American Chemical Society
Division of Cellulose and Renewable Materials
ACS Spring 2020 National Meeting

G. Larkin, Program Chair; W. Thielemans, Program Chair

SUNDAY MORNING

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson
K. J. Edgar, Organizer; U. Edlund, Organizer; M. Ek, Organizer; S. Percec, Organizer; V. Percec, Organizer; L. Berglund, Presiding; W. Thielemans, Presiding Papers 1-8

A Century of Cellulose: The Past, Present & Future of Cellulose & Renewable Materials
T. Budtova, Organizer; M. Godshall, Organizer; G. M. Larkin, Organizer; S. M. Murphy, Organizer; G. W. Selling, Organizer; G. Selling, Presiding; S. Vignolini, Presiding Papers 9-12

New Horizons: Early Career Researchers in Renewable Materials
B. Frka-Petesic, Organizer; S. Vignolini, Organizer; H. Yang, Organizer; B. Frka-Petesic, Presiding Papers 13-21

Lignin as a Renewable Substrate for Polymers: From Molecular Understanding & Isolation to Targeted Applications
L. Berglund, Organizer; M. K. Johansson, Organizer; M. Lawoko, Organizer; P. Olsén, Organizer; R. Rojas, Organizer; O. Sevastyanova, Organizer; M. Lawoko, Presiding; O. Sevastyanova, Presiding Papers 22-29

Advances in Methodology for Structural Characterization of Cellulosic & other Polysaccharide-Based Systems
S. Kim, Organizer; Y. Ogawa, Organizer; P. Penttilä, Organizer; Y. Ogawa, Presiding; P. Penttilä, Presiding; S. Kim, Presiding Papers 30-37

SUNDAY AFTERNOON

A Century of Cellulose: The Past, Present & Future of Cellulose & Renewable Materials
T. Budtova, Organizer; M. Godshall, Organizer; G. M. Larkin, Organizer; S. M. Murphy, Organizer; G. W. Selling, Organizer; G. Selling, Presiding; E. D. Cranston, Presiding Papers 38-40

New Horizons: Early Career Researchers in Renewable Materials
B. Frka-Petesic, Organizer; S. Vignolini, Organizer; H. Yang, Organizer; H. Yang, Presiding Papers 41-48

Lignin as a Renewable Substrate for Polymers: From Molecular Understanding & Isolation to Targeted Applications
L. Berglund, Organizer; M. K. Johansson, Organizer; M. Lawoko, Organizer; P. Olsén,
Organizer; R. Rojas, Organizer; O. Sevastyanova, Organizer; M. Lawoko, Presiding Papers 49-56

Advances in Methodology for Structural Characterization of Cellulosic & other Polysaccharide-Based Systems
S. Kim, Organizer; Y. Ogawa, Organizer; P. Penttilä, Organizer; Y. Ogawa, Presiding Papers 57-64

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson
K. J. Edgar, Organizer; U. Edlund, Organizer; M. Ek, Organizer; S. Percec, Organizer; V. Percec, Organizer; T. Iwata, Presiding Papers 199-206

SUNDAY EVENING

General Posters
G. M. Larkin, Organizer; W. Thielemans, Organizer; Papers 65-150

MONDAY MORNING

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson
K. J. Edgar, Organizer; U. Edlund, Organizer; M. Ek, Organizer; S. Percec, Organizer; V. Percec, Organizer; S. Percec, Presiding; L. Zhang, Presiding Papers 151-158

Functionalization of Nanocelluloses for Electrical, Optical, Magnetic, Barrier & Topochemical Properties
H. Jameel, Organizer; L. A. Lucia, Organizer; L. A. Lucia, Organizer; L. Pal, Presiding Papers 159-166

New Horizons: Early Career Researchers in Renewable Materials
B. Frka-Petesic, Organizer; S. Vignolini, Organizer; H. Yang, Organizer; S. Vignolini, Presiding Papers 167-174

Lignin as a Renewable Substrate for Polymers: From Molecular Understanding & Isolation to Targeted Applications
L. Berglund, Organizer; M. K. Johansson, Organizer; M. Lawoko, Organizer; P. Olsén, Organizer; R. Rojas, Organizer; O. Sevastyanova, Organizer; P. Olsén, Presiding; M. K. Johansson, Presiding Papers 175-182

Advances in Methodology for Structural Characterization of Cellulosic & other Polysaccharide-Based Systems
S. Kim, Organizer; Y. Ogawa, Organizer; P. Penttilä, Organizer; Y. Ogawa, Presiding; P. Penttilä, Presiding; S. Kim, Presiding Papers 183-190

MONDAY AFTERNOON
Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson
K. J. Edgar, Organizer; U. Edlund, Organizer; M. Ek, Organizer; S. Percec, Organizer; V. Percec, Organizer; U. Edlund, Presiding Papers 191-198

Functionalization of Nanocelluloses for Electrical, Optical, Magnetic, Barrier & Topochemical Properties
H. Jameel, Organizer; L. Pal, Organizer; L. Pal, Organizer; L. A. Lucia, Presiding Papers 207-212

3D Printing of Functional Biomaterials: Think Big!
L. A. Lucia, Organizer; L. Pal, Organizer; L. Pal, Presiding Papers 213-217

Lignin as a Renewable Substrate for Polymers: From Molecular Understanding & Isolation to Targeted Applications
L. Berglund, Organizer; M. K. Johansson, Organizer; M. Lawoko, Organizer; P. Olsén, Organizer; R. Rojas, Organizer; O. Sevastyanova, Organizer; L. Berglund, Presiding Papers 218-223

Innovative Lignin Upgrading: Smart Materials & Specialty Chemicals
C. Crestini, Organizer; H. Lange, Organizer; M. K. Osterberg, Organizer; M. Sipponen, Organizer; C. Crestini, Presiding; M. K. Osterberg, Presiding Papers 224-229

MONDAY EVENING

Sci-Mix
W. Thielemans, Organizer; G. M. Larkin, Organizer; Papers 142, 110, 106, 138, 94, 105, 125, 117, 108, 126, 81, 86, 144, 96, 98, 145, 134

TUESDAY MORNING

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson
K. J. Edgar, Organizer; U. Edlund, Organizer; M. Ek, Organizer; S. Percec, Organizer; V. Percec, Organizer; M. K. Ek, Presiding; R. Narayan, Presiding Papers 230-237

Nanocellulose: From Fundamentals to Function
T. Abitbol, Organizer; S. Kedzior, Organizer; E. Niinivaara, Organizer; M. Reid, Organizer; T. Abitbol, Presiding; S. Kedzior, Presiding; E. Niinivaara, Presiding; M. Reid, Presiding Papers 238-245

Pitch in Renewable Materials for Early Career Scientists
D. Gómez Maldonado, Organizer; M. C. Iglesias, Organizer; M. S. Peresin, Organizer; O. Rojas, Organizer; W. Schlemmer, Organizer; K. Solin, Organizer; S. Spirk, Organizer; M. S. Peresin, Presiding; S. Spirk, Presiding Papers 246-261
Innovative Lignin Upgrading: Smart Materials & Specialty Chemicals
C. Crestini, Organizer; H. Lange, Organizer; M. K. Osterberg, Organizer; M. Sipponen, Organizer; M. K. Osterberg, Presiding; H. Lange, Presiding Papers 262-269

Advances in Renewable Materials
N. Abidi, Organizer; S. M. Murphy, Organizer; N. Abidi, Presiding; S. M. Murphy, Presiding; M. Johns, Presiding Papers 270-277

TUESDAY AFTERNOON

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson
K. J. Edgar, Organizer; U. Edlund, Organizer; M. Ek, Organizer; S. Percec, Organizer; V. Percec, Organizer; L. Berglund, Presiding Papers 278-284

Historical Perspectives on Cellulose & other Renewable Materials
G. M. Larkin, Organizer; G. D. Patterson, Organizer; W. Thielemans, Organizer; N. V. Tsarevsky, Organizer; W. Thielemans, Presiding Papers 285-289

3D Printing of Functional Biomaterials: Think Big!
L. A. Lucia, Organizer; L. Pal, Organizer; L. A. Lucia, Presiding Papers 290-294

Innovative Lignin Upgrading: Smart Materials & Specialty Chemicals
C. Crestini, Organizer; H. Lange, Organizer; M. K. Osterberg, Organizer; M. Sipponen, Organizer; M. H. Sipponen, Presiding; H. Lange, Presiding Papers 295-300

Cellulose & Renewable Materials for Gas, Air & Water/Liquid Purification
U. Edlund, Organizer; A. Mathew, Organizer; A. Mautner, Organizer; T. Tammelin, Organizer; U. Edlund, Presiding; A. Mathew, Presiding Papers 301-306

WEDNESDAY MORNING

Colloidal Assembly of Renewable Materials
A. Bismarck, Organizer; I. Capron, Organizer; Y. Habibi, Organizer; S. Spirk, Presiding Papers 307-314

Nanocellulose: From Fundamentals to Function
T. Abitbol, Organizer; S. Kedzior, Organizer; E. Niinivaara, Organizer; M. Reid, Organizer; T. Abitbol, Presiding; S. Kedzior, Presiding; E. Niinivaara, Presiding; M. Reid, Presiding Papers 315-322

Wood Based Polymers to Tackle Global Challenges
K. Heise, Organizer; T. Nypelo, Organizer; S. Spirk, Organizer; K. Heise, Presiding; S. Spirk, Presiding Papers 323-330

Innovative Lignin Upgrading: Smart Materials & Specialty Chemicals
C. Crestini, Organizer; H. Lange, Organizer; M. K. Osterberg, Organizer; M. Sipponen, Organizer; H. Lange, Presiding; M. H. Sipponen, Presiding Papers 331-338

**Cellulose & Renewable Materials for Gas, Air & Water/Liquid Purification**
U. Edlund, Organizer; A. Mathew, Organizer; A. Mautner, Organizer; T. Tammelin, Organizer; U. Edlund, Presiding; A. Mathew, Presiding Papers 339-346

**WEDNESDAY AFTERNOON**

**Colloidal Assembly of Renewable Materials**
A. Bismarck, Organizer; I. Capron, Organizer; Y. Habibi, Organizer; G. W. Selling, Presiding Papers 347-354

**Nanocellulose: From Fundamentals to Function**
T. Abitbol, Organizer; S. Kedzior, Organizer; E. Niinivaara, Organizer; M. Reid, Organizer; T. Abitbol, Presiding; S. Kedzior, Presiding; E. Niinivaara, Presiding; M. Reid, Presiding Papers 355-362

**Wood Based Polymers to Tackle Global Challenges**
K. Heise, Organizer; T. Nypelo, Organizer; S. Spirk, Organizer; S. Spirk, Presiding; T. Nypelo, Presiding Papers 363-370

**Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems**
M. L. Auad, Organizer; J. Campos-Teran, Organizer; O. Rojas, Organizer; M. L. Auad, Presiding Papers 371-378

**Cellulose & Renewable Materials for Gas, Air & Water/Liquid Purification**
U. Edlund, Organizer; A. Mathew, Organizer; A. Mautner, Organizer; T. Tammelin, Organizer; T. Tammelin, Presiding; A. Mautner, Presiding Papers 379-386

**THURSDAY MORNING**

**Bio-Based Gels & Porous Materials**
T. Budtova, Organizer; F. Liebner, Organizer; F. Liebner, Presiding; T. Budtova, Presiding Papers 387-394

**Nanocellulose: From Fundamentals to Function**
T. Abitbol, Organizer; S. Kedzior, Organizer; E. Niinivaara, Organizer; M. Reid, Organizer; T. Abitbol, Presiding; S. Kedzior, Presiding; E. Niinivaara, Presiding; M. Reid, Presiding Papers 395-402

**Wood-Mimics: Hierarchical Structures & Architectures**
S. Gaidukovs, Organizer; Y. Habibi, Organizer; L. Hu, Organizer; F. Jiang, Presiding Papers 403-406
Wood Based Polymers to Tackle Global Challenges
K. Heise, Organizer; T. Nypelo, Organizer; S. Spirk, Organizer; T. Nypelo, Presiding; S. Spirk, Presiding Papers 407-411

Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems
M. L. Auad, Organizer; J. Campos-Teran, Organizer; O. Rojas, Organizer; Papers 412-419

Raman Spectroscopy Applications in the Field of Celluloses & Lignocelluloses & their Major Components
U. P. Agarwal, Organizer; N. Gierlinger, Organizer; N. Gierlinger, Presiding; J. Kneipp, Presiding Papers 420-428

THURSDAY AFTERNOON

Bio-Based Gels & Porous Materials
T. Budtova, Organizer; F. Liebner, Organizer; O. T. Ikkala, Presiding; B. Cathala, Presiding Papers 429-436

Nanocellulose: From Fundamentals to Function
T. Abitbol, Organizer; S. Kedzior, Organizer; E. Niinivaara, Organizer; M. Reid, Organizer; T. Abitbol, Presiding; S. Kedzior, Presiding; E. Niinivaara, Presiding; M. Reid, Presiding Papers 437-444

Wood-Mimics: Hierarchical Structures & Architectures
S. Gaidukovs, Organizer; Y. Habibi, Organizer; L. Hu, Organizer; T. Keplinger, Presiding Papers 445-452

Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems
M. L. Auad, Organizer; J. Campos-Teran, Organizer; O. Rojas, Organizer; Papers 453-460

Raman Spectroscopy Applications in the Field of Celluloses & Lignocelluloses & their Major Components
U. P. Agarwal, Organizer; N. Gierlinger, Organizer; S. J. Eichhorn, Presiding; T. Keplinger, Presiding Papers 461-469

####
CELL

DIVISION OF CELLULOSE AND RENEWABLE MATERIALS

G. Larkin and W. Thielemans, Program Chairs

SUNDAY MORNING

Section A

Pennsylvania Convention Center
126A

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson

Nanomaterials & Nanocomposites

Cosponsored by BIOT, PMSE, POLY and WCC
Financially supported by Svenska Cellulosa Aktiebolaget SCA Wallenberg Wood Science Center WWSC
Tetra Pak Billerud Korsnäs Essity EPNOE
K. J. Edgar, U. Edlund, M. Ek, S. Percec, V. Percec, Organizers
L. Berglund, W. Thielemans, Presiding

8:00 Introductory Remarks.

8:05 1. From modification of lignin, and starch and cellulose surfaces, to nanoparticle assembly and cell-growth materials: Playing around in Ann Christine's world. W. Thielemans

8:30 2. Lignocellulosic nanoparticles: From fundamental understanding of interactions to biomedical applications. M.K. Osterberg


9:20 4. Functionalization and patterning of nanocellulose-based foams and films with tannins. L. Bergstrom

9:45 Intermission.
10:00 5. Materials from cellulosic wood fibers or fibrils: Why are mechanical properties different?. L. Berglund


Section B
Pennsylvania Convention Center
126B

A Century of Cellulose: The Past, Present & Future of Cellulose & Renewable Materials

Cosponsored by BIOT
Financially supported by EPNOE
T. Budtova, M. Godshall, G. M. Larkin, S. M. Murphy, G. W. Selling, Organizers
G. Selling, S. Vignolini, Presiding

8:00 Introductory Remarks.


8:55 11. What we’ve learned about lignification since the 2014 Anselme Payen Award. J. Ralph

9:20 12. Microfibril structures based on distribution of C6-carboxy groups in TEMPO-oxidized wood, cotton, and algal cellulose nanofibrils. Y. Ono, Y. HoriKawa, A. Isogai

9:45 Intermission.

10:00 Panel discussion.

11:40 Concluding Remarks.

Section C
New Horizons: Early Career Researchers in Renewable Materials

Nanocellulose Characterization & Functionalization: Energy Materials

Cosponsored by BIOT and YCC
S. Vignolini, H. Yang, Organizers
B. Frka-Petesic, Organizer, Presiding

8:00 Introductory Remarks.

8:05 13. Twist geometry of nanocelluloses probed by electron microdiffraction. Y. Ogawa

8:30 14. Nanocellulose and 2D conductors: Interactions and forces studied by colloidal probe atomic force microscopy. M.S. Reid, L. Wagberg

8:55 15. Pickering emulsions as synthetic tool for nanocellulose modification. K. Heise, M. Kostiainen, E. Kontturi

9:20 16. Preparation of cellulose nanocrystals bearing diverse functional moieties for material design. K. Zhang

9:45 Intermission.

10:00 17. Sulfonyl-modification of cellulose nanocrystals and their interactions in aqueous media. R. Salminen, W. Thielemans


11:40 21. Emerging cellulose technologies for energy, water and sustainability. T. Li

Lignin as a Renewable Substrate for Polymers: From Molecular Understanding & Isolation to Targeted Applications

Section D
Biorefinery & Technical Lignins

Cosponsored by POLY
Financially supported by Wallenberg Wood Science Center
L. Berglund, M. K. Johansson, P. Olsén, R. Rojas, Organizers
M. Lawoko, O. Sevastyanova, Organizers, Presiding

8:00 Introductory Remarks.


8:30 23. Elucidating mechanisms and structural changes during organosolv lignin extraction. M. Karlsson, O. Sevastyanova, M. Lawoko


9:45 Intermission.

10:00 26. Unravelling insights on kraft lignin structure and composition. N. Giummarella, D. Areskogh, M. Lawoko

10:25 27. Formation of condensed structures during mild thermal treatment of kraft lignin with fatty acids through radical reactions. M.H. Lahtinen, J. Mikkilä, K.S. Mikkonen, P.O. Kilpelainen, I. Kilpeläinen


Section E

Pennsylvania Convention Center
Broad Street Atrium - Theater 13

Advances in Methodology for Structural Characterization of Cellulosic & other Polysaccharide-Based Systems
8:00 Introductory Remarks.

8:05 30. Small- and wide-angle x-ray scattering: Valuable tool for analyzing nanostructured materials using a compact laboratory system. **J. Brousseau**, H. Santner


8:55 32. X-ray fiber diffraction studies of the structure of cellulose microfibrils. **L.C. Makowski**

9:20 33. Using a combination of resonant soft X-ray scattering and grazing-incidence diffraction for the study of plant primary cell walls. **S. Rongpipi**, J. Del Mundo, S.N. Kiemle, W. Barnes, C. Anderson, D. Cosgrove, E. Gomez, **E. Gomez**

9:45 Intermission.

10:00 34. Combining deuterium-labeling and neutron scattering to gain insight into plant cell wall organization. **H.M. O'Neill**, R. Shah, S. Pingali, B.H. Davison, B.R. Evans

10:25 35. Application of X-ray and neutron scattering to understand lignocellulosic deconstruction for bioenergy. **G. Cheng**


**Microbial Metabolic & Bioprocess Engineering**

**Nonmodel Host Engineering & Bioreactor Engineering**

Sponsored by BIOT, Cosponsored by CELL

**Engineering Functionality into Bio(mimetic) Polymers**
Green Polymer Chemistry: New Products, Processes & Applications

Novel Materials & Applications

Sponsored by POLY, Cosponsored by AGFD and CELL

SUNDAY AFTERNOON

Pennsylvania Convention Center
126A

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson

Biorefineries & Bioengineering

Cosponsored by BIOT, PMSE, POLY and WCC
Financially supported by Svenska Cellulosa Aktiebolaget SCA Wallenberg Wood Science Center WWSC
Tetra Pak Billerud Korsnäs Essity EPNOE
K. J. Edgar, U. Edlund, M. Ek, S. Percec, V. Percec, Organizers
T. Iwata, Presiding


1:30 200. Protein plastics. M. Hedenqvist


2:45 Intermission.

3:00 203. Review of the tailoring of cellulose surfaces with the layer-by-layer technique to create new cellulose-based materials and devices. L. Wagberg


4:15 206. Bioproducts engineered from lignocelluloses: From plants and residues to next generation materials. O.J. Rojas

Section B

Pennsylvania Convention Center
126B

A Century of Cellulose: The Past, Present & Future of Cellulose & Renewable Materials

Cosponsored by BIOT
Financially supported by EPNOE
T. Budtova, M. Godshall, G. M. Larkin, S. M. Murphy, G. W. Selling, Organizers
E. D. Cranston, G. Selling, Presiding

1:00 Introductory Remarks.

1:05 38. Lessons from DFT quantum mechanics studies of disaccharide conformations. A.D. French


1:55 40. CELL as a springboard for dynamic research and networking. O. Rojas

2:20 Intermission.

2:35 Panel discussion.

4:15 Concluding remarks.

Section C

Pennsylvania Convention Center
Broad Street Atrium - Theater 11

New Horizons: Early Career Researchers in Renewable Materials

Composites & functional materials

Cosponsored by BIOT and YCC
B. Frka-Petesic, S. Vignolini, Organizers
H. Yang, Organizer, Presiding
1:00 Introductory Remarks.

1:05 41. Double-network bionanocomposites from nanocellulose and mycelium. N. Attias, Y.J. Grobman, T. Abitbol

1:30 42. Low-cost waste-derived mycelium nanopapers. A. Mautner, M. Jones, K. Weiland, E. Kontturi, S. John, A. Bismarck

1:55 43. 3-ingredient, 2-step, 1-pot process to obtain uniform esterified lignin derivatives. L. Liu, S. Chen, L. Ji, S. Renneckar


2:45 Intermission.

3:00 45. Rod-coil oligocellulose-elastomer- and polypeptide diblock copolymers for advanced biobased nanomaterials. J. Majoinen, R. Pylkkänen, M. Penttilä, O.J. Rojas


3:50 47. Substrate interactions as a handle to control long-range order in micro- and macro-structures formed from cellulose nanocrystals. B.L. Tardy, J. Richardson, L. Greca, J. Guo, H. Ejima, O. Rojas

4:15 48. Modifying materials using rod shaped fillers. J. Foster

Section D

Pennsylvania Convention Center
Broad Street Atrium - Theater 12

Lignin as a Renewable Substrate for Polymers: From Molecular Understanding & Isolation to Targeted Applications

Progress in Synthesis, Characterization & Modeling of Lignin

Cosponsored by POLY
Financially supported by Wallenberg Wood Science Center
L. Berglund, M. K. Johansson, P. Olsén, R. Rojas, O. Sevastyanova, Organizers
M. Lawoko, Organizer, Presiding

1:00 Introductory Remarks.
1:05 49. Novel lignin monomers: Another brick in the wall. J. del Río, J. Rencoret, A. Gutierrez, T. Elder, H. Kim, J. Ralph


1:55 51. Measuring the *in situ* glass transition of catechyl lignin. E. Ristanti, C.E. Frazier


2:45 Intermission.

3:00 53. On the visualization of lignin structure. M. Balakshin, E. Capanema, A. Potthast, T. Rosenau


Section E

Pennsylvania Convention Center
Broad Street Atrium - Theater 13

**Advances in Methodology for Structural Characterization of Cellulosic & other Polysaccharide-Based Systems**

Cosponsored by POLY
Financially supported by Anton Paar
S. Kim, Y. Ogawa, P. Penttilä, *Organizers*
Y. Ogawa, *Presiding*

1:00 Introductory Remarks.

1:05 57. Solid-state NMR as a powerful tool to characterize polysaccharide-based systems. F. D'Acierio, W.Y. Hamad, M.J. Maclachlan, C.A. Michal

1:30 58. Probing surface chemistry of functionalized cellulose nanofibrils enabled by dynamic nuclear polarization enhanced solid-state NMR. G. De Paepe

2:20 60. Beyond crystallinity: Developing Raman spectroscopy tools to better define cellulose supramolecular structure. U.P. Agarwal

2:45 Intermission.

3:00 61. Density functional theory modeling of cellulose and its interactions in plant cell walls. J.D. Kubicki, H. Yang

3:25 62. Advances in nanoscale infrared spectroscopy to explore the properties of lignocellulosic-based materials. L. Tetard

3:50 63. FTIR microspectroscopy investigation of biomolecules distribution in cotton seed coat. S.P. Liyanage, M. Hossain, N. Abidi

4:15 64. Mass spectrometry analysis of pyranose dehydrogenase action on xylooligosaccharides. M. Tenkanen, H. Zhao, J. Karppi, E. Master

Green Polymer Chemistry: New Products, Processes & Applications

Biobased Materials & their Preparation

Sponsored by POLY, Cosponsored by AGFD and CELL

SUNDAY EVENING

Pennsylvania Convention Center
Exhibit Hall A

General Posters

G. M. Larkin, W. Thielemans, Organizers

6:00 - 8:00
65. Removal of rare earth metal ions from contaminated water by sustainable carboxycellulose nanofibers derived from agave through nitro oxidation process. I. Brahmbhatt, S. Sharma, P.R. Sharma, M. Nolan, B.S. Hsiao


67. Isolation and characterization of cellulose nanofibrils from *cladophora glomerata* algae. W. Gao, J. Zeng, J. Xu, B. Wang, K. Chen

68. 3D printed UV curable hydrogels using cellulose nanocrystals as a rheological modifier. D. Kam, A. Braner, L. Larush, A. Chiappone, O. Shoseyov, S. Magdassi

69. From traditional use of Fique fibers (*Furcraea spp*) to novel bionanocomposite for dye degradation technologies. J.D. Sánchez Moreno, E. Gutiérrez Pineda, C. Blanco-Tirado, M.Y. Combariza

70. Nanocellulose based filaments as textile sensors. K. Gordeyeva, C. Brett, S. Roth, D. Soderberg

71. Effect of methacrylation on the thermoresponsive sol-gel transition of methylcellulose. N. Haq-Siddiqi, S.B. Nicoll

72. Hyper-production of cellulase based macromolecules by *Escherichia coli* engineered with UV & EMS mutated cellulase gene from *Aspergillus niger* for industrial applications. Q. Daud


74. Nitro-oxidation on raw agricultural residues. P.R. Sharma, S. Sharma

75. Comparing physicochemical properties and sorption behaviors of pyrolosis-derived and microwave-mediated biochar. C. Brickler, Y. Wu, S. Li, G. Chen, A. Swamy

76. High-efficiency, energy-saving and “green” route for fabrication of chitin-based materials. J. Cai


79. Trypsin active paper for sample preparation steps in paper-spray mass spectrometry applications. L.M. Riedler, U. Schwenke, T. Bock, G. Schwall, M. Biesalski


82. Development of rigid poliurethane foam from kraft lignin and renewable chain extender: Thermal insulation application. **L. Tavares**, S.E. Vidotti

83. Characterization of silk/cellulose biocomposites infused with rGO. **A. Morales**, B. Blessing, S. Love, S.M. O'Malley, X. Hu, D. Salas-de la Cruz

84. Crystallization behavior and thermal restoring of superhydrophobic flower-like structures using binary mixtures of cellulose-based polymers and waxes. **C. Cordt**, A. Geissler, M. Biesalski


86. Low-cost synthesis of cellulose-biochar composites for enhanced water and nitrogen use efficiency in agricultural fields. **Y. Wu**, C. Brickler, S. Li, G. Chen

87. Natural rubber nanocomposites with nanocellulose: Suspension rheology and elastomeric properties. **P. Samyn**, G. Reggers, R. Carleer, P. Adriaensens

88. Wood-inspired binder enabled vertical ink printing of g-C₃N₄ forest for highly efficient photocatalytic hydrogen evolution. **B. Jiang**, Z. Liang, **Y. Jin**

89. On the effect of the presence of lignin on feedstock and its effects on the properties of mechanically produced lignin-containing cellulose nanofibrils (LCNF). **M.C. Iglesias**, M.S. Peresin

90. Efficient production of glucose via acid-catalyzed hydrolysis of cation-modified microcrystalline cellulose. T. Zhang, H. Xiao, **Y. Jin**


92. Nanocellulose-based SERS sensor for the detection of explosives. J. Wu, Y. Feng, **W. Wu**

93. High-wet-strength lignocellulosic paper for heavy metal ion adsorption and oil/water separation. S. Jiang, H. Tian, **W. Wu**

94. Fluorescently-labelled cellulose nanofibrils for leaching detection. M. Karlsson, C. Aulin, A.B. Fall, **T. Abitbol**

96. Oxidative coupling of methyl furoate to form 5,5’-dicarboxylic-2,2’-bifuran methyl esters. **M. Ye**, R.F. Lobo


100. Effect of chemical modification of CNF on the properties of PVP/CNF hydrogel. **H. Youn**, W. Im, H. Lee, S. Park, S. Youk, S. Goo


102. Controlling barrier properties of composites using nonspherical particles. **A. Abbas**, V. Singh


104. Use of steam explosion to produce microfibrillated cellulose from *Posidonia oceanica* waste. **M. Khadraoui**, R. Khiari, N. Brosse, L. Bergaoui, E. Mauret


106. Guidance of corneal epithelial cells migration by co-operative effects of stretched bacterial cellulose/gelatin and DC electric fields. **I. Wang**, Z. Shi, M. Zhao, **G. Yang**

107. SElectiveLi: Novel electrochemical process using lignosulfonates to produce bio-based monomers & polymers. **J. Panther**, S.R. Waldvogel


111. Pectin and nanocellulose from soybean hulls as partial substituents in methylene diphenyl diisocyanate adhesive formulations. J.A. Hernandez, B. Soni, M.C. Iglesias, R.G. Richey, C.E. Frazier, M.S. Peresin


113. Catalytic access to alkylated cyclohexanoles. K. Alt, S.R. Waldvogel


117. Nanocellulose membranes in diagnostics. A. Piper, L. Wagberg, M. Hamedi

118. Operation of proton exchange membrane (PEM) fuel cells using natural cellulose fiber membranes. A. Raut, L. Wang, M. Rafailovich, S. Sharma, R. Isseroff


120. Incorporation of iron on nanocellulose for arsenic removal from water. M. Khan, W. Yang, J. Gao, B.S. Hsiao, D.G. Drueckhammer


124. Sustainable microwave assisted extraction of bioactive compounds from agricultural residues. A. Jimenez, M. Ramos, A. Mellinas, I. Solaberrieta, C. Pelegrin, Y. Flores, M. Garrigós

125. Fabrication and characterization of bacterial nanocellulose-based functional materials for biomedical applications. G. Yang

126. Antiplasticization behavior of biobased additives on the structure, properties, and solution spinning of regenerated cellulose fibers. M. Biswas, E. Ford


129. Fundamentals of cellulose nanocrystals (CNCs) in common organic solvents. A. Chang, A. Zheng, K.R. Carter


132. Eucalyptus nitens lignins by ionic liquid-based biorefinery methods. L. Penin, H. Lange, C. Crestini, V. Santos, J.C. Parajó

133. Carbohydrate polymers based value-added co-products from sorghum bran, bagasse and biomass. M.P. Yadav


139. Promise of bioplastics from lignin. **L. Liu, K. Bessler, S. Renneckar**

140. Mixing up lignin fractions: Tailoring thermal properties for ultralight nanofibrous lignin sponges. **M. Cho, J. Yiu, S. Renneckar**


142. Time-resolved structural transition during nanocellulose gel formation using an *in situ* SAXS/flow-focusing technique. **T. Rosen, R. Wang, H. He, C. Zhan, S. Chodankar, B.S. Hsiao**


144. Data analysis pipeline for scanning micro–diffraction measurements on plant tissues. **J. Liu, L. Yang**

145. Isosorbide-based low viscosity resins for additive manufacturing applications. **X. Chu, H. Berensmann, J.J. LaScala, G.R. Palmese**

146. Electron microscopy of cellulosics: Historical perspectives and technical challenges. **Y. Ogawa**


148. Thermal properties of treated date palm fibers. **H.J. Perera, B. Alatts**

149. Sunflower oil enriched with lycopene from pink guava (*Psidium guajava* L.) through a green process with Waring blender and Ultraturrax. M. Villegas, C. Molina, A. Serpa, J.A. Velasquez, P. Gañan Rojo, R. Zuluaga Gallego, **C. Gomez Hoyos**

150. Functionalization of ethyl cellulose by hydroxyl-yne click chemistry. B. Li, **J. Yu, Y. Fan**

**MONDAY MORNING**
Pennsylvania Convention Center
126A

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson

The Chemistry of Forest

Cosponsored by BIOT, PMSE, POLY and WCC
Financially supported by Svenska Cellulosa Aktiebolaget SCA Wallenberg Wood Science Center WWSC
Tetra Pak Billerud Korsnäs Essity EPNOE
K. J. Edgar, U. Edlund, M. Ek, V. Percec, Organizers
S. Percec, Organizer, Presiding
L. Zhang, Presiding

8:00 Introductory Remarks.

8:05 151. Putting cellulose from bacteria and plants to work. R.A. Gross, A. Amason, J.F. Nowak, J. Samuel

8:30 152. Cellulose-NaOH solutions: Influence of non-dissolved fibers on solution gelation and properties of all-cellulose composites. O. Korhonen, K. Labidi, T. Budtova

8:55 153. Sustainable polymers and fibers from lignin. M.L. Auad, J. Hinkle, A. Bansode

9:20 154. Segmentation and kink-formation mechanisms of TEMPO-oxidized cellulose fibrils during sonication in water to form TEMPO-CNCs. Y. Zhou, A. Isogai

9:45 Intermission.

10:00 155. Regio- and chemoselective synthesis of glycosaminoglycan analogs from simple precursors. C. Gao, K.J. Edgar


Section B
Pennsylvania Convention Center
126B

**Functionalization of Nanocelluloses for Electrical, Optical, Magnetic, Barrier & Topochemical Properties**

Cosponsored by COLL
H. Jameel, L. A. Lucia, *Organizers*
L. Pal, *Presiding*

8:00 Introductory Remarks.

8:05 159. Surface modified cellulose nanocrystals: Investigating cellulose in electronics. A. Chang, K.R. Carter


9:45 Intermission.

10:00 163. Modification of cellulose surfaces through strongly adsorbed polymer layers: Way to cellulose hydrophobization. W. Xu, O. Werzer, R. Resel, T. Pettersson, E. Kontturi


10:50 165. Fully biodegradable nanogenerators based on functional nanocellulose. z. shi, G. Yang


11:40 Concluding Remarks.

Section C
New Horizons: Early Career Researchers in Renewable Materials

Optical Properties of Cellulose-Based Materials

Cosponsored by BIOT and YCC
B. Frka-Petesic, H. Yang, Organizers
S. Vignolini, Organizer, Presiding

8:00 Introductory Remarks.


8:30 168. Optical materials based on cholesteric liquid crystals of cellulose nanocrystals. Y. Cao, M.J. Maclachlan

8:55 169. Optical consequences of distortions in cellulose nanocrystal films. B. Frka-Petesic, G. Kamita, G. Guidetti, S. Vignolini

9:20 170. Rationalising the cholesteric phase of cellulose nanocrystals in terms of entropic effects. M. Chiappini, S. Dussi, B. Frka-Petesic, S. Vignolini, M. Dijkstra

9:45 Intermission.


10:25 172. Understanding the structural diversity in chitins as a versatile template for optical biomimetics. A. Pui Ting Ho, M. Karacar, B. Aydemir, A.G. Dumanli

10:50 173. Cellulose building blocks design for scattering engineering. H. Yang, G. Jacucci, S. Vignolini


11:40 Concluding Remarks.

Section D

Pennsylvania Convention Center
Broad Street Atrium - Theater 12

Lignin as a Renewable Substrate for Polymers: From Molecular Understanding & Isolation to Targeted Applications
Lignin Platform Polymers & Thermosets

Cosponsored by POLY
Financially supported by Wallenberg Wood Science Center
L. Berglund, M. Lawoko, R. Rojas, O. Sevastyanova, Organizers
M. K. Johansson, P. Olsén, Organizers, Presiding

8:00 Introductory Remarks.

8:05 175. Synthesis of biobased building blocks from eugenol: Chemical platform approach for polymer synthesis. S. Caillol

8:30 176. Renewable, tunable polymers from lignin and 5-hydroxymethylfurfural. T.J. Schwartz

8:55 177. Green process for the direct functionalization of lignin for use in thermosets. D.C. Webster, E. Krall, A. Hart


9:45 Intermission.

10:00 179. Lignin-based epoxy-resins: understanding the influence of Lignin homo cross-linking during amination reaction to control final elastic properties of the bio-hybrid material. M.A. Biesalski, S. Trosien

10:25 180. Developing 100% bio based epoxy resin using lignin as bisphenol-A replacement. S. Nikafshar, J. Wang, M. Nejad


11:15 182. Unraveling the relationship between structure and material properties in lignin-derived epoxy resins. C. Gioia, M. Colonna, A. Tagami, L. Medina, O. Sevastyanova, L. Berglund, M. Lawoko

Section E

Pennsylvania Convention Center
Broad Street Atrium - Theater 13

Advances in Methodology for Structural Characterization of Cellulosic & other Polysaccharide-Based Systems
8:00 Introductory Remarks.

8:05 183. ForMAX: Multiscale structural characterization of fibrous materials. K. Nygard

8:30 184. Structural characterization of cellulose in plant tissues using X-ray microbeam scattering and scanning imaging. L. Yang


9:20 186. Scanning electron diffraction as a tool to study the local crystallinity of cellulose. T. Willhammar

9:45 Intermission.

10:00 187. Atomistic simulation studies of cellulose microfibril aggregates. A. Paajanen, S. Ceccherini, Y. Sonavane, T. Maloney, S. Paavilainen, J.A. Ketoja

10:25 188. New developments and strategies for high resolution characterization of secondary plant cell walls by atomic force microscopy. T. Keplinger, M. Adobes Vidal


11:40 Concluding Remarks.

History of Polymer Science

Sponsored by HIST, Cosponsored by CELL‡

Green Polymer Chemistry: New Products, Processes & Applications

Catalysts & Catalyzed Reactions
Sponsored by POLY, Cosponsored by AGFD and CELL

MONDAY AFTERNOON

Pennsylvania Convention Center
126A

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson

Biomaterials & Biomedicals

Cosponsored by BIOT, PMSE, POLY and WCC
Financially supported by Svenska Cellulosa Aktiebolaget SCA Wallenberg Wood Science Center WWSC
Tetra Pak Billerud Korsnäs Essity EPNOE
K. J. Edgar, M. Ek, S. Percec, V. Percec, Organizers
U. Edlund, Organizer, Presiding

1:05 191. Polymer nanostructures for bioapplications: From stem cells enrichment to drug delivery. M. Monteiro


1:55 193. Porous scaffolds of biodegradable polymers via templated techniques. R. Srivastava

2:20 194. Functionalized silk biomaterial systems. D.L. Kaplan

2:45 Intermission.


3:20 196. Using phase separation of cellulose derivatives to control the drug release rate. A. Larsson

3:45 197. Multifunctional hydrogels for rapid hemostasis and tissue repair. B. Guo

4:10 198. Forensic engineering of advanced polymeric biomaterials. M.M. Kowalczuk

Section B
Pennsylvania Convention Center
126B

**Functionalization of Nanocelluloses for Electrical, Optical, Magnetic, Barrier & Topochemical Properties**

Cosponsored by COLL
H. Jameel, L. Pal, L. Pal, *Organizers*
L. A. Lucia, *Presiding*

1:00 Introductory Remarks.


1:30 208. Nanocellulose-based polyelectrolyte membranes: Land of opportunities for application in fuel cells. **C. Vilela**, F. Figueiredo, A. Silvestre, C. Freire


2:45 211. Actuation modulation by modification of substrate morphology: Bacterial cellulose/PEDOT:PSS actuator. P. Maity, **S. C R**, M. Khandelwal


3:35 Concluding Remarks.

Section C

Pennsylvania Convention Center
Broad Street Atrium - Theater 11

**3D Printing of Functional Biomaterials: Think Big!**

Cosponsored by PMSE
L. A. Lucia, L. Pal, *Organizers*
L. Pal, *Presiding*

1:00 Introductory Remarks.
1:05 213. Two-phase, biomass emulgels for direct ink writing of hierarchical architectures. S. Huan, B. Mattos, R. Ajdary, W. Xiang, L. Bai, O. Rojas

1:30 214. Preparation and properties of 3D printer filament with poly(lactic acid)/lignin-containing microfibrillated cellulose(L-MFC) derived from organosolv. J. Ryu, J. Lee, K. Kim, T. Eom


2:20 216. 3D printing hydrogel scaffolds of wood nanocellulose with tunable mechanical strength towards biomedical applications. C. Xu, W. Xu, X. Wang, S. Willför


3:10 Concluding Remarks.

Section D

Pennsylvania Convention Center
Broad Street Atrium - Theater 12

Lignin as a Renewable Substrate for Polymers: From Molecular Understanding & Isolation to Targeted Applications

Lignin-Based Thermoplastics

Cosponsored by POLY
Financially supported by Wallenberg Wood Science Center
M. K. Johansson, M. Lawoko, P. Ölsén, R. Rojas, O. Sevastyanova, Organizers
L. Berglund, Organizer, Presiding

1:00 Introductory Remarks.

1:05 218. Lignin engineering for high-value applications. M. Balakshin, E. Capanema, O. Rojas

1:30 219. Dynamics of lignin glass transition. L. Petridis


2:20 221. Profitable eco-friendly plastics with kraft lignin contents above 90 wt%. Y. Chen, S. Sarkanen


3:35 Concluding Remarks.

Section E

Pennsylvania Convention Center
Broad Street Atrium - Theater 13

**Innovative Lignin Upgrading: Smart Materials & Specialty Chemicals**

**Advances in Functional Lignin Microstructures**

H. Lange, M. Sipponen, *Organizers*
C. Crestini, M. K. Osterberg, *Organizers, Presiding*

1:00 Introductory Remarks.


1:30 225. Supramolecular assembly of natural polyphenols/Fe(III) coordination complexes for versatile microcapsule engineering. H. Lange, **M. Gigli**, C. Crestini


3:35 Concluding Remarks.
History of Polymer Science
Sponsored by HIST, Cosponsored by CELL

Systems Biology, Synthetic Biology & Emerging Technologies

Microbial Processes: Systems & Synthetic Biology Tools
Sponsored by BIOT, Cosponsored by CELL

Green Polymer Chemistry: New Products, Processes & Applications

Advances in Polyesters
Sponsored by POLY, Cosponsored by AGFD and CELL

MONDAY EVENING
Section A
Pennsylvania Convention Center
Exhibit Hall A

Sci-Mix

G. M. Larkin, W. Thielemans, Organizers

8:00 - 10:00


TUESDAY MORNING
Section A
Pennsylvania Convention Center
126A
Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson

Hydrogels & Colloids

Cosponsored by BIOT, PMSE, POLY and WCC
Financially supported by Svenska Cellulosa Aktiebolaget SCA Wallenberg Wood Science Center WWSC
Tetra Pak Billerud Korsnäs Essity EPNOE

K. J. Edgar, U. Edlund, M. Ek, S. Percec, V. Percec, Organizers
M. K. Ek, R. Narayan, Presiding

8:00 Introductory Remarks.

8:05 230. High-performance materials derived from polysaccharide ester derivatives. T. Iwata


8:55 232. Everything degrades! Nanocellulose composites with on-demand degradability. F. Mayer, A. Mautner, A. Bismarck


9:45 Intermission.

10:00 234. Linear polyamidoamines derived from α-amino acids as phosphorus-free surface-confined intumescent flame retardants for cotton fabrics. J. Alongi, P. Ferruti, a. manfredi, F. Carosio, M. Hakkarainen, E. Ranucci


10:50 236. Lignocellulose derived hydrogels, thermosets and thermoplastic materials. M. Hakkarainen

11:15 237. Spatiotemporal migration of target nucleotide in partly oligonucleotide crosslinked hydrogels identifies toehold as a critical parameter in the swelling dynamics. E.P. Jonasova, A. Bjørkøy, B.T. Stokke

Section B

Pennsylvania Convention Center
126B
Nanocellulose: From Fundamentals to Function

Cosponsored by COLL and PMSE
Financially supported by RISE
T. Abitbol, S. Kedzior, E. Niinivaara, M. Reid, Organizers, Presiding

8:00 Introductory Remarks.


8:30 239. CNC-like cellulotic whiskers (C-LCWs): Production and evaluation of morphologically and chemically diversified lignocellulosic nanomaterials. J. Zhu, H. Wang, J. Zhu, U.P. Agarwal, R. Gleisner

8:55 240. CNF from pulp fibers with different hemicellulose and lignin content. C. Aulin, E. Brännvall, A.B. Fall


9:45 Intermission.

10:00 242. Nanofibrillated cellulose for sustainable textile coloration. S. Rai, R. Saremi, S. Sharma, S. Minko


10:50 244. Facile and comprehensive approach, accounting for substrate interactions, for the characterization of the dimensions of cellulose nanofibrils. B.L. Tardy, B. Mattos, O. Rojas


11:40 Concluding Remarks.

Section C

Pennsylvania Convention Center
Broad Street Atrium - Theater 11

Pitch in Renewable Materials for Early Career Scientists

Cosponsored by SCHB and YCC
Financially supported by EPNOE
8:00 Introductory Remarks.


8:30 248. Linking adhesion force to area in molecular contact measured by FRET spectroscopy. **M. Gaspar Simões**, G. Urstoger, R. Schennach, U. Hirn


9:45 Intermission.

10:00 254. Sustainable dimethyl ether recycle system for regenerating super absorbent polymers. C. Wu, **S. Raghavan**, **A. Pine**, D.I. Collias, B.J. Love

10:13 255. Enhancing the surface area and porosity characteristics of cellulose-based monoliths using inorganic salts. **P. Parajuli**, Y. Hu, N. Abidi


11:03 259. Effects of dehydration on plant primary cell wall cellulose from grazing-incidence wide angle X-ray scattering. J.T. Del Mundo, S. Rongpipi, D. Cosgrove, E. Gomez, E. Gomez

11:15 260. Use of high frequency ultrasound for the depolymerization of cellulose into glucose. S. haouache, I. Capron, f. jerome

11:28 261. Robust cathodes for structural batteries from cellulose nanofibrils and chiral cobalt oxide nanoparticles. H. Françon, P.A. Larsson, N. Kotov, L. Wagberg

11:40 Concluding Remarks.

Section D
Pennsylvania Convention Center
Broad Street Atrium - Theater 12

Innovative Lignin Upgrading: Smart Materials & Specialty Chemicals
Towards Platform Chemicals from Lignin

C. Crestini, H. Lange, M. Sipponen, Organizers
M. K. Osterberg, Organizer, Presiding
H. Lange, Presiding

8:00 Introductory Remarks.

8:05 262. Lignin first using benign catalysts. J.S. Samec

8:30 263. Formic acid fractionation of lignocellulosic biomass and valorization of lignin. Y. Zhang, X. Wang, P. Fatehi, Q. Hou, M. Qin, S. Willför, C. Xu


9:20 265. Can biogenic formaldehyde provide a novel lignin analysis?. N. Shivyari, C.E. Frazier

9:45 Intermission.

10:00 266. Electrochemical degradation of lignin. S.R. Waldvogel, M. Zirbes, J. Strugatchi, J. Panther, M. Breiner


11:15 269. Selective conversion of lignin to aromatic acids in high yield via two-step oxidation method. Z. Tong, H. Bao, w. peng

11:40 Concluding Remarks.

Section E

Pennsylvania Convention Center
Broad Street Atrium - Theater 13

Advances in Renewable Materials

N. Abidi, S. M. Murphy, Organizers, Presiding
M. Johns, Presiding

8:00 Introductory Remarks.

8:05 270. Fusion of fiber networks with ionic liquids to produce new type of cellulose materials for biodegradable packaging applications. H. Orelma, A. Tanaka, A. Khakalo, A. Korpela

8:30 271. Understanding cellulose dissolution in ionic liquids and their solutions in molecular solvents: Physical organic chemistry approach. O. El Seoud, M. Kostag, P.R. Pires, D.C. Ferreira

8:55 272. Conducting cellulose nanopapers as platform for sensing applications. E. Gutiérrez Pineda, C. Blanco-Tirado, M.Y. Combariza


9:45 Intermission.

10:00 274. Award Address (ACS Award for Affordable Green Chemistry sponsored by Dow and endowed by Rohm and Haas Company). Renewable Acrylic Acid enables Bio Economy of Superbsorbent Polymers, Coatings, Adhesives, etc.). D.I. Collias, J. Godlewski, J. Velasquez


11:15 277. Morphological change in the microphase separation of cellulose diacetate/diblock copolymer blends. S. Morimoto, K. Sugimura, T. Awano, H. Kamitakahara, Y. Nishio

11:40 Concluding Remarks.

Sustainability in Bioprocessing

Sponsored by BIOT, Cosponsored by CELL

Green Polymer Chemistry: New Products, Processes & Applications

Polymer Degradation & Recycling

Sponsored by POLY, Cosponsored by AGFD and CELL

TUESDAY AFTERNOON

Section A

Pennsylvania Convention Center
126A

Renewable Molecules & Materials: Anselme Payen Award Symposium in Honor of Ann-Christine Albertsson

Renewable: Synthetic & Structural Design

Cosponsored by BIOT, PMSE, POLY and WCC
Financially supported by Svenska Cellulosa Aktiebolaget SCA Wallenberg Wood Science Center WWSC Tetra Pak Billerud Korsnäs Essity EPNOE K. J. Edgar, U. Edlund, M. Ek, S. Percec, V. Percec, Organizers L. Berglund, Presiding

1:05 278. Potential uses of MVG (methyl vinyl glycolate) derived from glucose cracking. S. Lundmark, S.G. Elliot, B.M. Jessen, R. Madsen, E. Taarning, I. Tosi, P. Wennerberg

1:30 279. Opening Rings: From biopolymers, in water and beyond. P. Olsén

1:55 280. Polypeptides as functional nanomaterials toward achieving plant organellar engineering through cell walls. K. Numata

2:20 281. From ring-opening reactions to renewable functional materials. K. Odelius
2:45 282. Renewable fats and oils based long chain polyamides. J. Seppala, H.P. Nguyen

3:10 283. Synthetic cells and other assemblies from bio-renewable starting materials. V. Percec

3:35 Intermission.

3:50 284. New paradigm in the design of degradable and renewable polymeric materials. A. Albertsson

4:40 Concluding Remarks.

Section B

Pennsylvania Convention Center
126B

Historical Perspectives on Cellulose & other Renewable Materials

Cosponsored by BIOT, HIST‡ and MPPG‡
G. M. Larkin, G. D. Patterson, N. V. Tsarevsky, Organizers
W. Thielemans, Organizer, Presiding

1:00 Introductory Remarks.

1:05 285. History of CELL. G.D. Patterson

1:55 286. Anselme Payen: Forgotten histories of our pioneering founder. S.J. Eichhorn

2:20 287. Chemical history of cellulose. G.D. Patterson

2:45 288. Cellulose solutions: Early discoveries and applications. N.V. Tsarevsky

3:10 289. Study, stabilization and utilization of gun-cotton by Frederick Abel. S.H. Mauskopf

3:35 Concluding Remarks.

Section C

Pennsylvania Convention Center
Broad Street Atrium - Theater 11

3D Printing of Functional Biomaterials: Think Big!

Cosponsored by PMSE
L. Pal, Organizer
L. A. Lucia, Organizer, Presiding
1:00 Introduction.

1:05 290. Direct ink writing of lignin/hydroxypropyl cellulose solutions. L. Ebers, M.G. Laborie

1:30 291. Use of lignocellulosic-derived components to develop novel biobased 3D printable polymeric materials. N. Kasmi, G. Mertz, V. Berthé, R. Dieden, Y. Habibi

1:55 292. TPO nanoparticle as water-soluble photoinitiator and CNC as a rheological modifier for extrusion-based 3D printing technique. D. Kam, A. Briner, L. Larush, A. Chiappone, O. Shoseyov, S. Magdassi


3:10 Concluding Remarks.

Pennsylvania Convention Center
Broad Street Atrium - Theater 12

Innovative Lignin Upgrading: Smart Materials & Specialty Chemicals

Value-Added Products from Lignin

C. Crestini, H. Lange, M. K. Osterberg, M. Sipponen, Organizers
H. Lange, M. H. Sipponen, Presiding

1:00 Introductory Remarks.


2:45 299. Enhancing the broad-spectrum ultraviolet adsorption of lignin through grafting modification and reverse self-assembly. **Y. Qian**, Y. Wu, X. Qiu


3:35 Concluding Remarks.

Section E

Pennsylvania Convention Center
Broad Street Atrium - Theater 13

**Cellulose & Renewable Materials for Gas, Air & Water/Liquid Purification**

A. Mautner, T. Tammelin, **Organizers**
U. Edlund, A. Mathew, **Organizers, Presiding**

1:00 Introductory remarks.

1:05 301. Processing and upscaling potential of functionalized nanocellulose as films and coatings for various purification applications. **V. Kumar**, K. Vesa, A. Jaiswal, V. Rissanen, T. Kaljunen, T. Tammelin

1:30 302. Surface modification of commercial membranes using antifouling nanocellulose coatings. **A. Aguilar Sanchez**, B. Jalvo, A. Mautner, S. Nameer, A. Mathew


2:20 304. Tempo-CNF coated viscose: Water treatments applications. **A. Pérez Marz**

2:45 305. Lignin-based graphene encapsulated iron nanoparticles for water purification. **X. Zhang**, J. Zhang

Green Polymer Chemistry: New Products, Processes & Applications

Oil- & Lignin-Containing Materials

Sponsored by POLY, Cosponsored by AGFD and CELL

WEDNESDAY MORNING

Pennsylvania Convention Center
126A

Colloidal Assembly of Renewable Materials

Cosponsored by COLL and PMSE
A. Bismarck, I. Capron, Y. Habibi, Organizers
S. Spirk, Presiding

8:00 Introductory Remarks.


8:30 308. New high performance starch based emulsifiers using amylose inclusion complexes. *G.W. Selling*, W. Hay

8:55 309. Assembly of cellulose nanocrystals into 2D cellular networks during spin coating. *E. Kontturi*


9:45 Intermission.

10:00 311. Spherically confined cholesteric liquid crystals of hydroxypropyl cellulose. *A. Chakrabarty*, K. Miyagi, Y. Teramoto

10:50 313. Controlled supramolecular assembly of reducing end-functionalized tunicate cellulose nanocrystals. M. Chemin, C. Moreau, B. Cathala, A. Villares

11:15 314. Cellulose nanocrystal holograms. B. Frka-Petesic, R. Parker, C.A. Williams, S. Vignolini

Section B

Pennsylvania Convention Center
126B

Nanocellulose: From Fundamentals to Function

Cosponsored by COLL and PMSE
Financially supported by RISE
T. Abitbol, S. Kedzior, E. Niinivaara, M. Reid, Organizers, Presiding

8:00 Introductory Remarks.

8:05 315. Ion-specific assembly of nanocellulose: Theory and applications. T. Benselfelt, L. Wagberg

8:30 316. More than paper: Cellulose printing for custom-tailored photonics. c. guang, E. Zussman, O. Rojas


9:45 Intermission.


10:25 320. Bound oligosaccharides and their interactions with water on CNCs produced using aqueous versus gaseous acid hydrolyses. E. Niinivaara, T. Pääkkönen, E. Kontturi, E.D. Cranston


11:40 Concluding Remarks.

Section C

Pennsylvania Convention Center
Broad Street Atrium - Theater 11

Wood Based Polymers to Tackle Global Challenges

Tackling Global Challenges

Cosponsored by PMSE, POLY and SCHB
T. Nypelo, Organizer
K. Heise, S. Spirk, Organizers, Presiding

8:00 Introductory Remarks.

8:05 323. Swelling and visco-elastic behaviour of wood in mixed solvents: Stationary and transient states. J. Bossu, G. Dusfour, S. Corn, P. Trens, Q.K. Tran, N. Le Moigne, F. Di Renzo

8:30 324. Cationic starch in jet cooking: Dissolution, rheology and interaction with cellulosic surfaces. M. Gabriel, F. Gomernik, F. Thaler, A. Chemelli, S. Spirk


9:45 Intermission.

10:00 327. Wood-based cellulosic fibers and how they can help solving environmental issues. M. Opietnik, C. Weilach, S. Kulka, J. Innerlohinger

10:25 328. Wood for energy 2.0. K. Miettunen, J. Vapaavuori, O. Rojas


Section D
Innovative Lignin Upgrading: Smart Materials & Specialty Chemicals

Advances in Lignin Nanoparticles

C. Crestini, H. Lange, M. K. Osterberg, M. Sipponen, Organizers
H. Lange, M. H. Sipponen, Presiding

8:00 Introductory Remarks.

8:05 331. Green, rapid and direct preparation of lignin nanoparticles from alkaline pulping liquor. M.B. Agustin, P. Penttilä, M.H. Lahtinen, K.S. Mikkonen


8:55 333. Lignin nanoparticles as vehicles for transport and release of actives. S. Caiotto, M. Gigli, C. Crestini


9:45 Intermission.

10:00 335. Facile method to stabilize colloidal lignin particles by intraparticle cross-linking. T. Zou, M. Sipponen, M.K. Osterberg

10:25 336. Lignin/Fe3O4 nanoparticles derived from different eucalyptus lignin fractions. I. Pylypchuk, A.V. Riazanova, M. Lindström, O. Sevastyanova


11:40 Concluding Remarks.
Pennsylvania Convention Center  
Broad Street Atrium - Theater 13

**Cellulose & Renewable Materials for Gas, Air & Water/Liquid Purification**

**Water Purification Materials & Aspects**

A. Mautner, T. Tammelin, *Organizers*  
U. Edlund, A. Mathew, *Organizers, Presiding*

8:00 Introductory remarks.

8:05 339. Sustainable water purification using biomass nanofibers. **B.S. Hsiao**, P.R. Sharmar

8:30 340. Water filters by foam coating of TEMPO-CN. **A. Mautner**, Q. Jiang, K. Vesa, A. Jaiswal, A. Bismarck


9:45 Intermission.

10:00 343. Bioinspired concepts for clean water and air. **T. Tammelin**


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**Green Polymer Chemistry: New Products, Processes & Applications**

**Peptides, Proteins & Polyimides**

Sponsored by POLY, Cosponsored by AGFD and CELL
WEDNESDAY AFTERNOON

Pennsylvania Convention Center
126A

Colloidal Assembly of Renewable Materials

Cosponsored by COLL and PMSE
A. Bismarck, I. Capron, Y. Habibi, Organizers
G. W. Selling, Presiding


1:30 348. Mercerized cellulose nanocrystals: From structure to interface organization. I. Capron, S. haouache, C. Jimenez-Saelices, f. jerome


2:20 350. Cellulose based devices based on thin film composites. G. Trimmel, S. Spirk

2:45 Intermission.

3:00 351. Mechanisms controlling mobility of cellulose nanofibers in the dilute to semi-dilute regime: Influence of semi-flexibility?. D. Soderberg

3:25 352. Interaction of cellulose nanocrystals with lipid bilayers. y. navon, B.R. Jean, A. Bernheim, L. Heux


4:15 354. Microstructure arrays of cellulose nanocrystals in liquid crystal bubbles via topographical control. W. Xiang, G. Chu, O. Rojas

4:40 Concluding Remarks.

Section B

Pennsylvania Convention Center
126B
Nanocellulose: From Fundamentals to Function

Cosponsored by COLL and PMSE
Financially supported by RISE
T. Abitbol, S. Kedzior, E. Niinivaara, M. Reid, Organizers, Presiding

1:00 Introductory Remarks.


1:55 357. Tuning the thermal conductivity of phonon-engineered cellulose nanomaterial-based foams by modifying the surface chemistry. V. Apostolopoulou Kalkavoura, T. Kaldéus, P. Munier, L. Dlugozima, E.E. Malmstrom, L. Bergstrom


2:45 Intermission.

3:00 359. Time-dependent behavior of cellulose nanofiber networks: Effect of grammage on creep properties and strain-rate dependency. A. Santmarti, H. Liu, K. Lee


3:50 361. Structuration of hard materials using cellulose nanomaterials. J. Foster


4:40 Concluding Remarks.

Section C

Pennsylvania Convention Center
Broad Street Atrium - Theater 11

Wood Based Polymers to Tackle Global Challenges

Energy & Interfaces


2:45 Intermission.


Section D

Pennsylvania Convention Center
Broad Street Atrium - Theater 12

**Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems**

J. Campos-Teran, O. Rojas, Organizers
M. L. Auad, Organizer, Presiding

1:00 Introductory Remarks.


1:55 373. Characterization of lignin for preparing lignin modified phenolic resin as wood adhesives. A. Bansode


2:45 Intermission.

3:00 375. Sustainable rice hull pretreatment for bioproducts. J. Lynam


3:50 377. Valorization of cocoa shells: Effect of two different chemical treatments on physical and chemical properties of cellulose nanofibers. C. Gomez Hoyos, J.A. Velasquez, P. Mazo, L. Penagos, R. Zuluaga Gallego


Section E

Pennsylvania Convention Center
Broad Street Atrium - Theater 13

Cellulose & Renewable Materials for Gas, Air & Water/Liquid Purification

Water & Air

U. Edlund, A. Mathew, Organizers
A. Mautner, T. Tammelin, Organizers, Presiding

1:00 Introductory remarks.

1:05 379. Atomic force microscopy as a tool to probe nanocellulose interactions with water pollutants. A. Mathew
1:30 380. Thin films of nanocellulose: Interactions with water, vapor, and gases. **E. Kontturi**

1:55 381. Unravelling the spontaneous formation of metal oxide nanoparticles on cellulose nanofibrils during adsorption of metal ions: Green alternative towards multifunctional hybrid materials. **L.A. Valencia, A. Mathew**

2:20 382. Design of nanoscaled environmental scavengers from biomass: Descriptive and predictive computational modelling as support to the experimental strategies. **S. Monti, A. Mathew**

2:45 Intermission.

3:00 383. Toward smart and safe engineered materials and devices for clean air and water. **U. Edlund**


3:50 385. *In situ* fermentation derived micro-nano composites with contrast wettabilities and application in oil-water filtration. **S. C R, a.P. Veedu, M. Khandelwal**


4:40 Concluding Remarks.

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**Green Polymer Chemistry: New Products, Processes & Applications**

**Polysaccharides & Related Materials**

Sponsored by POLY, Cosponsored by AGFD and CELL

**THURSDAY MORNING**

Pennsylvania Convention Center
103A

**Bio-Based Gels & Porous Materials**

Cosponsored by COLL and PMSE
T. Budtova, F. Liebner, *Organizers, Presiding*
8:00 Introductory Remarks.

8:05 387. Aerogels from pulps: Influence of pulp composition and non-solvent type on aerogels’ properties. L. Druel, L. Salmen, E. Brännvall, F. Alvarado, T. Budtova

8:30 388. Aerogels directly from whole biomass: Fabrication and mechanistic study. Y. Liao, Z. Pang, X. Pan


9:20 390. Amphiphilic to hydrophobic nanocellulose aerogels via ice-templating, sol-gel and organogel. Y. Hsieh

9:45 Intermission.


Section B

Pennsylvania Convention Center
103B

Nanocellulose: From Fundamentals to Function

Cosponsored by COLL and PMSE
Financially supported by RISE
T. Abitbol, S. Kedzior, E. Niinivaara, M. Reid, Organizers, Presiding

8:00 Introductory Remarks.

8:05 395. Reinforcement of guayule and natural rubber latex using nitro-oxidized jute nanofibers. P.R. Sharma, S. Sharma, B. Hsiao
8:30 396. TEMPO oxidized cellulose-reinforced composites: Pulp or nanofibrillated-cellulose?. A. Gaduan, K. Lee


9:20 398. In situ Modification of beads from regenerated cellulose: Creating all-cellulose composites. K. Mystek, M. Reid, P.A. Larsson, L. Wagberg

9:45 Intermission.

10:00 399. Molecular mobility and structure of cellulose nanofibrils composites as revealed by broadband dielectric spectroscopy and fast scanning calorimetry. A.M. Elert, P. Szymoniak, M. Farooq, J. Valle-Delgado, M.K. Osterberg, H. Sturm, A. Schoenhals


11:40 Concluding Remarks.

Pennsylvania Convention Center
103C

Wood-Mimics: Hierarchical Structures & Architectures

S. Gaidukovs, Y. Habibi, L. Hu, Organizers
F. Jiang, Presiding

8:00 Introductory Remarks.

8:05 403. Case study tuneable wood: Transfer of bioinspired concepts into bio-based materials. T. Keplinger, M. Frey

8:30 404. Super strong anisotropic cellulose-based films from wood by a cellulose DP protection strategy. Z. Fang, Y. Liu, J. Zhou, X. Qiu
8:55 405. Advanced wood technologies for energy efficient buildings. T. Li

9:20 406. Wood nanotechnologies. L. Hu

9:45 Intermission.

Section C

Pennsylvania Convention Center
103C

Wood Based Polymers to Tackle Global Challenges

Nanofibers & Applications

Cosponsored by PMSE, POLY and SCHB
K. Heise, Organizer
T. Nypelo, S. Spirk, Organizers, Presiding


10:50 409. Poly(ethylene glycol) as a coating agent to prevent hornification of cellulose nanofibres. A. Santmarti, K. Lee

11:15 410. Fabrication and properties of electrospun cellulose nanofibres from ionic liquid. S. Sriubaite, M. Bulota, E. Krugly, D. Ciuzas, D. Martuzevicius

11:40 411. Safer-by-design approach for the elaboration of versatile nanocellulose-based hybrid particles for photocatalytic applications. H. Voisin, I. Capron

12:05 Concluding Remarks.

Section D

Pennsylvania Convention Center
106B

Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems
8:00 Introductory Remarks.

8:05 412. Robust poultry feather fibre preform: Upcycling waste feathers with (nano)cellulose. V. Vilchez, E. Dieckmann, C. Cheeseman, K. Lee

8:30 413. Combining tannins with cellulose biocolloids towards functional materials. B. Mattos, A. Missio, E. Hahnert, B. Tardy, O. Rojas


9:45 Intermission.

10:00 416. Integrated process to recover extractable, starch- and cellulose-derived sugars from food waste. Q. Jin, N. Poe, H. Wang, H. Huang

10:25 417. Carboxylated cellulose nanofibrils (R-CNFS) as an additive in water based drilling fluids (WBMs) applied to shale formatio. Y. Villada Villada, M.C. Iglesias, J. Zhu, N. Casis, M.S. Peresin, D. Estenoz

10:50 418. Wet stable nanocellulose-based materials with tannins. K. Kriechbaum, L. Bergstrom


Section E

Pennsylvania Convention Center
107A

Raman Spectroscopy Applications in the Field of Celluloses & Lignocelluloses & their Major Components

U. P. Agarwal, Organizer
8:00 Introductory Remarks.

8:05 420. Non-destructive imaging of lignin chemistry in plant cell wall using hyperspectral stimulated Raman scattering microscopy. S. Ding

8:30 421. Deformation and imaging of cellulose using Raman spectroscopy. S.J. Eichhorn


9:20 423. Raman spectra of Valonia and Tunicata: Questions they raise about the structures of celluloses Iα & Iβ. R.H. Atalla

9:45 Intermission.

10:00 424. New insights into wood-based nanocomposites by Raman spectroscopy imaging. T. Keplinger


11:40 428. From the soft to the hard: Changes in microchemistry during cell wall maturation of walnut shells. N. Xiao, N. Gierlinger

Green Polymer Chemistry: New Products, Processes & Applications

Novel Polymers

Sponsored by POLY, Cosponsored by AGFD and CELL

THURSDAY AFTERNOON

Pennsylvania Convention Center
103A
Bio-Based Gels & Porous Materials

Cosponsored by COLL and PMSE
T. Budtova, F. Liebner, Organizers
B. Cathala, O. T. Ikkala, Presiding

1:00 Introductory Remarks.


1:30 430. Pineapple aerogels from agricultural waste for engineering applications. N.H. Do, T. Luu, Q.B. Thai, D.K. Le, P.K. Le, H. Duong


2:20 432. Self-healing and conductive double network hydrogel with enhanced mechanical property. Y. Zou

2:45 Intermission.

3:00 433. UV-triggered on-demand thermoreversible and irreversible gelation of cellulose nanocrystals. O.T. Ikkala, C. Hoerenz, K. Bertula, T. Tiainen, S. Hietala, V. Hynninen


4:40 Concluding Remarks.

Section B

Pennsylvania Convention Center
103B

Nanocellulose: From Fundamentals to Function
Cosponsored by COLL and PMSE
Financially supported by RISE
T. Abitbol, S. Kedzior, E. Niinivaara, M. Reid, Organizers, Presiding

1:00 Introductory Remarks.

1:05 437. Drying induced brittle-to-ductile transition of bacterial cellulose nanofiber network. W. Song, N. Herrera-Vargas, J. Li, K. Lee

1:30 438. Understanding the mechanical performance of nanocellulose nanopapers and bioinspired nanocomposites. A. Walther


2:45 Intermission.

3:00 441. Tough bacterial cellulose films for transparent composite applications. N. Herrera-Vargas, K. Lee

3:25 442. Synthesis of microcapsules consisting of a hexadecane core and a cellulosic shell for thermal energy management. G. Bahsi Kaya, Y. Kim


4:15 444. Nanocelluloses as texturizers in industrial applications. E. Heggset, K. Syverud

4:40 Concluding Remarks.

Section C

Pennsylvania Convention Center
103C

Wood-Mimics: Hierarchical Structures & Architectures

S. Gaidukovs, Y. Habibi, L. Hu, Organizers
T. Keplinger, Presiding
1:05 445. Hydrogen-bonding-induced assembly of aligned cellulose nanofibers into ultrastrong and tough bulk materials. X. Han, Y. Ye, F. Jiang

1:30 446. Additive manufacturing of 3D structures composed of wood materials. D. Kam, M. Layani, O. Shoseyov, S. Magdassi


2:20 448. Wood-like biodegradable polybutylene succinate / nanocellulose composites with controlled interface properties. S. Gaidukovs, A. Barkane, O. Platnieks, I. Filipova, V. Thakur

2:45 Intermission.

3:00 449. Mechanics of cellulose nanomaterials using a bottom-up scalable modeling scheme. T. Li


4:15 452. Wood-derived materials and structures for multiple applications. H. Zhu

4:40 Concluding Remarks.

Section D

Pennsylvania Convention Center
106B

Valorization of Renewable Resources & Residuals into New Materials & Multiphase Systems

M. L. Auad, J. Campos-Teran, O. Rojas, Organizers

1:00 Introductory Remarks.


1:30 454. Swelling and softening mechanisms of natural fibres under hygro- and hydrothermal conditions. W. Garat, N. Le Moigne, S. Corn, J. Beaugrand, A. Bergeret


2:45 Intermission.

3:00 457. Valorization of agro-food residues to obtain multifunctional biopolymers for building and automotive parts processed through additive manufacturing, BARBARA project. **A. Jimenez**, F. Vilaplana, D. Puglia, L. García, M. Garrigós


4:40 Concluding Remarks.

Section E

Pennsylvania Convention Center
107A

**Raman Spectroscopy Applications in the Field of Celluloses & Lignocelluloses & their Major Components**

U. P. Agarwal, N. Gierlinger, *Organizers*
S. J. Eichhorn, T. Keplinger, *Presiding*

1:05 461. Linear (IR & Raman) versus non-linear (SFG) vibrational spectroscopy for plant cell wall study: Pros and cons. **S.H. Kim**, M. Makarem


2:45 Intermission.

3:00 465. Insight into plant cell morphological and molecular structure by combination of Raman scattering with multimodal micro-spectroscopy at different scales. J. Kneipp, R. Elbaum, V.R. Zancajo, Z. Heiner, I. Liedtke, S. Diehn

3:25 466. Label-free visualization of fungal cell and spore wall architecture by confocal Raman microscopy. H. Noothalapati, T. Yamamoto


4:40 469. Raman spectroscopy for analyzing cellulosic and cellulose materials. U.P. Agarwal

5:05 Concluding Remarks.

Green Polymer Chemistry: New Products, Processes & Applications

Additive Manufacturing & Advanced Processes

Sponsored by POLY, Cosponsored by AGFD and CELL
CELL 1

From modification of lignin, and starch and cellulose surfaces, to nanoparticle assembly and cell-growth materials: Playing around in Ann Christine’s world

_Wim Thielemans, wim.thielemans@kuleuven.be_. Chemical Engineering, KU Leuven, Kortrijk, Belgium

Over the past 15 years, I have worked on wide variety of renewable materials and molecules that have touched on Ann-Christine’s work and interests in renewable materials. In honor of Ann-Christine Albertsson, this year’s Anselme Payen award winner, I will present a selection of this effort using our published work in Biomacromolecules as a thread:

1. Modification of kraft lignin for use in petroleum and plant-oil based thermosets and natural fiber composites,
2. Surface modification of starch and cellulose nanocrystals for different applications,
3. Gelation and assembly of modified cellulose nanocrystals, and
4. Use of cellulose and starch nanocrystals in cell-growth materials.

The links between the different studies and cross-fertilization between projects will be highlighted, together with work branching from this central thread.

CELL 2

Lignocellulosic nanoparticles: From fundamental understanding of interactions to biomedical applications

_Monica K. Osterberg, monika.osterberg@aalto.fi_. Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland

There is a growing interest to replace synthetic polymers and animal based proteins with plant-based nanomaterials for biomedical applications. Cellulose nanofibril (CNF) hydrogels have been used both for cell culture and for 3D bioprinting of tissue mimics. Spherical lignin nanoparticles or colloidal lignin particles (CLPs) have also recently gained interest for applications ranging from drug delivery to emulsion stabilization and energy storage. However, the lignocellulosic nanoparticles need surface modification or additives for optimal performance. For example, the 3D printed constructs need modification for dimensional stability during storage and use in physiological conditions. To enable surface tailoring it is essential to understand the interactions between the lignocellulosic nanoparticles and living cells or proteins. Well-defined model substrates from CLPs were prepared and microgravimetry (QCM-D) was employed to study their swelling behavior and stability as a function of pH as well as adsorption of proteins and cationic lignin used for surface modification. Furthermore, direct surface forces between CNF and extracellular matrix (ECM) proteins like laminin and collagens were studied using atomic force microscopy (AFM). The forces between living cells (human hepatocellular carcinoma cells, HepG2 and human pluripotent stem cells, WA07) and CNF were also measured. The results were compared to forces between cells and ECM
proteins like laminin and collagens, that are commonly used in cell culture. Different concentrations of CLPs were added to CNF-alginate hydrogels to improve the shape stability of 3D-printed constructs. The prepared scaffolds showed improved stability in cell culture medium. The cell viability of HepG2 cells in the modified hydrogels was investigated. The number of living cells increased at least two times for all the formulated scaffolds within a 5 days of cell culturing. The biocompatibility and mechanical properties of the lignocellulosic nanoparticles makes them promising for biomedical applications and the gained fundamental understanding of surface interactions will enable their tailoring.

CELL 3

Entropy-driven adsorption of cellulose ethers to cellulose nanocrystals: Comparing 2D vs. 3D adsorption trends and Pickering emulsion performance

Lingli Liu¹, Stephanie A. Kedzior², Zhen Hu¹, Marco Maccagno⁴, Jing Guo⁵, Tiffany Abitbol³, Isabel Mira⁴, Emily D. Cranston⁶,⁷, emily.cranston@ubc.ca. (1) Chemical Engineering, McMaster University, Hamilton, Ontario, Canada (2) Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada (3) RISE Bioeconomy, Stockholm, Sweden (4) RISE Bioscience and Materials, Stockholm, Sweden (5) Dupont Nutrition & Bioscience, Midland, Michigan, United States (6) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (7) Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada

The interactions between common food-grade polymers and nanocellulose are important for the design of formulated products and hybrid materials such as emulsions, gels, foams and films. In this work, the interactions between 11 cellulose ether types (two commercial METHOCEL™ series) and cellulose nanocrystals (CNCs) were investigated by comparing polymer adsorption to model CNC films and to CNCs in aqueous suspension. It was found that methylcellulose and hydroxypropyl methylcellulose irreversibly adsorbed to CNCs in 2D and 3D, and higher hydroxypropyl content and lower methoxy content led to more adsorption. Isothermal titration calorimetry and quartz crystal microbalance (at varying temperature) indicated that adsorption was entropically driven, by the release of water molecules from the CNC surface and the cellulose ethers. Partial least squares multivariate statistical analysis suggested that the degree of substitution was the primary factor governing cellulose ether adsorption in 2D, whereas molecular weight and degree of substitution were significant factors in 3D adsorption. The use of CNCs and cellulose ethers as co-stabilizers was found to impart “extreme stability” to Pickering emulsions, e.g. emulsions that remain stable after multiple freeze-thaw and heat-cool cycles, emulsions that stay intact through the majority of the (simulated) digestive tract, and emulsions that can be completely dried to remove the continuous water phase for encapsulation applications. Similarly, CNC–cellulose ether combinations were used to stabilize microsuspension polymerization and allowed for latex morphology and surface properties to be tailored. The ability to make stable emulsions and latexes in a controlled manner using non-toxic
nanoparticles is relevant for envisioned products across a range of industrial sectors including food, cosmetics, adhesives, paints/coatings, oil and gas, and pharmaceuticals.

**CELL 4**

**Functionalization and patterning of nanocellulose-based foams and films with tannins**

*Lennart Bergstrom, lennart.bergstrom@mmk.su.se.* Stockholm University, Stockholm, Sweden

Versatile processing routes that utilize renewable or Earth abundant resources and additives are needed to enable scalable production of multifunctional foams, aerogels and films for applications including packaging, sensors and energy storage, e.g. thermal insulation. This presentation will give examples how tannins, the second most abundant aromatic polymer, can be used to both control and tune the rheological properties and to infer specific functionalities to nanocellulose-based foams and films.

We have developed and investigated polysaccharide-based composite foams for 3D printing of lightweight structures. The rheological properties of the wet foams and the resistance to shrinkage during drying were tuned by addition of e.g. tannic acid and glyoxal and the drying temperature. Tannic acid addition optimized the microstructure and the viscoelastic properties of the wet foam for direct ink writing of lightweight and water-resilient structures that could be post-functionalized. Inspired by the ancient *Bogolanfini* dyeing technique from Mali, we have functionalized and patterned nanocellulose films by surface-bound nanoparticles of hydrolyzable tannins and multivalent metal ions with tunable colors. AFM and electron microscopy showed that the tannin-metal ion nanoparticles formed by an in-fibre reaction between the pre-impregnated tannin and the metal ions in the printing ink. Patterning of CNF films with metal ion-hydrolyzable tannin nanoparticles is a versatile route to functional films based on organic materials derived from trees and abundant metal ions.

**CELL 5**

**Materials from cellulosic wood fibers or fibrils: Why are mechanical properties different?**

*Lars Berglund, blund@kth.se.* Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Cellulose nanofibrils from wood are important building blocks in new materials, and typically have diameters in the 3-15 nm range. One argument in favor of nanocellulose materials is that very high mechanical properties can be achieved. This is also true for materials from cellulosic wood fibers, although they have mm-scale length and diameters of 20-30μm. In order to make fair comparison of films, they need to have similar porosity and fiber/fibril organization (random-in-plane, oriented etc). Such comparisons are important, not only for the selection of fiber and fibrils, but also...
because absolute numbers for material properties are important for comparisons with molded glass fiber reinforced plastics from petroleum-based polymers.

Data indicate that materials from cellulosic wood fibers can even have higher modulus than films based on cellulose nanofibrils. Reasons for this are analyzed. When it comes to ultimate strength, the nanocellulose films show better properties since damage development is delayed to larger strains, compared with materials based on 30μm diameter fibers. The properties of cellulose fiber/fibril composites with a polymer matrix can be modulated by the choice of fiber volume fraction, polymer matrix and fiber orientation distribution. Interestingly, wood fiber/polymer composites can show very high strength, provided the wood fiber is well preserved in terms of limited mechanical damage and chemical degradation. There are favorable effects not only from preserving cellulose structure, but also from the preservation of hemicelluloses and their distribution in the fiber cell wall.

CELL 6

Nanocellulose as a versatile platform for 3D-printed functional materials

Aji Mathew, aji.mathew@mmk.su.se, Sahar Sultan. Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

3D printing using cellulose nanomaterials is explored as a processing route for developing materials for different functional applications due to the inherent shear thinning property of nanocellulose aqueous gels. We have recently shown that the remarkable mechanical, chemical and biological properties, and the possibility to support living cells delivers tremendous possibilities for developing nanocellulose based medical implants and scaffolds via 3D printing. For eg. nanocellulose based porous hydrogel scaffold was successfully 3D printed to have gradient porosity / density and cellulose nanocrystal orientation in the pore walls which favors cartilage tissue regeneration. The biocompatibility and cartilage regeneration potential of these scaffolds with osteoblast cells was further enhanced by coating the printed scaffolds with dopamine and growth factors as Fibroblast growth factor (FGF-18). Nanocellulose can also act as template for in situ processing of hybrids with metallic organic frameworks or hydroxyapatite which generates 3D printable inks for hierarchically porous multi-functional materials for targeted drug release and tissue regeneration. Nanocellulose gel based 3D printing thus provides a flexible and green platform for producing a variety of functional materials for biomedical implants, environmental remediation, wearable electronics, etc.

CELL 7

Molecular interface engineering of nano cellulose for improved bio-nanocomposites
In recent works, it has been highlighted the potential of the "bottom-up" design of a molecularly engineered interface nano cellulose for the improvement of targeted properties of the bio-nanocomposite. In order to tackle the challenge of a controlled interface between the nano cellulose and biodegradable polymer matrices, different strategies have been explored.

In this frame, a water-borne reactive compatibilizer was designed for the tuning of the polycaprolactone (PCL)/cellulose nanofibril (CNF) interface, with the aim to tailor the mechanical properties of the corresponding nanocomposite for an improved stress transfer efficiency. This design of an amphiphilic random copolymer, carrying a hydrophilic quaternized ammonium and methacrylate moieties as hydrophobic reactive groups, allowed for self-assembly in the aqueous medium into nanoparticles. A uniform core-shell nanohybrid was formed by adsorbing the reactive compatibilizer adsorbed onto CNF in water dispersion, due to electrostatic interactions as confirmed by AFM. The manually premixed polymer matrix with the water dispersion of the core-shell nanohybrid allowed for a wet feeding approach with efficient evaporation of the water during the melt compounding, (see Figure). A remarkable improvement of the mechanical properties is demonstrated.

In another system, to overcome the intrinsic brittleness of the poly(hydroxybutyrate)-co-poly(hydroxy valerate) PHBV matrix, and at the same time improve their dispersion in the hydrophobic PHBV matrix, cellulose nanocrystals (CNCs) have been synthesized with an innovative green method called one-pot acid hydrolysis/Fischer esterification. The rationale behind this approach has been to overcome the intrinsic brittleness of the PHBV matrix, by using a low amount of tailored surface-modified CNCs as a nucleating agent, for PHBV’s crystallites size reduction. The blend of functionalized CNCs and PHBV has allowed the production of fully biodegradable nanocomposites with improved thermo-mechanical properties.
Figure. Schematic overview of the electrostatic adsorption reactive wet feeding melt processing of the bio-nanocomposites. The PCL radicals are formed by hydrogen abstraction by the peroxide (Luperox®).

CELL 8

Effect of hydrophobized nanocelluloses on synergistic gelation of xanthan and locust bean gums

Rinat Nigmatullin¹, Marcus Johns¹, Valeria Gabrielli², Juan-Carloz Muñoz-Garcia², Saffron Bryant³, Yaroslav Khimyak², Jesus Angulo², Janet Scott⁴, Karen Edler⁵, Stephen J. Eichhorn¹, s.j.eichhorn@bristol.ac.uk. (1) Bristol Composites Institute, University of Bristol, Bristol, United Kingdom (2) School of Pharmacy, University of East Anglia, Norwich, United Kingdom (3) Department of Chemistry, University of Bath, Bath, United Kingdom (4) Building 1S, Centre for Sustainable Chemical Technologies, Bath, United Kingdom (5) University of Bath, Bath, United Kingdom

Polysaccharide mixtures with synergistic effects are exploited in various industrial applications due to their potential in the modification of rheological, or structural, properties of water-based systems; gel formation; and colloid stabilisation. Moreover, colloidal particle – especially nanoparticle – additives have proven to be versatile tools for further alteration of rheological properties. In this contribution, additives of nanocellulose particles have been explored for the modification of gel properties in xanthan and glucomannan mixtures, a well-known polysaccharide combination with synergetic interactions resulting in stronger gels. Highly charged sulphated nanocrystals (CNCs) and TEMPO-oxidized cellulose nanofibrils (OCNFs) and their hydrophobically modified counterparts, hCNCs and hOCNFs, were studied as additives to soluble polysaccharide mixtures. Hydrophobized nanocelluloses were derived from CNCs and OCNFs via coupling with octylamine. Additives of highly charged nanocelluloses had
only marginal effect on the rheological properties of xanthan gum and locust bean gum mixtures (XG/LBG). However, hydrophobized nanocelluloses induced significant increases in gel strength and viscosity. Moreover, hydrophobized nanocelluloses only affected the synergistic gel; rheological properties of neither XG, nor LBG, solutions were affected by the addition of hydrophobized nanocelluloses. The rheological properties of gels with different polysaccharide concentrations and nanocellulose content were studied via oscillatory rheology and steady-shear viscosity measurements. The structure and interactions between components of the complex ternary polysaccharide system were investigated by SAXS, spectral confocal microscopy, Raman and NMR spectroscopy.

CELL 9

Adventures in olefin cross-metathesis of polysaccharides

Kevin J. Edgar¹, kjedgar@vt.edu, Diana Novo², Junyi Chen³, Xiangtao Meng³, Yifan Dong⁴. (1) Virginia Tech, Blacksburg, Virginia, United States (2) Chemistry, Virginia Polytechnic Institute and State University, Miami, Virginia, United States (4) Chemistry, Virginia Tech, Blacksburg, Virginia, United States

Olefin cross-metathesis (CM) was introduced primarily by the group of Robert Grubbs, and contributed to his Nobel Prize in chemistry. Like many other reactions that work well with small molecules, translation of this chemistry to polysaccharides proves to be challenging and often in unexpected ways. Yet olefin CM is extremely attractive in the sense that it is highly chemoselective, fast, mild, and can afford very high, frequently quantitative conversions. Our lab introduced olefin CM to polysaccharide chemistry, and in this presentation we will describe our work in this area, including how we overcame issues of reactivity, selectivity, restricted approach angles, and failed hypotheses. We will describe how olefin CM can provide exciting new polymers for drug delivery, introduce diverse functionality to polysaccharides, append complex entities that have multiple reactive sites like bile acid derivatives, and create highly efficient routes to complex derivatives. We will describe in addition the combination of this click-like reaction with another click reaction, thiol-Michael addition, to efficiently prepare even more highly functionalized derivatives.

CELL 10

Ultrahigh tough regenerated cellulose materials constructed from cellulose solution via double cross-linking

Lina Zhang, zhangln@whu.edu.cn, Ang Lu, Jie Cai, Chunyu Chang, Kunkun Zhu, Dongdong Ye. Wuhan University, Wuhan Hubei, China

Faced with the serious pollution caused by plastics wasters and depletion of petroleum & coal resources, it makes a growing urgency to utilize the renewable resources for producing the environmentally friendly materials. Herein, we have established a new
strategy, namely by combining the aligned nanofibers and the dual-crosslinking the simultaneous strengthening and ultrahigh toughness in the regenerated cellulose materials can be realized. A series of ultrahigh tough and highly strength cellulose materials including fibers, films and hydrogels were constructed from the cellulose solution in alkali/urea aqueous system with cooling, in which the extended stiff chains of cellulose aggregated easily in parallel manner under mild coagulating environment to form dense nanofibers with mean diameter of about 30 nm, displaying an orientation microstructure and excellent mechanical properties. On the basis of the pre-stretching ability of the chemically cross-linking networks and the removability of the cellulose nanofibers and molecular bundles in the hydrogel state, a highly ordered structure in the chemically and physically crosslinked double networks containing nanofibers was created through strong self-aggregation force of the cellulose driven by hydrogen bonds. After thorough washing, the strong interactions in the cellulose hydrogel generated enough forces to tightly fix ("freeze") the oriented nanofibrinous structure and designed shape, leading to the formation of the ultrahigh tough materials. For example, the tensile strength and specific strength of the cellulose films achieved to 253 MPa and 217±15 MPa g⁻¹ cm³, to close the lightweight titanium alloy (244 MPa g⁻¹ cm³).

CELL 11

What we’ve learned about lignification since the 2014 Anselme Payen Award

John Ralph, jralph@wisc.edu. U. Wisconsin-Madison, Madison, Wisconsin, United States

Lignins, the aromatic polymers deposited in plant secondary cell walls during lignification, continue to fascinate plant researchers. The traditional definition, that lignins derive from the primary monomers, the three monolignols, no longer suffices to describe the range of polymers found. Each year, the nature of what constitutes a lignin monomer, and the definition of lignin itself has had to evolve. We describe some of the intriguing findings since the 2014 Anselme Payen event, mainly from our lab and its collaborators, that is causing not only an evolving redefinition of lignin but, inspired by Nature herself, is allowing us to consider actually redesigning the polymer for improved properties and value.

CELL 12

Microfibril structures based on distribution of C6-carboxy groups in TEMPO-oxidized wood, cotton, and algal cellulose nanofibrils

Yuko Ono¹, Yoshiki HORIKAWA², Akira Isogai¹, aisogai@mail.ecc.u-tokyo.ac.jp. (1) Univ Tokyo, Tokyo, Japan (2) Tokyo University of Agriculture and Technology, Tokyo, Japan

TEMPO-mediated oxidation has opened new chemistry field of cellulose science and technology. This is because C6-OH groups exposed on native cellulose microfibril
surfaces are position-selectively oxidized to sodium C6-carboxylate groups in water at room temperature under moderate conditions. Osmotic effects and electrostatic repulsions efficiently work between the anionically charged TEMPO-oxidized cellulose microfibrils, resulting in complete individualization of TEMPO-oxidized cellulose nanofibrils by gentle mechanical disintegration in water. Therefore, individualized and isolated cellulose microfibrils without any aggregation are visualized as TEMPO-oxidized cellulose nanofibrils by TEM or AFM. In this study, distributions of carboxy groups among the molecules in TEMPO-oxidized cellulose nanofibrils prepared from wood, cotton, and algal celluloses were investigated. Most C6-carboxy groups in TEMPO-oxidized cellulose nanofibrils were esterified with anthracene-methyl groups, showing an UV absorption peak at 365 nm. The anthracene-methylated TEMPO-oxidized cellulose nanofibrils were dissolved in 8% LiCl/DMAC. After dilution to 1% LiCl/DMAC, the solutions were subjected to size-exclusion chromatography with multi-angle laser-light scattering, refractive index, and UV detection. For TEMPO-oxidized algal cellulose nanofibril, C6-carboxy group-rich molecules were present predominantly in the low-molar-mass region, which was consistent with the core-clad cellulose chain packing structures in individual algal cellulose microfibrils and partial depolymerization of the oxidized cellulose molecules. In contrast, TEMPO-oxidized wood and cotton cellulose nanofibrils had almost homogeneous distributions of C6-carboxy groups in all molar mass regions, indicating that each cellulose microfibril in higher plants consisted of interdigitated cellulose chain packing structures. Because formation of the interdigitated packing structures are possibly caused by the formation of periodically disordered regions present along the longitudinal direction of each cellulose microfibril, never-dried plant cellulose samples were used as starting materials for TEMPO-mediated oxidation, disintegration in water to prepare nanofibrils, and distribution analysis of C6-carboxy groups in the TEMPO-oxidized cellulose nanofibrils.

**CELL 13**

**Twist geometry of nanocelluloses probed by electron microdiffraction**

**Yu Ogawa**, ogawa@cermav.cnrs.fr. Cermav, CNRS, Grenoble, France

The intrinsic chirality of cellulose crystals provides them with high added values such as chiral induction ability. At the nanoscale, this chirality is connected to the right-handed longitudinal twisting of these fibrous crystallites. However, this nanoscale fibrillar twist has been a matter of debate due to contradictory observations between microscopic analyses and molecular simulations and so far, the exact twist geometry has not been elucidated.

In this study, I performed an electron microdiffraction analysis of tunicate cellulose nanocrystals (CNCs) under cryo-frozen and dry conditions. Sequential microED acquisitions along a longitudinal axis of single nanocrystal revealed the continuous twisting of CNCs in aqueous suspension. This regular twist was drastically modified to discontinuous sharp twists when the CNCs are dried on a flat surface. In this presentation, I will also discuss the variations of twist geometries among different cellulose specimens.
Nanocellulose and 2D conductors: Interactions and forces studied by colloidal probe atomic force microscopy

Michael S. Reid, reidms@mcmaster.ca, Lars Wagberg. Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

With the continued demand for renewable and biodegradable technologies, the potential applications of nanocellulose has expanded to include biomedical devices, catalyst supports, coatings, advanced papers and electronics just to name a few. In many of these applications cellulose nanofibrils (CNFs) or cellulose nanocrystals (CNCs) are used synergistically with small molecules, polymers and other nanoparticles to create advanced hybrid materials. Yet for many applications the interactions between the components are not well understood. While adsorption studies can provide insight, in many cases it can be difficult to predict and measure specifically how nanocellulose interacts with other constituents in hybrid materials. Moreover, adsorption studies do not address how cellulose-cellulose interactions are altered by the incorporation of other materials. By using colloidal probe atomic force microscopy (CP-AFM), nanoscale interactions such as van der Waals, electrostatic double layer and steric forces can be directly measured in a variety of environments. In this work we explore how CPAFM can be used to extract nanoscale interactions to support the design and processing of renewable composite materials. Specifically, we investigate the interactions between nanocellulose and 2D conductors such as graphene in varying ionic strength and pH. Additionally, substrate composition, layer number and chemical functionalization are investigated to provide deeper insight into these interactions. This work aims to highlight that understanding nanoscale interactions is essential for the development of nanocellulose applications as many hybrid materials contain a complex mixture of components.

Pickering emulsions as synthetic tool for nanocellulose modification

Katja Heise\textsuperscript{1}, katja.heise@aalto.fi, Mauri Kostiainen\textsuperscript{2}, Eero Kontturi\textsuperscript{3}. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (3) Department of Bioproducts and Biosystems, Aalto University, Aalto, Finland

Cellulose nanocrystals (CNCs) offer an enormous potential for high-end material applications, not least based on their high tensile properties, long-range chirality, and unique water-response. This property spectrum has been largely expanded by tailored surface modifications. However, owing to the CNCs anionic nature and inherent hydrophilicity, chemical surface modifications are often confronted with a loss in accessibility associated with an uncontrolled aggregation of CNCs in the presence of most organic solvents, salts, or reaction by-products. In this study, we explore the oil-water interface as synthetic environment for controllable chemical CNC modifications,
exploiting the CNCs irreversible self-assembly at the interface forming the so-called oil-in-water Pickering emulsions (o/w PEs). Starting from 2,2,6,6- tetramethyl-piperidinyl-1-oxy radical oxidized CNCs (TCNCs), which provide C6-carboxylates reaction sites, our investigations initially targeted a thorough evaluation of the PEs stability by systematically altering the bulk-water phase conditions (e.g. presence of co-solvents, pH, ionic strength) and the TCNC concentrations (0.5 - 0.5 wt%). The emulsions where thereby monitored using microscopic (optical and scanning) and light-scattering techniques. The accessibility of TCNCs assembled to the interface and the controllability of the reactions system were further evaluated by applying well-established electrostatic (quaternary amine) and covalent (carbodiimide-mediated peptide coupling) modification strategies, which enabled mild functionalization of the droplets in the water phase with low-molecular-weight building blocks. This functionalization was assessed by advanced solution-state 1D and 2D NMR techniques. Compared to conventional, dispersion-state CNC modifications, we foresee an enormous potential for PEs as neoteric synthetic tool, which may be the answer towards challenges related to the controllability of CNC surface modifications and which may open up totally new avenues for the large-scale fabrication of sophisticated nanocellulose-based materials.

CELL 16

Preparation of cellulose nanocrystals bearing diverse functional moieties for material design

Kai Zhang, khang1@uni-goettingen.de. Wood Technology and Wood Chemistry, University of Goettingen, Goettingen, Germany

Cellulose nanocrystals as one important type of nanocellulose have great potential for various applications. Although there are already a couple of methods for their preparation, efficient and sustainable methods are still desired. A novel method based on the periodate oxidation for the preparation of cellulose nanocrystals bearing carboxyl groups as functional moieties on surface was developed, which can stabilize high internal phase oil-in-water Pickering emulsions. In comparison, esterification of cellulose using acid chloride leads to cellulose nanocrystals that are well dispersed in organic solvents due to surface-attached hydrophobic chains. These organo-dispersible cellulose nanocrystals form microsized helices during the evaporation-driven self-assembly, which is affected by several surroundings parameters, such as substrates, concentrations of cellulose nanocrystals and surface-attached alkane chains. Furthermore, cellulose nanocrystals via TEMPO-oxidation can be well aligned in dynamic hydrogels by constructing the polymeric hydrogel networks using dynamic covalent bonds. Due to highly different relaxation behaviors between cellulose nanocrystals and the hydrogel matrix, combined solid and liquid material behaviors can be observed, which allows the fabrication of a broad range of functional materials.

CELL 17
Sulfonyl-modification of cellulose nanocrystals and their interactions in aqueous media

Reeta Salminen¹, reeta.salminen@kuleuven.be, Wim Thielemans². (1) Chemical Engineering, KU Leuven Kulak, Kortrijk, Belgium (2) Chemical Engineering, KU Leuven, Kortrijk, Belgium

Surface modification of cellulose nanocrystals (CNC) have been well-studied for the possible tuning of the CNC properties and applications. One of the properties that is affected by CNC surface modification is their interactions among themselves and with other moieties. In this study, CNCs were modified by an autocatalyzed esterification using (4-chlorosulfonyl) benzoic acid, which results in anionic benzosulfonyl grafts on the CNC surface. The reaction mechanism follows a tosyl chloride-catalyzed esterification. However, (4-chlorosulfonyl) benzoic acid contains both the catalyst and a carboxylic acid required for the esterification. As the intermediate sulfonyl ester is replaced with a more stable ester bond, the sulfonyl group is left pointing outwards in the final product. The degree of substitution could be tuned by the reaction time and the amine co-catalyst (pyridine, triethylamine, and diisopropylethylamine). The maximum degree of substitution reached was 0.3 which roughly translates to a surface degree of substitution of 1. Additionally, due to the acidic nature of the sulfonyl, the protonated amine co-catalyst remained in the product as the sulfonyl counter ion. The counter ion was found to affect the interactions between CNCs and hence their colloidal stability. Therefore, the counterion-sulfonyl interaction were investigateds by isothermal titration calorimetry and correlated with the degree of substitution and acid content. Finally, CNC interactions with di- and tetravalent ammonia were also investigated.

CELL 18

Conductive cellulosic materials for flexible organic electronic applications

Mehr Mirvakili, mirvakili.chbe@gmail.com, Siham Atifi, Wadood Y. Hamad. Biomaterials Division, FPInnovations, Vancouver, British Columbia, Canada

Organic semiconducting polymers are promising candidates for various flexible optoelectronic devices application due to their competitive price and low processability requirements. Poly (3,4- ethylene dioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) is the most successful conducting polymer that is commercially available. In this study, cellulose nanocrystals (CNCs) have been used as a polyanionic material to stabilize PEDOT during oxidative polymerization of the EDOT monomer. We were able to form films with tunable conductivity and optical properties comparable to PEDOT:PSS. However, unlike PSS, CNCs are nontoxic. Moreover, while the viscoelastic properties of PEDOT:PSS is stable and shows a minor shear-thinning behaviour, PEDOT:CNC behaves as a rheological gel where the viscosity profile shows a single shear-thinning behaviour over the whole range of shear rates investigated, making it attractive for processing purposes. The aqueous solution of PEDOT:CNC can be deposited with different processes to provide controllably thin and
flexible films. We believe our current findings provide novel sustainable solutions for producing a new generation of conductive inks and ingredients for flexible electronics.

**CELL 19**

**Nanocellulose as a building block for renewable energy**

*Jaana Vapaavuori¹, jaana.vapaavuori@umontreal.ca, Tyler Or², Arto Hiltunen⁶, Kati Miettunen³, Jose Moran-Mirabal², Emily D. Cranston⁴,⁵. (1) Chemistry and Materials Science, Aalto University, Espoo, Finland (2) Dept Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario, Canada (3) Bioproducts and Biosystems, Aalto University, Espoo, Finland (4) Chemical Engineering, McMaster University, Hamilton, Ontario, Canada (5) University of British Columbia, Vancouver, British Columbia, Canada (6) Tampere University, Tampere, Finland*

One of the main bottlenecks in the development of materials for applications in the fields of opto- and nanoelectronics, catalysis, separation, and energy conversion is the difficulty of fabricating porous large surface area 3D inorganic semiconducting nanostructures in a precisely-controlled and inexpensive manner. In this presentation, we demonstrate that covalently-linked cellulose nanocrystal (CNC) aerogels can be used both as scaffolds for liquid electrolytes of dye-sensitized solar cells (DSSCs) and as templates for atomic layer deposition (ALD) of titanium dioxide (TiO₂). Furthermore, these templates can be removed upon calcination of the porous network structure, which can then serve as an electrode for photoelectrochemical (PEC) water splitting cells producing energy in the form of H₂(g). When the functional TiO₂ coating was 15 nm thick, 100 % improvement in solar water splitting efficiency over a planar device was obtained, clearly demonstrating the vast possibilities for optimization with respect to device performance and material consumption. Moreover, when the TiO₂ coating thickness was further reduced to 7 nm, we were able to demonstrate the thinnest self-supporting mesoporous semiconductive structure fabricated directly on a conductive substrate by using sacrificial aerogel templates. On top of the potential for opening new markets for the use of nanocellulose aerogels in renewable energy, novel understanding and unexpected properties can emerge from combining the ultrahigh precision ALD and the large-area 3D nanostructured templates made out of CNCs.

**CELL 20**

**Synthetic approach to study carbohydrate materials**

*Martina Delbianco, martina.delbianco@mpikg.mpg.de. Max Planck Institute of Colloids and Interfaces, Potsdam, Germany*

Polysaccharides are the most abundant organic materials in nature, yet correlations between their three-dimensional structure and macroscopic properties have not been established. Automated glycan assembly (AGA) enables the preparation of well-defined
oligo- and polysaccharides resembling natural as well as unnatural structures. A collection of related compounds, modified at specific positions of the chain, is presented. These synthetic glycans are ideal probes for the fundamental study of polysaccharides, shedding light on how the modification patterns affect the polysaccharides properties (i.e. solubility and crystallinity). Molecular dynamics simulations and NMR analysis show that different classes of polysaccharides adopt fundamentally different conformations, drastically altered by single-site substitutions. Moreover, these synthetic oligosaccharides are able to self-assemble into nanostructures of varying morphologies. Well-defined differences in chain length, monomer modification, and aggregation methods yield glycomaterials with distinct shapes and properties.

CELL 21

Emerging cellulose technologies for energy, water and sustainability

Tian Li, mytian1211@gmail.com. Materials Science and Engineering, University of Maryland, College Park, College Park, Maryland, United States

When aided by advances in the fundamental understanding and atomic characterization, cellulose offers immense opportunities with diverse length scale and provides a sustainable solution for energy, water and sustainability. I will first talk about energy management using cellulose including the development of radiative cooling wood, thermally insulting wood, and transparent wood. The microfluidic, nanofluidic and molecular scale ion regulation capability of cellulose has also been explored. An expansive array of aligned cellulose nanofibers have been used as a high-performance ion regulation membrane from which an electrically gated ionic transistor was demonstrated. The dimension of the ion transport channels shows excellent tunability from tens of nm to sub-nm via structural and molecular engineering. The transport of sodium ions within the molecular chains of cellulose was utilized for ionic...
thermoelectrics (~24 mV/K) to convert abundant low-grade thermal energy to electricity².

**CELL 22**

**Tunable molecular features of CELF lignin and CELF lignin-based polyurethanes**

Yun-Yan Wang¹, Priya Sengupta², Charles Caì³, Charles Wyman⁴, Yunqiao Pu⁶, puy1@ornl.gov, Arthur J. Ragauskas⁵. (1) Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee, United States (2) Department of Chemical and Environmental Engineering, University of California, Riverside, California, United States (6) Bioseiences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Owing to its diverse chemical functionality, lignin from lignocellulosic biomass have recently gained significant interest as a suitable green replacement for petro-based polyols in polyurethane industry which represents total annual production of 5.8 billion pounds. Recent advancements in biomass pretreatment have improved extraction and recovery of clean lignin streams from biomass while minimizing impact to sugars to support the development of high performance lignin-based polyurethanes (LPUs) capable of supplanting existing targetted nonrenewable polyurethane applications such as foams and films. Here we use Co-solvent Enhanced Lignocellulosic Fractionation (CELF) as an advanced lignin-first biomass pretreatment method to efficiently extract and recover highly pure technical lignin product from hardwood poplar. CELF uniquely applies tetrahydrofuran (THF) as a water co-solvent in mild acidic reaction to achieve high levels of fractionation between biomass lignin and sugar fractions while minimizing their degradation. By varying the CELF pretreatment reaction conditions, we had generated different CELF lignin samples comprising a range of different molecular composition, as analyzed by HSQC NMR. We determined that the tunable molecular features of CELF lignin products including hydroxyl contents, molecular weight, and polymer chain flexibility have a significant impact on the mechanical and thermal behaviors of CELF-LPUs that we had synthesized. By mapping the functional changes of CELF-LPUs to changes in lignin macromolecular structures, as obtained during CELF pretreatment, we may better understand how to develop precise methods for tuning the performance of LPUs for target applications.

**CELL 23**

**Elucidating mechanisms and structural changes during organosolv lignin extraction**

Maria Karlsson¹, maria11@kth.se, Olena Sevastyanova², Martin Lawoko¹. (1) Fibre and Polymer Technology, Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Teknikringen 56, Sweden (2) Fibre Wood Tech/Wood Chem Pulp Tech, Stockholm, Sweden
Lignin is the most abundant natural resource of aromatics on earth. Due to the societal changes towards a bioeconomy where replacements of fossil-based aromatics by renewable ones is targeted, lignin is of high interest as a polymer precursor for different applications. About one third of the lignocellulosic biomass is constituted of lignin, and today technical lignin that are obtained from the kraft and sulfite pulping is used as an energy source. One problem with technical lignin for material applications is the heterogeneity.

Alcohol-based organosolv pulping is a well-known pulping process that has been tested in small scale plants. It has shown promising results with less heterogeneous lignin compared to kraft lignin. The process is also more green and sustainable pulping technique due to the solvent systems that are used. Ethanol, that is often used as the organic solvent in the solvent system, is a green solvent that can be produced from biomass.

The mechanisms involved in organosolv lignin have to our knowledge not been subject to deep structural- and mechanistic studies, which can be central to designing and optimizing the process for production of more homogeneous lignins with attractive chemical and physical characteristics for use as polymer precursors. This study therefore aims at elucidating mechanisms during lignin extraction with ethanol. The adopted approach is unique and performed in two steps. In the first step hemicellulose is extracted with water at sub-critical conditions. This is followed by organosolv ethanol extraction with acid catalyst. The extracted lignin’s are investigated in function of time, where time dependent changes are studied and are connected to reaction mechanisms. Detailed NMR characterization for structure include both 1D and 2D techniques, while size exclusion chromatography will be used to study the molar mass.

CELL 24

**Acid hydro tropic lignin (AHL): Low temperature fractionation and characterization**

*Junyong Zhu¹, jzhu@fs.fed.us, Cheng Cai², Kolby Hirth¹, Zhaojiang Wang³, Jinlan Cheng⁴. (1) USDA Forest Service, Madison, Wisconsin, United States (2) South China University of Technology, Guangzhou, China (3) Qilu University of Technology, Jinan, China (4) Nanjing Forestry University, Nanjing, China*

Acid hydro tropic fractionation (AHF) of lignocelluloses has recently been demonstrated several advantages over traditional alkaline, sulfite, organosolv, ionic liquid, deep eutectic solvents (DESs). Specifically, AHF can achieve rapid (< 20 min) near complete (~90%) dissolution of wood lignin at 80°C in aqueous systems without organic solvent. The dissolved lignin can be easily separated through precipitation by simply diluting the spent liquor with water to the minimal hydro trope concentration (MHC). The dissolved xylose can be efficiently dehydrated into furfural, a high value chemical, using the acid hydro trope in the spent liquor without additional catalyst. The rapid solubilization of lignin at low temperatures resulted in lignin with low degree of condensation and low glass transition temperature, which facilitate direct valorization as polymers or aromatics through subsequent depolymerization. In this presentation we will present two acid hydro tropes: p-Toluenesulfonic acid (p-TsOH) and Maleic acid for fractionating birth
wood. We will compare their performance in terms of the extent of delignification, water usage for lignin precipitation, resultant lignin properties, as well as the utility of resultant solid cellulosic fraction for production lignin containing cellulose nanomaterials (LCM) and sugars through enzymatic saccharification. The low acidity of Maleic acid resulted in a maximal delignification of 55% compare with 85% for p-TsOH, but favorable for its higher MHC of 25 wt% than 11 wt% for p-TsOH, i.e., less water is needed for lignin precipitation. Lignin esterification by Maleic acid also facilitated nanofibrillation of the resultant lignocellulosic solids and reduced nonproductive binding of cellulase to residual lignin through pH mediation. The Maleic acid is also favorable for acid recovery due to low solubility and non-corrosive.

CELL 25

Analytical insights on lignin-carbohydrate complexes in hardwood and softwood extracts

Danila Carvalho¹, carvalho.danila@gmail.com, Maarit H. Lahtinen¹, Martin Lawoko³, Kirsi S. Mikkonen². (1) Department of Food and Nutrition, University of Helsinki, Helsinki, Finland (2) University of Helsinki, Helsinki, Finland (3) Royal Institute of Technology, Stockholm, Sweden
Galactoglucomannans (GGM) and glucoronoxylans (GX) are the most abundant hemicelluloses in softwood and hardwood, respectively. Recently, GGM- and GX-rich assemblies obtained through pressurized hot water flow-through extraction (PHWE) of wood saw meal proved to be more efficient emulsifiers than conventional food hydrocolloids, and they also protected emulsified lipids against oxidation. Our hypothesis is that hemicelluloses and phenolic residues in the extracts are covalently linked forming lignin-carbohydrate complexes (LCC). The presence of LCC in the GGM- and GX-rich assemblies likely enhances their functionality in colloidal systems. To confirm this hypothesis, the presence of LCC in GGM- and GX-rich assemblies was investigated. Firstly, GGM- and GX-rich assemblies were recovered from spruce and birch PHWE extracts, respectively, by freeze-drying, spray-drying, ethanol-solubilization and ethanol-precipitation. The chemical structure of the samples was investigated in detail by specialized techniques including high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD), size-exclusion chromatography (SEC) and nuclear magnetic resonance spectroscopy (NMR). Then, further fractionation was performed using the spray-dried (s) GGM sample, which was chosen due to its excellent functionality in emulsions. The sGGM sample was fractionated using anti-solvent precipitation (ethanol/water mixtures), extraction with binary systems (ethyl acetate/water), acid hydrolysis and by a combination of physical (centrifugation and nanofiltration) and enzymatic treatments (sequential and semi-simultaneous) and assessed regarding to the presence of LCC. The presence of phenylglycoside and γ-ester bonds in GGM- and GX-rich assemblies was confirmed, especially in freeze-dried, spray-dried and ethanol-soluble samples. The ethanol-precipitation favored the fractionation of higher-molar mass and more pure GGM and GX fractions. Consequently, the ethanol-soluble samples were concentrated with LCC structures. Among the fractionation methods, the combination of physical and enzymatic treatments resulted in concentration of low molar mass hemicelluloses and LCC structures. Thus, the findings suggest that GGM- and GX-rich extracts are functionalized by the presence of LCCs, which may contribute to their excellent emulsion stabilization capacity.

CELL 26

Unravelling insights on kraft lignin structure and composition

Nicola Giummarella¹, nicolag@kth.se, Dimitri Areskogh², Martin Lawoko¹. (1) Fiber and Polymer Technology, Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden, Sweden (2) Innovation Center for Biomaterials, Stora Enso, Stockholm, Sweden, Sweden

Lignocellulosic biomass represents the most attractive sustainable and renewable resource. About 20-30% of lignocellulosics consists of lignin, the most abundant source of renewable aromatics in polymeric form. Industrially, lignin is obtained as a by-product from the conversion of wood to chemical pulp. Nowadays, most of it is just burn as a fuel to supply part of the energy demand of the pulp mill. However, lignin has a huge potential as a substrate for the production of more high value application such as
biomaterials and functional biopolymers. Recent progress in retrieving kraft lignin from the black liquor has opened possibilities for the use of such technical lignins to produce valuable bio-based products. Nevertheless, the major issue to be addressed is the structural- and size heterogeneity. Herein, we report our strategy intended to refine lignin by sustainable and sequential solvents extraction. Advanced characterization techniques are needed to successfully unravel structural insights of the refined fractions. Insights at the molecular scale have been carried out by both 2D NMR (DEPT-Edited HSQC, TOCSY, HMBC) and 1D NMR (APT-, DEPT-13C) while functionalities were quantified by 31P-NMR. Using these techniques, we identify a new linkage type that can be associated with radical coupling reactions in lignin.

CELL 27

Formation of condensed structures during mild thermal treatment of kraft lignin with fatty acids through radical reactions

Maarit H. Lahtinen¹, maarit.lahtinen@helsinki.fi, Joona Mikkilä², Kirsi S. Mikkonen¹, Petri O. Kilpeläinen³, Ilkka Kilpeläinen². (1) Department of Food and Nutrition, University of Helsinki, Helsingin yliopisto, Finland (2) Department of Chemistry, University of Helsinki, Helsinki, Finland (3) Natural Resources Institute Finland, Vantaa, I am not in the U.S. or Canada, Finland

The presence of condensed lignin structures formed during kraft pulping process have been identified and characterized in previous studies. Resinol-type structures, namely pinoresinol and secoisolariciresinol, have been characterized in kraft lignin and residual kraft lignin samples. It has been suggested that the difficult removal of residual lignin from pulp is affected by these structures, which are also associated with fatty acids. Sulphur has been suggested to play a role in initiation of radical reactions involved, but our hypothesis is that similar reactions can also take place in novel processes and applications involving other possible radical initiators.

As new processes and applications for biomaterials are being developed, it is essential to understand the underlying mechanisms of existing technologies. To get new insight to the mechanisms involved in formation of condensed structures, kraft lignin was heated in temperatures used in many processes used for biomaterials, namely 160-170 °C. In order to understand the role of fatty acids in the reactions, heat treatments were performed using tall oil fatty acids or the organic solvent decane as the reaction media. The washed and dried products were practically insoluble in organic solvents, but they could be analyzed using FT-IR. To increase the solubility of the samples, each were acetylated in a mixture of pyridine and acetic anhydride at 80 °C. As a result, main part of the samples was soluble in d6-DMSO for structural analysis with NMR, and in THF for analysis of molar masses with GPC. The thermal properties of the products were also characterized with TGA and DSC. In addition, the role of fatty acids in the reaction was examined by analyzing lignin samples with py-GC/MS in the presence and absence of fatty acids.
The structural analysis by NMR confirmed the presence of condensed structures in both samples. In addition, fatty acids were present in sample heated with tall oil fatty acids as the solvent, according to both NMR and FT-IR. Thermal analyses suggested that the materials were fused together instead of behaving as separate materials. Analysis with py-GC/MS at 200 °C showed that the composition of lignin-based volatiles were affected by the presence of fatty acids in the sample. Therefore, it is highly possible that similar reactions occur in processing and applications of biomaterials containing lignin and fatty acid-type extractives.

CELL 28

Alkali lignin fractionation by size exclusion chromatography: Analysis of fractions

Anastasia Andrianova3, Audrey LaVallie1, Bin Yao1, Joshua Schumaker1, Sarah Reagen2, Shelly Lu1, Julia Zhao1, Irina P Smoliakova1, Evgenii Kozliak2, Alena Kubatova2, alena.kubatova@und.edu. (1) Chemistry, University of North Dakota, Grand forks, North Dakota, United States (2) Chemistry Department, University of North Dakota, Grand Forks, North Dakota, United States (3) Agilent, Wilmington, Delaware, United States

Lignin is a highly abundant yet recalcitrant polymer finding only limited use. In this study, we subjected alkali lignin to size exclusion chromatography verified by extensive calibration using both polar and non-polar standards, to obtain six lignin fractions distinguished by molecular weight (MW). Then we performed a comprehensive characterization of these fractions utilizing a suite of methods including high performance SEC, direct infusion high resolution mass spectrometry, gas chromatography-mass spectrometry (GC-MS), thermal desorption/pyrolysis-GC-MS, phosphorus-31 NMR spectroscopy and thermal carbon analysis. Unlike commonly used fractionation methods, i.e., precipitation, solvent extraction and membrane filtration, preparative SEC with a properly selected stationary phase enabled the fraction collection with a desired narrow MW range. Alkali lignin was shown to contain impurities of a lower MW, apparently of carbohydrate nature, which eluted prior to high MW lignin species in SEC; this common feature may skew the determined MW values if the detector other than DAD is used. NMR data suggest that the obtained SEC fractions feature a different functional groups composition. A preliminary TEM evaluation of the particle size distribution in the solution showed that the high-MW fractions form larger size nanoparticles in water than original lignin. By contrast, lower MW fractions either featured high zeta-potential, forming unstable nanoparticles or none, with zero diameter.

CELL 29

Renewable chemicals from wood and technical lignins
Armando Cordova¹, armando.cordova@miun.se, Luca Deiana¹, Ismail Ibrahem¹, Italo Sanhueza¹, Rana Alimohammadzadeh¹, Shuangzheng Lin². (1) Mid Sweden University, Sundsvall, Sweden (2) Organofuel Sweden, Sundsvall, Sweden

New eco-friendly heterogeneous and cascade catalysis technology for converting lignin and wood to high value renewable fine chemicals and monomers is disclosed. Lignin is one of the most abundant sustainable raw materials on earth. However, it is a highly complex bio-polymeric material, which have made it hard to find useful applications for it. In fact, most to the technical lignins derived from the side streams of different pulping processes have low prices. The current largest application for this lignin is combustion and regeneration of the energy to the mills. In this presentation, all types of lignins can be converted to renewable chemicals using nature inspired cascade catalysis, non-toxic conditions and sustainable oxidants (oxygen/air).

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Small- and wide-angle x-ray scattering: Valuable tool for analyzing nanostructured materials using a compact laboratory system

Jean-Luc Brousseau¹, Jean-Luc.Brousseau@anton-paar.com, Heiner Santner². (1) Anton Paar USA, Ashland, Virginia, United States (2) Anton Paar Graz, Graz, Austria

The small- and wide-angle X-ray scattering (SAXS and WAXS) method draws increasing attention in the characterization of nanostructured materials. SAXS determines the size, shape and internal structure of colloidal structures in a range from typically 1 nm to 300 nm. Materials that can be analyzed include nanoparticles, surfactants, emulsions, liquid crystals, porous media, polymers and fibers. WAXS ideally complements results obtained by SAXS since it provides essential information on a sample’s crystallinity at the atomic level. For example, WAXS straightforwardly determines if a sample is monomorphous or contains polymorphous phases; the sample’s crystalline structure can often be directly related to its properties like melting point, taste, etc. Both WAXS and (GI-) SAXS, are ideally suited to analyze samples under changing external conditions, e.g. in-situ monitoring of processes in dependence of temperature, pH, additives, humidity, pressure, tensile stress, rheological shear, etc.

In this contribution we will discuss selected applications of the SAXS/WAXS/GISAXS technique for characterizing different nanostructured materials, including dispersions of very large silica nanoparticles, BioSAXS studies of proteins and polysaccharides in solution, GISAXS characterization of nanosized thin film samples and combined rheological-scattering measurements. All measurements were performed with the SAXSpoint 2.0 system, the most compact and versatile laboratory SAXS/WAXS/GiSAXS system.

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Accessibility of the nanoscale components of biomass to water govern their reactivity and processability in treatments taking place in aqueous environments. Currently, the limited understanding on the interactions between water and the nanoscale structure of (ligno)celluloses restricts the full utilization of plant-based biomass. However, only a few methods are capable of directly characterizing the effects of moisture on the sensitive multicomponent structure of the plant cell wall.

Due to their non-invasive nature, X-ray and neutron scattering offer extremely valuable methods for studying the response of wood and other cellulosic materials to moisture changes. They can be used to follow the swelling and shrinkage of microfibril bundles and changes in their crystalline domains, with minimal sample preparation procedures and in real time as a response to the changing environment. We have used small and wide-angle X-ray scattering (SAXS and WAXS) and small-angle neutron scattering (SANS) to detect irreversible aggregation of cellulose microfibrils and other nanostructural effects during the first drying of wood from the green state, and to follow the effects of moisture changes on wood nanostructure in situ. Most recently, we have addressed the accessibility of water in the nanopores of wood especially with the aid of SANS and contrast variation.

Our results show, that these techniques can be used to investigate moisture-related changes in the plant cell wall nanostructure that are difficult to observe with other methods. With a more complete understanding on how the plant cell wall structure is displayed in X-ray and neutron scattering data and improvement of tools for the data analysis, we expect these methods to yield highly useful new information on the plant cell wall nanostructure and its relation to moisture.

**CELL 32**

**X-ray fiber diffraction studies of the structure of cellulose microfibrils**

*Lee C. Makowski, l.makowski@neu.edu.* Bioengineering, Northeastern University, Boston, Massachusetts, United States

X-ray fiber diffraction from cellulose microfibrils contains information on the size, shape and polymorphism of microfibril structure. Using a combination of data from the small-angle (SAXS) and wide-angle (WAXS) regimes of these scattering patterns, we re-visit the question of the arrangement and number of cellulose chains present in microfibrils. Direct methods that utilize the SAXS data are used to calculate microfibril size and
cross-sectional shape. Large scale simulations of the twist of microfibrils are used to create molecular models that are then used to compute intensities in both small angle and wide angle data. Comparison of the results of these two approaches are used to predict the most likely arrangements of cellulose chains in microfibrils from multiple natural sources.

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Using a combination of resonant soft X-ray scattering and grazing-incidence diffraction for the study of plant primary cell walls

Sintu Rongpipi, Joshua Del Mundo, Sarah N. Kiemle, Will Barnes, Charlie Anderson, Daniel Cosgrove, Esther Gomez, Enrique Gomez, edg12@psu.edu. Penn State University, University Park, Pennsylvania, United States

Cellulose microfibrils are crucial for many of the remarkable mechanical properties of primary cell walls. Nevertheless, many structural features of cellulose microfibril organization in cell walls are not yet fully described. Although direct imaging can provide some information on cell wall organization over limited sample sizes, scattering yields structural information in reciprocal space over large sample areas. Using onion epidermal wall and Arabidopsis hypocotyls, we introduce resonant soft X-ray scattering (RSoXS) to directly quantify the average interfibril spacing. Tuning the X-ray energy to the calcium L-edge enhances the contrast between cellulose and pectin due to the localization of calcium ions to homogalacturonan in the pectin matrix. As a consequence, the chemical-specificity of RSoXS enables the study of the interplay between cellulose and matrix polysaccharides, by revealing the average center-to-center distance between cellulose microfibrils or microfibril bundles of about 20 nm to 30 nm. Furthermore, we use grazing-incidence wide-angle X-ray scattering to reveal a texturing of cellulose crystals within the cell wall. We find a degree of preferred orientation of crystals along the thickness of the wall that depends on developmental age and source. Using a combination of Arabidopsis mutants, we can reveal the role of matrix polysaccharides on cellulose crystal texturing and organization.

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Combining deuterium-labeling and neutron scattering to gain insight into plant cell wall organization

Hugh M. O'Neill¹, oneilhm@ornl.gov, Riddhi Shah⁴, Sai Venkatesh Pingali², Brian H. Davison³, Barbara R. Evans². (1) Biology and Soft Matter Division, Oak Ridge Natl Lab, Oak Ridge, Tennessee, United States (2) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (3) Oak Ridge Natl Lab, Knoxville, Tennessee, United States (4) Bredesen Center, University of Tennessee, Knoxville, Knoxville, Tennessee, United States
The plant cell wall is an intricate hierarchical structure that is primarily composed of the biopolymers, cellulose, lignin and hemicellulose. Understanding how the plant cell wall is assembled and also the changes that occur when it is deconstructed to produce fuels and chemicals is of critical importance for the development of a sustainable bioenergy economy. Although there has been significant progress towards these goals, the molecular level interactions between the component biomass polymers is poorly understood. Neutron scattering has emerged as a versatile tool to investigate the structure and dynamics of biomass and related model materials to obtain information that is unattainable by other means. We will discuss how the mesoscale organization of the plant cell walls is influenced by lignin content and composition and how these differences affect sugar release during thermochemical pretreatment. The neutron scattering cross-sections of hydrogen and deuterium are very different making it possible to selectively highlight different components within a complex system. A deuterated bacterial cellulose was produced as a model material to investigate different aspects of biomass structure and dynamics that are relevant to biomass deconstruction. We will present a molecular description of water-cellulose dynamics to enhance our understanding of water’s role and how it partitions in the cellulose supramolecular structure, potentially leading to more efficient pretreatment approaches. These examples will demonstrate how the combination of neutron scattering with biodeuteration can enhance our knowledge of the plant cell wall structure and the underlying processes that occur that change biomass morphology during thermochemical pretreatment for biofuels production.

**CELL 35**

**Application of X-ray and neutron scattering to understand lignocellulosic deconstruction for bioenergy**

**Gang Cheng, gchengbuct@gmail.com.** Life Science and Technology, Beijing University of Chemical Technology, Beijing, China

Lignocellulosic biomass, consisting of cellulose, hemicellulose and lignin, is being explored as a sustainable source of sugars and platform chemicals for conversion into fuels and industrial chemicals. However, biomass must be pre-treated to deconstruct plant cell walls, thereby improving enzyme accessibility to cellulose and the economics of lignocellulosic bio-refineries. The interactions between plant cell walls and biomass pretreatment generate recalcitrance-related changes in physical structures on multiple length scales. Scattering techniques including x-ray and neutron scattering, complementary to imaging techniques, offer several advantages like minimal sample preparation, versatile sample environment and in situ dynamic investigation of cell wall structures. The combination of wide and small angle scattering (WAS and SAS) techniques covers length scales from a few angstroms to several hundred nanometers. We mainly used x-ray diffraction (XRD) and small angle neutron scattering (SANS) to study the interactions between biomass and ionic liquids during biomass pretreatment, with the aim of better understand the mechanism of ionic liquid pretreatment. SANS also was used to investigate solution structures of cellulose in ionic liquids and lignin in
several common solvents, which benefits both cellulose and lignin processing for high value products. In addition, we applied neutron reflectivity to study cellulose films/cellulases interactions.

**CELL 36**

**Switchgrass lignin and hemicellulose structural reorganization observed *in situ* during dilute acid pretreatment**

Sai Venkatesh Pingali¹, pingalis@ornl.gov, Zhi Yang¹, Marcus Foston², Hugh M. O'Neil³, Volker Urban¹, Arthur J. Ragauskas¹, Barbara Evans¹, Brian H. Davison⁴. (1) University of Tennessee, Knoxville, Tennessee, United States (2) Washington University in St. Louis, St Louis, Missouri, United States (3) Biology and Soft Matter Division, Oak Ridge Natl Lab, Oak Ridge, Tennessee, United States (4) Oak Ridge Natl Lab, Knoxville, Tennessee, United States

Production of second-generation bioethanol from lignocellulosic biomass requires pretreatment to open the plant cell wall structure and improve enzyme access. Many different thermochemical pretreatments have been extensively developed and employed but, the exact nature of plant cell wall recalcitrance and the most efficient and economical approach to alter plant cell wall structure via pretreatment still remains elusive. In order to understand the role that non-cellulosic plant cell wall polymers have on the overall efficiency of pretreatment, the structural evolution of the amorphous plant cell wall polymers was investigated during dilute acid pretreatment by employing *in-situ* small-angle neutron scattering (*in-situ* SANS). In this study, we observed real-time structural changes not possible by any other technique. To deconvolute the structural contributions of the lignin and hemicellulose, raw switchgrass (NATV) and isolated fractions of holocellulose (HOLO) and cellulose (CELL) from NATV were studied. Our results show aggregate particles first appear around 80 °C for NATV and HOLO samples. These particles at a low severity are presumably composed of hemicellulose oligomers. The formation of much larger aggregate particles presumably composed of lignin were only observed in the NATV sample. For HOLO sample, an increase in the aggregate particle size presumably composed of pseudo-lignin was observed at relatively much higher severity. These particles become progressively more compact and denser with increasing pretreatment temperature/time. Consistent with our interpretation of structural evolutions in NATV and HOLO samples, no such aggregate particles were observed in CELL samples for the entire duration of the pretreatment. These results suggest that not only lignin, but also hemicellulose can form aggregate particles within the plant cell wall during pretreatment and potentially have an influence on the pretreatment efficiency.

**CELL 37**

**Structural changes during drying of regenerated cellulose beads**
The recently developed nanometer-smooth cellulose beads have turned out to be excellent model systems for determining the fundamental interactions between cellulose surfaces. It is hence important to fully characterize these beads in order to show how suitable they are as models for cellulose-rich fibres. In the present work the macro- and micro-structural evolution of water swollen and ethanol swollen regenerated cellulose gel beads have been determined during the drying process by optical microscopy combined with analytical balance measurements, small-angle X-ray scattering (SAXS), and wide-angle X-ray scattering (WAXS). The results clearly show that the drying of cellulose from water is different compared to drying from ethanol. For the drying of ethanol swollen beads there are only small changes in the detected structures from both SAXS and WAXS measurements during the entire drying process. However, for the drying of water swollen beads, the dimensions of the internal structures and also the morphology changes during drying. After complete drying from water the cellulose microstructure is characterized by elongated small structures and spherical aggregates. Moreover, it is observed by WAXS that cellulose IIhydrate appears and transforms to cellulose II during water evaporation but it is not possible to determine the degree of crystallinity of the beads from the results of the WAXS measurements.

**CELL 38**

**Lessons from DFT quantum mechanics studies of disaccharide conformation**

*Alfred D. French*, Al.French@ars.usda.gov. Southern Regional Research Center, U.S. Department of Agriculture, Metairie, Louisiana, United States

Given a computer cluster with a few hundred cpu cores, it is possible to create Ramachandran-style energy maps for disaccharides and their analogs. At the time of writing this abstract, calculations have been completed for cellobiose and β-(1->4)-xylobiose, and maltose is more than 80% finished. These disaccharides are of special interest because they are the shortest representatives of cellulose, xylan hemicellulose, and amylose (starch). The energies for each 20° increment of φ and ψ were computed with B3LYP theory, and M062X theory is being used on maltose as well. In the cases of cellobiose and xylobiose, the use of SMD continuum solvation was necessary for prediction of crystallographically observed structures, while the effect on maltose structures was smaller. The energy calculations were validated by crystal structures taken from both the Cambridge Crystal Structure Database and the Protein Data Bank. The cyclodextrin structures furnish thousands of φ,ψ pairs for maltose linkages but have structural constraints, and there are numerous structures from the Protein Data Bank that do not correspond to low energies. It is clear, however, that these calculations are quite predictive for conformations observed in crystals, and that the average energy of φ,ψ distortion due to crystal packing is small, with majorities falling inside the 1 kcal mol⁻¹ contours.
Lyocell chemistry: From explosion to fibers

Thomas Rosenau¹, thomas.rosenau@boku.ac.at, Antje Potthast¹, Hubert Hettegger¹, Paul Kosma¹, Thomas Roeder². (1) Dept of Chemistry, BOKU University Vienna, Vienna, Austria (2) Lenzing AG, Lenzing, Austria

N-Methylmorpholine-N-oxide monohydrate (NMMO) is used as a solvent for direct dissolution of cellulose in industrial fiber-making (Lyocell process), which is today a major source of man-made cellulosics. Lyocell fiber manufacture is seen as an eco-friendly alternative to other, environmentally more challenging processes, such as viscose (rayon) production.

In the idealized case, Lyocell fiber production could be seen as an entirely physical process, which does not cause any chemical changes in pulp or solvent. Following this idea, process development in its early phases has concentrated on technological issues, so that the chemical side of the process was somewhat neglected. In fact, chemical safety issues, euphemistically called “exothermicities” or “thermal runaway reaction” brought the process to the rim of abandonment, and elucidation of the underlying Lyocell chemistry and elaboration of suitable stabilization approaches became critical for the process to survive.

The chemistry of the Lyocell process has been comprehensively studied in our, elucidating side reactions and byproducts, developing efficient stabilizers and elaborating safe process conditions, rendering Lyocell production the safe and secure process it is today. Side reactions can be divided into homolytic (radical) and heterolytic (non-radical, ionic) processes. The former mainly involve NMMO-derived radicals as well as metal ions, the latter entail Polonowski-type reactions and autocatalytic decomposition processes involving carbenium-iminium ions. All of these degradation processes contribute to chromophore formation which is another important aspect of Lyocell chemistry. Investigations into NMMO and other cellulose solvent systems have meanwhile evolved into a separate field of cellulose chemistry.

In this paper, the chemistry of the Lyocell process will be briefly introduced and also recalled from a historical perspective, covering the basics of the process chemistry and the underlying reaction mechanism, including some key aspects, such as cellulose degradation, chromophore formation, thermal runaway reactions, and stabilizers.

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CELL as a springboard for dynamic research and networking

Orlando Rojas¹,², orlando.rojas@aalto.fi. (1) Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Aalto, Finland (2) Departments of Chemical & Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada
The CELL division has been a critical factor in the academic life of many of us. I will present my personal experience, beginning with the first symposium on cellulose nanotechnology that we organized more than 10 year ago. Over this time, together with my students, we have enjoyed the conference series as the place to go to share knowledge and learn from each other. It is because of CELL that initiatives such as the Boreal Alliance are taking shape. Here, a group of members is nucleating ideas to develop solution for the materials needs within the future bioeconomy. I will share some of my successful experiences and highlight the factors that I think have helped us to nucleate initiatives with a large impact. These include the recently launched FinnCERES flagship between VTT and Aalto University, in Finland and the renewal of the BioProducts Institute in the University of British Columbia. Together with many other efforts that are being deployed globally, there is a huge opportunity to produce the science and the talent needed to sustainably better our lives and the environment.

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Double-network bionanocomposites from nanocellulose and mycelium

Noam Attias², Yasha J. Grobman², Tiffany Abitbol¹, tiffany.abitbol@ri.se. (1) RISE Bioeconomy, Stockholm, Sweden (2) Faculty of Architecture and Town Planning, Technion, Haifa, Israel

Bionanocomposites are prepared from nanocellulose and a white rot fungus (T. multicolor) using a new approach. Mycelium is the vegetative part of the fungus and presents as a branched network structure composed of thread-like hyphae, which are in turn largely composed of chitin. So far, the natural ability of white rot fungi to decompose cellulose and lignin has been used in composting, bioremediation, and bleaching, but in this work, the networked structure of the fungal mycelium is used as a structural element with distinct physicochemical properties compared to nanocellulose. The overall aim of the work is to develop all-forest-based cellulosic-chitinous composite with tunable properties (e.g. strength and hydrophobicity) depending on the relative amount of each component. Different materials are presented and characterized in terms of appearance and network structure, wettability, thermal degradation, water uptake, and mechanical properties.

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Low-cost waste-derived mycelium nanopapers

Andreas Mautner¹, andreas.mautner@univie.ac.at, Mitchell Jones¹,², Kathrin Weiland¹, Eero Kontturi³, Sabu John², Alexander Bismarck¹. (1) Institute for Materials Chemistry & Research, University of Vienna, Wien, Austria (2) School of Engineering, RMIT University, Melbourne, Victoria, Australia (3) Department of Forest Products Technology, Aalto University, Aalto, Finland
Mycelium, which is the vegetative growth of filamentous fungi, has attracted significant academic and commercial interest in recent years due to its ability to upcycle agricultural and industrial wastes into low-cost, sustainable composite materials. However, so far mycelium composites typically exhibit mechanical properties similar to polymer foams rather than bulk polymers, which primarily originates from their weak organic filler constituents. However, fungal growth can be also utilized as a low-cost method for on-demand generation of natural nanofibrils, such as chitin and chitosan. These base constituents of fungi can be grown and isolated from liquid agricultural wastes and byproducts in the form of fungal microfilaments.

Here, we characterized polymer extracts and nanopapers produced from a common mushroom reference and various species of fungal mycelium grown on sugarcane byproduct molasses. Polymer yields of $\sim$10–26% were achieved, which are comparable to those of crustacean-derived chitin, and the nanopapers produced exhibited much higher tensile strengths than the existing mycelium materials, with values of up to $\sim$25 MPa (mycelium) and $\sim$100 MPa (mushroom), in addition to useful hydrophobic surface properties resulting from the presence of organic lipid residues in the nanopapers. Treatments with HCl or H$_2$O$_2$ were utilized to remove these impurities thus facilitating tuning of mechanical, thermal, and surface properties of the nanopapers produced. This enables their use in a wide range of potential applications including coatings, membranes, packaging, and paper.

**CELL 43**

3-ingredient, 2-step, 1-pot process to obtain uniform esterified lignin derivatives

Li-Yang Liu, liyang.liu@alumni.ubc.ca, Siwei Chen, Lun Ji, Scott Renneckar. Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

Kraft lignin can be blended with traditional thermoplastic materials, but this can lead to well-known embrittlement. The esterification of hydroxyl groups in kraft lignin with fatty acids can significantly improve their compatibility with aliphatic polyesters by the promotion of secondary interactions. However, this route has two problems: 1) the traditional non-green approach of derivatization causes environmental issues; and 2) blending the lignin derivatives above the 25 - 40% level leads to significant phase separation that severely impacts mechanical properties. Understanding the structure-property relationship for this type of material is vital to solving this problem. However, it is challenging because of the unknown physicochemical properties of kraft lignin and how they change during heating. In this study, we adopt a one-pot process to obtain a highly uniform esterified kraft lignin with a well-characterized structure. The greener esterification route was selected to modify the hydroxyethyl kraft lignin in a one-pot process with a 90% degree of substitution. A simple downward fractionation method was further used to obtain five fully esterified lignin fractions with specific absolute molar mass, well-characterized thermal properties. We anticipate these uniform esterified lignin fractions with well-characterized structures can greatly aid in the preparation of lignin-polymer blends materials providing insight into structure-property relationships.
Towards sustainable and renewable carbon products: Comprehensive analytical and statistical study of graphitization in lignin carbon

Valerie Garcia-Negron¹, vgarcian@utk.edu, Dayton Kizzire¹, Orlando Rios², David Keffer³, David P. Harper³. (1) Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, United States (2) Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (3) Center for Renewable Carbon, The University of Tennessee, Knoxville, Tennessee, United States

Sustainable and renewable carbon products are experiencing an accelerating interest due to the high-energy demand societal activities require. Lignin, a by-product of the pulping process, is an abundant biopolymer composed of carbon-rich chemical structures with potential for “green” solutions in energy-related applications such as carbon fibers, batteries, solar cells, adsorbents, and chemicals. The relative abundance of the principal monomeric units—guaiacyl, p-hydroxyphenyl, and syringyl— VARIES with lignin feedstock. The relationships between lignin feedstock, processing conditions, and structure of the composite product as a result of carbonization (pyrolysis and reduction) are not well-established. This work combines analytical and statistical techniques to elucidate such relationships which provide a foundation for engineering application- and performance-specific carbon materials. Lignin feedstocks obtained from softwoods, hardwoods, and grasses were carbonized at reduction temperatures of 1050, 1500, and 2000 °C. Materials were characterized during carbonization at the atomic- and micro-scales using x-ray diffraction, chemical analysis, and high-resolution transmission electron microscopy. Results suggest the evolution of carbon structures consist of graphene sheets that assemble as both crystalline (stacked nanocrystallites) and amorphous (disordered fragments) domains. The crystalline domain reveals larger crystal sizes as reduction temperature increases. Specifically, kraft softwood and organosolv switchgrass carbon composites contain higher graphitization, thus are favorable sources for graphite substitutes. Correlations and PCA of x-ray data and reduction temperature suggest that there are intrinsic structural properties dependent on feedstock and wood extraction method, and independent from humidity. In addition, electrochemical studies were performed on batteries containing lignin-based anodes with promising performance comparable to traditional graphite anodes.

Rod-coil oligocellulose-elastomer- and polypeptide diblock copolymers for advanced biobased nanomaterials

Johanna Majoinen¹, johanna.majoinen@aalto.fi, Robert Pylkkänen², Merja Penttilä², Orlando J. Rojas¹. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) VTT, Espoo, Finland
Biobased block copolymers (BCPs) are interesting candidates to replace traditional coil-coil BCP analogues with enhances self-assembly and effective downsizing of feature nanostructures for future sustainable materials. We introduce biosynthetically produced oligocellulose as a crystallizing rod-like block to act as highly immiscible block with small size to serve as high $\chi$ low N BCP with wanted properties. The BCPs are synthetizes from ready (end-functionalized) sub-blocks using copper alkyne azide cycloaddition witch creates a triazole ring at the interface between the different blocks. Triazole ring N-alkylation introduces single point charge to the ring and at the interface between blocks. Newly formed ionic moieties reorient formed structures utilizing electrostatic interactions effective long range.

In this study, we demonstrate synthesis and full characterization of oligocellulose-elastomer -and oligopeptide rod-coil diblock copolymers. With highly crystallizing and hydrogen bond self-associating oligocellulose rod blocks, liquid crystalline BCP properties are expected and highly favorable for orienting self-assembled nanostructures. The concepts introduced in this work can be widely used among biopolymer advanced material processing towards future cellulose based BCP high-end applications.

**CELL 46**

**High precision 3-D printing of nanocellulose into super strong yet flexible structure**

Jungang Jiang, Hale Oguzlu, Mingyao Song, Feng Jiang, feng.jiang@ubc.ca.
Department of Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

3-D printing or additive manufacturing is a high-resolution computer-aided design and fabricating technology that enables producing 3-D objects in a controlled manner. Using direct ink writing (DIW) technique, cellulose and nanocellulose suspension have been demonstrated to be applicable for 3D printing application, and the printed 3-D structures have been widely used for biomedical applications. In general, 3-D printed nanocellulose structure shows porous morphology and therefore the strength can be hampered. In this presentation, I will introduce our most recent research in 3D printing super strong yet flexible structure from nanocellulose. Several 3D printing nanocellulose examples will be presented, and the properties affecting the printability, shape fidelity, and mechanical properties will be discussed. The 3D printed structure demonstrated great flexibility when wet and can be rolled, twisted, and folded. However, when it is dry, the cellulosic structure is very strong and can support over 15000 times of its own weight. This 3D printed cellulose structure is much stronger than some of other 3-D printed carbon materials, bio-based polymers, ceramic and even metallic materials. We envision that it could be useful for lightweight structural materials and substrate for a variety of advanced applications.

**CELL 47**
Substrate interactions as a handle to control long-range order in micro- and macro- structures formed from cellulose nanocrystals

Blaise L. Tardy1, blaise.tardy@aalto.fi, Joseph Richardson2, Luiz Greca1, Junling Guo3,4, Hirotaka Ejima2, Orlando Rojas1,5. (1) Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Materials Engineering, Tokyo University, Tokyo, Japan (3) Wyss Institute, Harvard University, Boston, Massachusetts, United States (4) School of Biomass Science and Engineering, Sichuan University, Chengdu, China (5) University of British Columbia, Vancouver, British Columbia, Canada

Cellulose nanocrystals (CNCs) have recently undergone mass production and are expected to be key building blocks for the developing bioeconomy. At the nanoscale, CNCs present outstanding mechanical characteristics, with tensile strengths as high as 7 GPa, and elastic moduli above 150 GPa. The transfer of these mechanical properties into the macro-scale is an exciting challenge, with a high potential to revolutionize materials science, and bottom-up fabrication.

For the successful transfer of the mechanical properties of CNCs into larger scales, control over their long-range order is required as it determines their self-cohesive behavior, i.e. the extent to which supramolecular interactions occur. Herein, we used substrates with varying compliance to control interfacial interactions during the assembly of CNCs. We demonstrate that substrates can be exploited to tether microstructures formed from CNCs and the arrangement of CNCs within these microstructures. We explore the substrate dependency on the formation of microstructures, and their relation with the cohesive strength of the formed materials. The development of the long-range order was further evaluated as a function of substrate roughness, and surface energy. The mechanical robustness of the CNC constructs were correlated with the substrate properties, the microstructures, and the use of additives (e.g. electrolytes). The optical properties of the systems were evaluated to obtain insights on the long-range order of CNCs. This was achieved using scanning electron microscopy, small-angle X-ray scattering, as well as bright field microscopy—in various configurations. The presented findings are expected to represent an important step towards exploiting the interfacial behavior of nanocelluloses to reach new ordered structures with outstanding mechanical properties. With the wider range of bio-colloids, other than nanocelluloses, being under development, the ramifications of our findings are wide.

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Modifying materials using rod shaped fillers

Johan Foster, johanf@vt.edu. Virginia Tech, Blacksburg, Virginia, United States

We present our work on making reinforced, light-weight materials using rod shaped, bio-based fillers. In pursuit of creating materials that have favorable mechanical and chemical characteristics, cellulose nanocrystals (CNCs) have provided not only the structural reinforcement component needed to effectively replace damaged tissue and
aid in healing, but also a handle to introduce favorable interactions. CNCs are mechanically stiff, high-aspect-ratio, bio-sourced and bio-renewable fibers which can be utilized as both a reinforcing element in nanocomposites, but also a convenient chemical handle for adding stimuli responsiveness to a material. We present our research focused on the creation of reinforced, structured and functional bionanocomposite materials created using CNCs.

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Novel lignin monomers: Another brick in the wall

José C. del Río¹, delrio@irmase.csic.es, Jorge Rencoret¹, Ana Gutierrez¹, Thomas Elder², Hoon Kim³, John Ralph³. (1) IRNAS-CSIC, Seville, Spain (2) USDA-Forest Service, Auburn, Alabama, United States (3) U. Wisconsin-Madison, Madison, Wisconsin, United States

Lignin is a phenylpropanoid polymer derived essentially from the oxidative radical coupling of three \( p \)-hydroxycinnamyl alcohols (so-called “monolignols”) differing in their degree of methoxylation, \( p \)-coumaryl, coniferyl, and sinapyl alcohols. Several other phenolic compounds, all deriving from the shikimate-derived monolignol biosynthetic pathway, have been found to behave as lignin monomers in many plants, including the monolignol ester conjugates (with acetate, \( p \)-coumarate, ferulate, and \( p \)-hydroxybenzoate) or the incompletely methylated monomers caffeyl and 5-hydroxyconiferyl alcohols, among others. However, recent studies have revealed that some phenolic compounds derived from other biosynthetic pathways also act as true lignin monomers participating in coupling and cross-coupling reactions during lignification in several plants. This is the case for the flavone tricin recently established as a monomer in the lignins from grasses and other monocots, the newly discovered hydroxystilbenes (resveratrol, isorhapontigenin and piceatannol) that are implicated as monomers in the lignin of palm fruit endocarps, the respective hydroxystilbene glucosides that have been found in the lignin of spruce bark or the diferuloylputrescine that has been found as a monomer in the lignin of maize kernels. The discovery in lignins of ‘non-conventional’ phenolic precursors arising from other biosynthetic pathways expands the traditional definition of lignin and reveals that any phenolic compound that is delivered to the cell wall may be oxidized and incorporated into the lignin polymer during lignification, subject exclusively to its chemical compatibility. On the other hand, these discoveries reveal that valuable flavonoids and hydroxystilbenes could also be obtained from agricultural residues (cereal straws, palm fruit shells of tree barks) or from low-value lignin side-streams in lignocellulose processing mills, which will open new opportunities for the valorization of these residues that are considered as wastes.

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Benzoates in C4H/C3H downregulated Populus trichocarpa transgenic lignin
Hoon Kim1, hoonkim@wisc.edu, Quanzi Li2, Steven D. Karlen1, Rebecca Smith1, Rui Shi3, Jie Liu3, Chenmin Yang3, Sermsawat Tunlaya-Anukit3, Jack Wang3, Hou-min Chang3, Ronald Sederoff3, John Ralph4, Vincent Chiang3. (1) Great Lakes Bioenergy Research Center, University of Wisconsin-Madison, Madison, Wisconsin, United States (2) Chinese Academy of Forestry, Beijing, China (3) North Carolina State University, Raleigh, North Carolina, United States (4) U. Wisconsin-Madison, Madison, Wisconsin, United States

Lignin is an essential macromolecule in terrestrial plants. Genetic modifications of the monolignol biosynthetic pathway are becoming increasingly explored for improving the lignin and biomass quality and for producing high-value commodity chemical feedstocks. Here we report the ability to engineer lignin-bound benzoate (BA) from a triple-transgenic Populus trichocarpa downregulated in genes for the three key P450 enzymes, two 4-hydroxylases (PtrC4H1 and PtrC4H2) and one 3-hydroxylase (PtrC3H3), in the monolignol biosynthetic pathway. Surprising lignin benzoylation derives from the incorporation of monolignol benzoate (ML-BA) conjugates into the transgenic plant’s lignin monomer pool at a significant (5.5%) level. The ML-BA structure was found to be increased by ~16-fold when compared to the trace amounts in wild type (WT). The total lignin content in the transgenics was decreased to 50% of the WT level, and lignin H-unit levels were significantly increased (70-fold). The results suggest that the co-downregulation of PtrC4H1/PtrC4H2/PtrC3H3 genes causes a modification of the pathway that can be explained by connecting the benzoate biosynthetic pathway to the conventional monolignol biosynthetic pathway. Consequently, the BA and p-hydroxybenzoate (pBA) can be augmented and incorporated into the lignin. Moreover, the transgenic’s wood in this study showed reduced recalcitrance toward enzymatic saccharification, which has value for the conversion of plant biomass to bioenergy.

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Measuring the in situ glass transition of catechyl lignin

Eky Ristanti, ekyyr@vt.edu, Charles E. Frazier. Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States

In 2013, an entirely novel lignin was reported to occur in the seed coat of vanilla orchid (Vanilla planifolia) and Melocactus cacti. This lignin is a homopolymer of caffeoyl alcohol; it is commonly referred to as catechyl lignin, and it has since been discovered to occur also in the nutshell of Aleurites moluccanus (candlenut). In this presentation, we describe our efforts to measure the in situ glass transition in candlenut shells and vanilla bean seed coats. Neither of these sample types provides typical bar-shaped specimens that are amenable to simple bending or tensile analysis. Consequently, we employed compressive-torsion where particulate and/or misshaped specimens may be compressed between parallel-plates while subjected to torsional oscillation. Furthermore, we conducted these analyses with specimens immersed in plasticizers like ethylene glycol and N-methyl-2-pyrrolidone. Measurements using ground or solid
candlenut shell are relatively easy- as expected they revealed glass transitions about 30°C higher than for in situ guaiacyl lignins. Measurements of vanilla bean seed coats are much more difficult because of the need to isolate the seed coat from the seed endosperm and embryo. We describe the isolation process and the progression of glass transition measurement as a function of seed coat purity.

**CELL 52**

**Useful monomeric products from lignins and ‘clip-offs’**

*John Ralph*¹, *jralph@wisc.edu*, *Yanding Li*¹, *Ming-Jie Chen*¹, *Ruili Gao*¹, *Justin K. Mobley*², *Jorge Rencoret*³, *Steven D. Karlen*¹, *José C. del Río*⁴, *Jeremy Luterbacher*⁵, *James A. Dumesic*⁶. (1) U. Wisconsin-Madison, Madison, Wisconsin, United States (2) Chemistry, University of Kentucky, Lexington, Kentucky, United States (3) IRNAS, CSIC, Seville, Spain (4) IRNAS-CSIC, Seville, Spain (5) EPFL, Lausanne, Switzerland (6) Univ of Wisconsin, Madison, Wisconsin, United States

Hydrogenolytic, oxidative, or reductive cleavage methods can produce good yields of monomeric phenols from relatively native (i.e., ‘uncondensed’) polymeric lignins under various ‘lignin-first’ scenarios; such products include the hydroxyphenylpropanols/propanes, hydroxybenzaldehydes, hydroxybenzoic acids and even hydroxycinnamyl alcohols or even hydroxycinnamaldehydes from novel processes. A variety of ‘clip-offs’ is also available from simple chemistry; these include all the acids found acylating cell wall polysaccharides and lignins, as well as a few of the phenolics that are incorporated into lignins by relatively simple means. All of these compounds should find wide applications if available in bulk at modest prices, and a few already have obvious uses today, such as in making Tylenol™ (paracetamol, acetaminophen) from p-hydroxybenzoate.

**CELL 53**

**On the visualization of lignin structure**

*Mikhail Balakshin*¹, *mikhail.balakshin@renmatix.com*, *Ewellyn Capanema*³, *Antje Potthast*², *Thomas Rosenaur*⁴. (1) Aalto University, Espoo, Finland (2) Chemistry, BOKU Vienna, Wien, Wien, Austria (3) RISE, Stockholm, Sweden (4) Dept of Chemistry, BOKU University Vienna, Vienna, Austria

Despite the vast amount of information available, it is impossible to draw the exact chemical structure of native and technical lignins. There is incomplete information on the exact chemical structures of all lignin structural units, their linkage modes and more importantly the sequence of lignin subunits in the macromolecule. However, visualization of current information in a plausible lignin structural model is certainly useful for understanding structural features of lignin. Herein, we combine available analytical data, both from own work and literature, with recent findings on the absolute molecular weights of MWL to suggest an up-to-date
structural model of softwood and hardwood MWLs as well as main technical lignins. Spruce MWL consists of 25 C9-units on average being highly branched and crosslinked with short chains. In addition to etherified 5-5’ moieties, as widely accepted branching/crosslinking points, our analysis indicates that about half of lignin branching/crosslinking points are located in the side chain. Quantitative $^{13}$C NMR indicates that the branches are apparently of aliphatic ether (alkyl-O-alkyl) type at the a- or/and g-positions of the side chain (with intact b-O-4 linkages). The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation. The exact structure of these moieties is not fully defined yet: spectral data indicates slight structural diversity, offering challenges for precise 2D NMR elucidation.

CELL 54

New methods for quantitation of lignin in lignocellulosic materials

*Ning Li, Tianjiao Qu, Xuejun Pan, xpan@wisc.edu*. Biological Systems Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States

In the areas of biomass conversion, pulp & paper, and forage, lignin quantitation is an indispensable and routine procedure for composition analysis of lignocellulosic materials. The most commonly used methods are Klason method and acetyl bromide method. This presentation introduces two new methods recently developed for quantitation of lignin in lignocellulosic biomass using a molten salt hydrate (lithium bromide trihydrate) as a solvent or medium. The first method uses acidic lithium bromide trihydrate (ALBTH) to quickly and completely dissolve and hydrolyze cellulose and hemicellulose in the biomass under mild conditions and leaves lignin as an insoluble residue for gravimetric quantitation, and the soluble fraction of the lignin formed in the ALBTH assay is determined by UV spectrophotometry. The second method uses lithium bromide-acetic acid (LBAA) system to solubilize whole biomass, and the dissolved lignin is spectrophotometrically quantitated on an ultraviolet (UV) spectrophotometer. Specifically, in the LBAA method, acidic lithium bromide trihydrate is used to dissolve and hydrolyze cellulose and hemicellulose and depolymerize lignin first, and then acetic acid is added to dissolve the lignin. Both the ALBTH and LBAA methods were applied to softwood, hardwood, and herbage biomass and compared with acetyl bromide and Klason methods for lignin quantitation. The results indicated that the ALBTH and LBAA methods gave reliable and comparable lignin quantitation. The new methods are facial and fast for lignin quantification. In particular, the LBAA method is attractive in the screening experiments involving a large number of samples using a high throughput automatic analysis system.

CELL 55
Lignocellulosic materials in hydrolysis liquors: Isolation and properties

Dmitry Tarasov\textsuperscript{1,2}, dmitry.tarasov@aalto.fi, Mathew Leitch\textsuperscript{1}, Pedram Fatehi\textsuperscript{3}. (1) Natural Resources Management, Lakehead University, Thunder Bay, Ontario, Canada (2) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (3) Chemical Engineering, Lakehead University, Thunder Bay, Ontario, Canada

Autohydrolysis is the chemical-free and environmentally friendly pretreatment technology, which leads to lignin and polysaccharide dissolutions in hydrolysate. Lignin and carbohydrates presented in hydrolysates can be used for manufacturing value-added products. However, the direct conversion of lignocellulosic materials present in hydrolysates to value-added products is expensive due to their low concentrations in the hydrolysates.

In this study, the effect of autohydrolysis parameters on the properties, structure and composition of lignocelluloses extracted from softwood chips via flow through autohydrolysis pretreatment was investigated. To isolate lignocellulosic materials from hydrolysates, acidification and ethanol precipitation were employed. The highest temperatures applied in the autohydrolysis process were found to yield the maximum removal of lignin from wood; whereas, prolonged hydrothermal treatment increased the removal of hemicelluloses from wood. In addition, it was discovered that a low flow velocity led to higher lignocellulose removals. However, at a high liquid flow rate, hemicelluloses with larger molecular weights (Mw) were extracted. Gel permeation chromatography (GPC) analysis revealed the presence of lignin-carbohydrate complexes (LCC) in the hydrolysates. In addition, LCCs were also detected in the precipitates generated via acidification and ethanol treatment, but their removals depended on the hydrolysis conditions. The isolated material produced from hydrolysates due to ethanol or acid addition showed approximately twice as much heat capacity values as that of dried hydrolysates. The \textsuperscript{1}H-NMR analysis revealed that the extracted materials via acidification contained more methoxy groups and less cross-linking than those present in hydrolysates. These results suggested that the materials obtained after acid or ethanol treatment of hydrolysates could be considered as additives for heat-resistant biopolymers or hemicellulose-based films, respectively.

CELL 56

Coupling and reactions of monolignols and new lignin monomers: Density functional study

Thomas J. Elder\textsuperscript{1}, telder@fs.fed.us, José C. del Río\textsuperscript{2}, John Ralph\textsuperscript{3}, Jorge Rencoret\textsuperscript{4}, Hoon Kim\textsuperscript{5}, Gregg Beckham\textsuperscript{6}, Michael F. Crowley\textsuperscript{7}. (1) USDA Forest Service, Pineville, Louisiana, United States (2) IRNAS-CSIC, Seville, Spain (3) U. Wisconsin-Madison, Madison, Wisconsin, United States (4) IRNAS, CSIC, Seville, Spain (5) Wisconsin Energy Institute, University of Wisconsin-Madison, Madison, Wisconsin, United States (6) NREL, Golden, Colorado, United States (7) National Renewable Energy Lab, Lakewood, Colorado, United States
According to the strictest and traditional definition, lignin is a polymer of the hydroxycinnamyl alcohols, p-coumaryl, coniferyl, and sinapyl alcohol. Increasingly, however, it is being found that other compounds can serve as nucleation sites or be fully integrated into the lignin polymer. These non-canonical compounds may be the result of natural mutations, induced genetic modifications or through naturally occurring lignin monomers. Examples of the latter include caffeyl alcohol, found in various seed coats, hydroxystilbenes (especially piceatannol) identified in lignins from palm fruit endocarps, hydroxystilbene glucosides from spruce bark, diferuloylputrescine in maize kernels, and tricin from wheat straw and other monocotyledons. Indeed, it has been recently reported that 35 different monomers have been detected in natural lignins. The current work reports on the thermodynamics of coupling between monolignols and the new lignin monomers and bond dissociation energies of the resultant complexes by the application of density functional theory calculations.

**CELL 57**

Solid-state NMR as a powerful tool to characterize polysaccharide-based systems

*Francesco D’Acierno*\(^{2,1}\), fradaci@yahoo.it, Wadood Y. Hamad\(^{3}\), Mark J. Maclachlan\(^{2,4,5}\), Carl A. Michal\(^{1,2}\). (1) Department of Physics, The University of British Columbia, Vancouver, British Columbia, Canada (2) Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada (3) Biomaterials Division, FPInnovations, Vancouver, British Columbia, Canada (4) Stewart Blossom Quantum Matter Institute, University of British Columbia, Vancouver, British Columbia, Canada (5) WPI Nano Life Science Institute, Kanazawa University, Kanazawa, Japan

An accurate structural characterization of polysaccharide-based systems is crucial in understanding the properties of the materials. Among all the characterization techniques, solid-state NMR spectroscopy proves to be fundamental for a clear picture of complex polysaccharide-based systems.

An example of complexity in these systems is represented by disordered structures. Polysaccharides with large fractions of amorphous regions can be analyzed using \(^{1}\text{H}-^{13}\text{C}\) cross-polarization (CP) magic-angle-spinning (MAS) to resolve their molecular sites. The same experiment can be applied to biochars obtained by thermal degradation of biopolymers to quantitatively characterize the forms of carbon present, in combination with direct polarization (DP) MAS to determine the size of the carbonaceous char clusters.

Solid-state NMR is also effective in the structural characterization of porous materials. Some polysaccharides, such as chitin, self-assemble in mesoporous architectures directly in nature, while for others, such as cellulose, reduction to a nanocrystalline form is required to obtain these types of networks. Mesoporous polysaccharide-based materials can often be used as templates to create inorganic materials with complementary porosity, such as alumina aerogels, which can be exploited as catalyst supports, absorbents, or thermal insulators. Solid-state NMR enables the structural
characterization of the biotemplated materials, when the corresponding isotope is NMR-sensitive.

In this presentation, I will discuss our use of solid-state NMR techniques to probe the structures of new materials developed from biopolymers. This technique gives insight into the structure of the materials that is not available from other analytical methods.
Probing surface chemistry of functionalized cellulose nanofibrils enabled by dynamic nuclear polarization enhanced solid-state NMR

Gael De Paepe, gael.depaep@cea.fr. IRIG, CEA - Univ. Grenoble Alpes, Grenoble, France

Cellulose nanofibrils (CNF) are renewable, biodegradable and biocompatible, which makes them ideal candidates as carriers in drug delivery applications. However, in-depth chemical and structural characterization of the CNF surface chemistry is often a challenge, especially for low weight percentage of functionalization compatible with drug delivery applications. Solid-state NMR spectroscopy is, in principle, a key technique to obtaining local structural information on this type of system and was indeed used in the past for studying CNF surface chemistry but either with a high level of grafting (5 to 10 \%) or with the use of isotopically labeled molecules. Nevertheless, solid-state NMR fails to address application-driven systems that rely on a much lower level of grafting (~1 wt\% or lower) and the use of non-isotopically enriched grafted molecules. This is notably the case for the system we have studied in this work, namely CNF functionalized with an anti-bacterial molecule (modified-metronidazole). This new CNF-based system is biologically active and represents an innovative drug carrier formulation with “on demand” release ability in the presence of esterase enzymes. There is thus a need to probe and quantify the mode of fixation, whether through adsorption or covalent binding, since this will directly influence the delivery kinetics and the overall dosage of the drug. In this work, we will show how we use Dynamic Nuclear Polarization to overcome the sensitivity limitation of conventional solid-state NMR and gain insight into the surface chemistry of this biologically active material. Notably, we will show how the data can be used to differentiate unambiguously adsorption from covalent grafting (~1 wt\% in our case), locate the position of functionalization and estimate the efficiency of a two-step functionalization reaction. In addition, we will also show that these results cannot be obtained using other characterization techniques, such as FT-IR and elemental analysis. The main reason is that these techniques cannot differentiate unambiguously grafting versus adsorption and fail to report the presence of residual coupling agents (used during the synthesis) at the surface of the CNF. The latter are clearly evidenced from our NMR data with a wt\% similar to the functionalizing molecules. This has direct implications for drug delivery, especially the evaluation of efficiency.

Meso-scale polarity of cellulose microfibrils in plant cell walls: Distinguishing bidirectional vs. unidirectional arrangement of fibers using sum frequency generation spectroscopy
In plant cell walls, movement of cellulose synthase complex (CSC) regulates the cellulose microfibril deposition. By tagging CSCs with fluorescent tags and monitoring their movements with fluorescent microscopic imaging, previous studies have shown that the CSC movement is bidirectional in primary walls, while it can be biased toward unidirectional in induced secondary walls. This study explores the use of non-linear optical spectroscopy technique called sum frequency generation (SFG) to determine the net polarity of cellulose microfibrils in plant cell walls. Previously, DFT calculations suggested that SFG can distinguish parallel vs antiparallel packing of adjacent cellulose crystallites. The current study considers the effect of phase-mismatch between incoming and outgoing beams as well as the inter-crystallite separation. Theoretical calculations based on the nonlinear optics theory predicted how the SFG intensity will vary with the inter-crystallite distance for a given experimental geometry with a fixed coherence length of the SFG process. The theoretically-predicted trend was confirmed by measuring cellulose suspension solutions with varying concentrations. Then, the finding was applied to determine net polar order of uniaxially-aligned cellulose microfibrils along the fibril axis in a secondary xylem wall induced in the epidermis of Arabidopsis hypocotyl and cellulose fibers isolated from in vascular bundles of celery stem. To the best of our knowledge, these are the first spectroscopic evidence for biased directionality of cellulose microfibrils in certain types of plant cell walls.

**CELL 60**

**Beyond crystallinity: Developing Raman spectroscopy tools to better define cellulose supramolecular structure**

**Umesh P. Agarwal, uagarwal@fs.fed.us.** Forest Products Lab, Madison, Wisconsin, United States

Cellulose crystallinity measurement is one way to define the supramolecular structure of cellulose. However, from the vast literature on crystallinity, it’s clear that irrespective of the method used, the measurement inadequately defines the aggregated state of cellulose. Therefore, better approaches are needed. Raman spectroscopy is particularly well suited to this task because several pieces of information, beyond crystallinity, can be generated that when taken together provide a more accurate description of the aggregated state. Additionally, the information in Raman is more resolved because it comes from spectral features that represent both the aggregated and the molecular states of cellulose. Few examples will be presented to illustrate this capability.

**CELL 61**
Density functional theory modeling of cellulose and its interactions in plant cell walls

James D. Kubicki¹, jdkubicki@utep.edu, Hui Yang². (1) Geological Sciences, University of Texas at El Paso, El Paso, Texas, United States (2) Biology, Penn State, University Park, Pennsylvania, United States

The combination of X-ray, neutron, vibrational and nuclear magnetic resonance (NMR) spectroscopies has led to detail insights into the molecular structure of cellulose and its interactions with other plant cell wall components in muro. No technique provides an unambiguous interpretation of the molecular and nanoscale structure and chemistry however. Density functional theory (DFT) calculations are useful in this regard because they can be used to model structure, thermodynamics and kinetics with atomistic detail. The key is to ensure that the model results are consistent with experimental observables to the greatest extent possible. Our work focuses on reproducing known cellulose structures, vibrational frequencies and ¹³C NMR chemical shifts to benchmark the DFT predictions. DFT models can then be used to understand cellulose surface structure and interactions with other components that make up the foundation of the plant cell wall.

CELL 62

Advances in nanoscale infrared spectroscopy to explore the properties of lignocellulosic-based materials

Laurene Tetard, laurene.tetard@ucf.edu. NanoScience Technology Center, University of Central Florida, Orlando, Florida, United States

Advances to attain nanoscale spatial resolution with infrared spectroscopy are greatly needed to deepen our fundamental understanding of heterogeneous lignocellulosic-based. Meanwhile, the challenges associated with exploring molecular interactions locally remain, which impede the development of more efficient schemes to deconstruct lignocellulosic biomass and form new value-added materials derived from these processes. Novel platforms combining atomic force microscopy (AFM) and infrared spectroscopy (IR) with spatial resolution beyond 100 nm were recently proposed to explore the variations in chemical content of plant cell walls both in their native states and after chemical processing. They complement other multiscale interdisciplinary efforts required to grasp the complexity of the systems.

In this talk, we will discuss promising nanoscale infrared spectroscopy approaches that have been proposed to probe the composition of plant cell walls at the nanoscale (sub-100nm). To illustrate the potential of such technologies, we will compare the information accessed with various spatially resolved infrared spectroscopy methods on plant cell walls treated. The results will highlight the importance of statistical tools to establish connections between the observations made at the nanoscale and at larger scales to better take into account the complexity of natural variations associated with such systems.
FTIR microspectroscopy investigation of biomolecules distribution in cotton seed coat

Sumedha P. Liyanage, sumedha.liyanage@ttu.edu, Md. Tanjim Hossain, Noureddine Abidi. Fiber and Biopolymer Research Institute, Texas Tech University, Lubbock, Texas, United States

Cotton seed coat, which has a complex macromolecular composition, consists of cellulose, hemicellulose, lignin, pectin, and wax substances. The presence of seed coat fragments (SCFs) is a major problem in the textile industry because SCFs create weak points in the yarn and differences in dye uptake. The number of SCFs in the lint is cultivar-dependent. Understanding the amount and distribution of lignin and other macromolecules in the fiber base and the associated seed coat will provide a new insight into their contributions to produce SCFs. We identified two F3 cotton lines with differences in the number of SCFs in cotton lint. Then, we developed an integrated approach using Fourier transform infrared (FTIR) spectroscopy and microspectroscopy imaging, scanning electron microscopy, stereo microscopy, and thermogravimetric analysis to identify structural, compositional, and spatial distribution of biomolecules in SCFs. Infrared images of thin seed coat sections were analyzed by functional group distribution images and $k$-mean cluster analysis. Our results show that the distributions of pectic acids or hemicellulose (vibrations 1734 and 1624 cm$^{-1}$), and lignin (vibration $\sim$1504 cm$^{-1}$) are different in these cultivars. $k$-mean clustering produced different clusters and a representative spectrum for each layer of seed coats, which can be further analyzed to identify their biochemical differences. This study demonstrated that FTIR imaging could be used as a powerful non-destructive technique to investigate biochemical composition and distribution of biomolecules in seed coat sections.

Mass spectrometry analysis of pyranose dehydrogenase action on xylooligosaccharides

Maija Tenkanen$^1$, maija.tenkanen@helsinki.fi, Hongbo Zhao$^1$, Johanna Karppi$^2$, Emma Master$^{3,2}$. (1) University of Helsinki, Helsinki, Finland (2) Aalto University, Espoo, Finland (3) University of Toronto, Toronto, Ontario, Canada

Pyranose dehydrogenases (PDHs) are enzymes with ability to oxidize diverse carbohydrates in multiple positions. Oxidation of the anomeric carbon results in lactone which spontaneously hydrolyses to carboxylic acid in water. Secondary hydroxyls are oxidized to ketones which exist primary as hydrates in water complicating the analysis. In addition to monosaccharides, PDHs have shown activity on some di- and trisaccharides. Targeted enzymatic oxidation of carbohydrates facilitates their further derivatization or polymerization into bio-based chemicals and materials. We have compared activity and performance of two PDHs from Agaricus bisporus and
Leucoagaricus meleagris on linear (XOS) and arabinofuranosyl substituted (AXOS) xylooligosaccharides with degree of polymerization of two to five. Reaction mixtures were analyzed by UPLC-MS-ELSD to quantify the different oxidation products and ESI-MSn to reveal oxidized positions along the oligosaccharide. A workable method was developed applying sodium borodeuteride reduction for labeling of formed carbonyls to facilitate the identification, quantification and structural analysis of oxidized products. Activity of both enzymes was found to decrease with increasing length of the (A)XOS. Oxidation of linear XOS mostly led to bifunctionalized double oxidized products, and the oxidation was clearly targeted to the reducing and non-reducing xylopyranosyl residues. Single oxidized products dominated in AXOS reactions. Selectivity between oxidation of specific secondary hydroxyls versus the reducing end C1 was found to depend on both the enzyme and the substrate. The developed MS methods and data analysis, with the obtained results will be discussed in detail in the current paper. The sensitive and fast MS methods will be shown to have broad applicability to study carbohydrate oxidoreductases in general.

CELL 65

Removal of rare earth metal ions from contaminated water by sustainable carboxycellulose nanofibers derived from agave through nitro oxidation process

Isha Brahmbhatt1, ishabrahmbhatt02@gmail.com, Sunil Sharma1, Priyanka R. Sharma2,1, Marc Nolan1, Benjamin S. Hsiao3. (1) Chemistry, Stony Brook University, Ardsley, New York, United States (2) Polymer science and engineering division, National chemical laboratory, Dr.Homi Bhaba Road, Pune-411008, India (3) Stony Brook University, Stony Brook, New York, United States

There is a growing need for rare earth metal ions such as lanthanides for use in electronics, fuel cells, and various other applications. These precious ions are currently derived by mining, causing major pollution and contamination in nearby water sources. As cellulose is the most abundant organic material, we derived carboxycellulose nanofibers from raw agave biomass using the simple nitro oxidation process for the removal of lanthanide ions. The nitro oxidation method converts untreated biomass to carboxycellulose nanofibers in a one step process using nitric acid and sodium nitrite. Zeta potential indicates that the fibers are highly electronegative (zeta potential -117.3 mV), and the conductometric titration method reveals that the fibers have a high carboxylate content (0.75 mmol/g). SEM measurements show that the fibers contain clearly visible fibrous structures. The TEM measurements of the fibers record fiber lengths of 55-690 nm and average fiber widths of 5-6 nm, and AFM data displayed an average thickness of 1.6 nm. The oxidation of the agave nanofibers was confirmed with 13C CPMAS NMR data. The lower crystallinity of the agave nitro oxidized carboxycellulose nanofibers compared to raw agave was determined by WAXD. The nitro oxidation approach also offers beneficial reductions in the consumption of water and electric energy as well as the need for multi-chemicals when compared with conventional multiple-step processes at bench scale (e.g. TEMPO oxidation). Remediation studies on lanthanide ions showed a floc formation between the ions and
nanofibers. The Langmuir isotherm generated from ICP-MS studies indicated a 285.7 mg/g adsorption capacity and over a 90% adsorption efficiency for all lanthanide concentrations, which supersedes current water purification mechanisms such as iron oxide beads (123.6 mg/g adsorption capacity). These results suggest that the agave nitro oxidized carboxycellulose nanofibers are effective for the removal of lanthanide ions for drinking water purification and lanthanide ion industry.

CELL 66

High-strength and high-toughness double-cross-linked chitosan hydrogels: One-pot synthesis from chitin KOH/urea aqueous solution

Yi Zhong, 372821627@qq.com, Lina Zhang, Jie Cai. College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei, China

Construction of high value-added products from natural renewable bioresources is challenging and rewarding. High crystalline polysaccharides like cellulose and chitin, are insoluble in common solvents, suffering from insufficient development and utilization. Chitosan, the N-deacetylated product of chitin, is soluble in acid aqueous solution, having attracted much attention. However, the utilization of chitosan-based materials has been hampered by the weak mechanical properties when regenerated from acidic media. Recently, a sequential chemical crosslinking and physical crosslinking strategy has been proposed by us to prepare double-cross-linked (DC) chitin and cellulose hydrogels with both strength and toughness significantly improved. Herein, high-strength and high-toughness chitosan hydrogels were successfully prepared from chitin aqueous solutions, using the "green" and high-efficiency aqueous KOH/urea solution as solvent for chitin. The "one-pot" synthesis of chitosan hydrogels from chitin aqueous solution is based on a combination of in-situ deacetylation and sequential chemical and physical crosslinking strategy. Atomic force microscopic (AFM) images of DC chitosan hydrogels show that chitosan nanofibers self-assembled into a homogeneous 3D network structure. The incorporation of chemically and physically cross-linked domains imbues the DC chitosan hydrogels with relatively high-strength and high-toughness. The DC chitosan hydrogels are promising candidates for potential applications in biomedical materials, soft robots and environment-responsive materials.
Isolation and characterization of cellulose nanofibrils from \textit{cladophora glomerata} algae

\textbf{Wenhua Gao}, segaowenhua@scut.edu.cn, Jinsong Zeng, Jun Xu, Bin Wang, Kefu Chen. Scholl of Light Industry and Engeering, South China University of Technology, Guangzhou, Guangdong, China

\textit{Cladophora glomerata (C. glomerata)}, a fresh-water green macroalgae, has unique cellulose properties and thus may be promising for production of cellulose nanofibrils (CNFs). In this study, the main chemical components and polyose were tested by GC-
MS and ion chromatography respectively. The potential values of biodiesel and bioethanol were also analyzed. Then, the cellulose from *C. glomerata* was extracted and subjected to microfluidization with or without enzymatic hydrolysis pretreatment to produce CNFs. The results showed that the main lipid in *C. glomerata* were palmitic acid ester, stearic acid methyl ester and linoleic acid methyl ester. Compared to microcrystalline cellulose, the extracted cellulose from C. glomerata showed the same FT-IR characteristic groups and fast pyrolysis temperature range from TG analysis. The width of extracted cellulose from *C. glomerata* was not uniform, but the width of its constitutional unit was similar with bacterial cellulose. Increasing microfluidization passes produced smaller algal CNFs with more uniform sizes and lower crystallinity. Combining microfluidization with an enzymatic hydrolysis pretreatment, the crystallinity of algal CNFs decreased further, but the diameter distribution showed little change. The algal CNFs has significantly higher crystallinity, smaller diameter and better thermal stability. AFM analysis indicated that the diameter of Cladophora-CNFS was 15~30 nm.

**CELL 68**

**3D printed UV curable hydrogels using cellulose nanocrystals as a rheological modifier**

*Doron Kam*¹,², *Ariel Braner*¹,³, arielbraner@gmail.com, *Liraz Larush*¹, *Annalisa Chiappone*⁴, *Oded Shoseyov*², *Shlomo Magdassi*¹. (1) Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel (2) Plant Sciences and Genetics in Agriculture, The Hebrew University of Jerusalem, Rehovot, Israel (3) Alpha program, Future scientist center, Jerusalem, Israel (4) Applied Science and Technology, Politecnico di Torino, Torino, Italy

3D printing through extrusion-based technologies, requires flow of the ink during the extrusion, and rapid fixation upon contact with the printing platform. Here we present new hydrogel compositions, which are based on combining the rheological properties of cellulose nanocrystals, with rapid fixation by UV triggers polymerization. Hydrogels containing 54% water were 3D printed by Direct Write Process, while using nanoparticles of water-insoluble photoinitiator, 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (TPO). The 3D printing ink contained acrylic acid as a monomer with PEGDA as a cross-linker and cellulose nanocrystals (CNCs) for controlling the rheology. The latter provides a pseudo-plastic behavior, in which the ink has a low viscosity while printed and high viscosity at rest. The UV triggered photopolymerization was investigated by photo-rheology measurements. It was found that the CNCs improved the Young’s modulus of the printed objects, without disrupting strain to break.

**CELL 69**

**From traditional use of Fique fibers (*Furcraea spp*) to novel bionanocomposite for dye degradation technologies**
**Juan David D. Sánchez Moreno, jusanchez18.94@gmail.com, Eduart Gutiérrez Pineda, Cristian Blanco-Tirado, Marianny Y. Combariza. Escuela de Química, Universidad Industrial de Santander, Bucaramanga, Santander, Colombia**

*Furcraea spp*, commonly known as fique, was traditionally used as raw material for manufacturing of craftwork and artisanal products. Nowadays, it has gained radical importance in local Colombian science because of its functionality as a renewable biomass source. In previous studies, our research group has shown that fique fibers work as optimal matrices in nanocomposite materials used in wastewater dye degradation. However, nanoparticles (NPs) leaching appears to be the main problem during the application of these bionanocomposite (BNC) materials, generating short life cycles of use. In this research, we considered an initial surface modification as one of the most appropriate procedures to enhance the chemical interaction between cellulose and NPs. The overall process starts with the delignification of the fique fibers to obtain white and highly pure cellulose. These carbohydrate chains expose a highly porous and elevated hydroxyl group density on its surface, which makes them suitable for chemical modifications. Whereby, the surface was activated by the addition of N,N'-carbonildiimidazole and later amine anchoring. Fourier Transformed Infrared Spectroscopy (FTIR), Thermal characterization (TGA/DTG) and X-ray Photoelectron Spectroscopy (XPS) analysis confirmed the formation of a carbamate bond on the sixth carbon of the anhydroglucose units of cellulose and proved the presence of amine groups over the fibers. Subsequently, these modified fibers were decorated with manganese and iron oxide NPs. Scanning Electron Microscopy (SEM) and XPS analysis were respectively used to study the morphological and chemical composition of these bionanocomposites. To the best of our knowledge, this new BNC overcome the price-performance ratio of any previously reported fique nanocomposite applied in water treatment, and enables an effective route to obtain novel cellulose-based materials for future technological applications in the degradation of dyes.

**CELL 70**

**Nanocellulose based filaments as textile sensors**

*Korneliya Gordeyeva¹, gorde@kth.se, Calvin Brett², Stephan Roth³, Daniel Soderberg¹*. (1) Fluid Mechanics, KTH Royal Institute of Technology, Stockholm, Sweden (2) KTH Royal Institute of Technology & DESY, Stockholm, Sweden (3) DESY, Hamburg, Germany

During the last decades the demands of the society facilitated the development of electronic devices. Especially the production of smart technical textiles would be of great value for biomedical applications and health care. The most effort so far was placed in integration of optical fibers into textiles. Unfortunately, they have limitations in mechanical performance, they are typically expensive and hard to handle. Cellulose nanofibers (CNFs) seem to be a suitable replacement. They are nanoparticles that can be extracted from wood, an abundant and renewable material. Due to their biodegradability, mechanical strength and lightweight, CNFs have a potential in
production of green smart textiles. Recently it has been shown that strong and stiff biofibers can be produced using a dilute dispersions of CNFs by aligning the nanoparticles with shear and extensional flows, and that properties can be tuned by controlling interactions on the nanoscale.\(^1\)\(^,\)\(^2\)

In this work we are utilizing the flow-focusing fabrication route to produce stiff and strong filaments where TEMPO-mediated oxidized CNFs are playing the role of a strong and flexible matrix, and silver nanorods are used to provide conductivity. The fabricated filaments are evaluated with respect to hierarchical structure using electron microscopy as well as x-ray scattering techniques, and the structural information and impact on external mechanical load is correlated to conductivity. Furthermore, it is demonstrated that the obtained material is suitable for production of textile sensors based on nanocellulose.

**CELL 71**

**Effect of methacrylation on the thermoresponsive sol-gel transition of methylcellulose**

*Nada Haq-Siddiqi, nhaqsiddiqi@gmail.com, Steven B. Nicoll. Biomedical Engineering, City College of New York, Brooklyn, New York, United States*

Methylcellulose (MC) is a water-soluble cellulose derivative with a thermogelling property which allows it form physically crosslinked hydrogels as it undergoes sol-gel transition, driven by the aggregation of hydrophobic methoxy groups with increasing temperature. This property makes MC an appealing material for biomedical applications that require a sol-gel transition initiated at \(\leq 37^\circ\)C, enabling ease of injection as a liquid followed by gel formation post-injection within the body. However, physical crosslinking of MC alone does not result in adequate mechanical stability for most biomedical applications. To overcome this, we have added methacrylates to MC to enable chemical crosslinking via free-radical polymerization to form robust, stable hydrogels. The following study characterizes the influence of methacrylates on the thermoresponsiveness of MC. Methacrylated MC (mMC) was synthesized by reacting MC with methacrylic anhydride. Degree of methacrylation was quantified via \(^1\)H NMR (7.55%). Rheological analysis of mMC and unmodified MC (uMC) (3% w/v) showed that the thermoresponsiveness of MC (characterized by a sharp increase in \(G'\) at the thermogelation onset temperature) was preserved in mMC (\(n=3\)). Both uMC and mMC showed characteristic “salt-out” responses of lower gelation temperature when dissolved in PBS vs H\(_2\)O. The presence of methacrylate groups on the mMC significantly lowered the thermogelation temperature (~14°C) compared to uMC in both solutes. In addition, the rate of increase in \(G'\) was lower in mMC than uMC, indicating the potential role of steric interactions of the methacrylate group on the kinetics of MC aggregation. Thermogelation onset was at or below 37°C only in the mMC dissolved in PBS. The combined effect of thermogelation onset at or below physiologic temperatures with free-radical crosslinking results in a physiologically relevant injectable hydrogel with a wide variety of biomedical applications.
Hyper-production of cellulase based macromolecules by *Escherichia coli* engineered with UV & EMS mutated cellulase gene from *Aspergillus niger* for industrial applications

**Qurat-ul-ain Daud**, anniedaudkhan@yahoo.com. Biochemistry and Biotechnology, University of Gujrat, Mirpur, Pakistan

By every passing moment there seems to be an energy crisis everywhere in the world. Natural resources are depleting day by day. The increasing need of energy resources can be fulfilled by degrading cellulosic biomaterial by help of cellulasic material coated on macromolecules. Cellulases are the group of extracellular enzymes commonly employed for the hydrolytic breakdown of cellulolytic material. Cellulase enzyme has applications in almost every field including waste treatment, food processing, paper industries, etc. Due to high industrial demand, the high production cost of cellulases have always been major problem. The production of the cellulase enzyme from *Aspergillus niger* is the most economical way. Thus the study was designed to enhance the efficiency and cost effective production of cellulase enzyme. The strain of *A. niger* was genetically modified by the random mutation to obtain high efficiency cellulase producing strain. The hyperexpressed cellulase enzyme coated on macromolecules in the form of microfiblis on iron oxide carboxymethylcellulose macromolecules. The
random mutation was performed by physical and chemical methods. The physical mutagenesis was performed by the UV treatment at different time intervals. The maximum enzyme activity 324 μmol/mL was obtained at 10 mins UV exposure. The chemical mutagenesis was done by the treatment of Ethyl methane sulfonate concentrations 50, 100, 150, 200 and 250 μg/mL. The cellulase assay was performed using CMC as substrate following the method of DNS. The maximum enzyme activity obtained was 395 μmol/mL at 150 μg/mL. Then the maximum enzyme activity 427.6 μmol/mL obtained by the combined mutagenesis done by exposure of 10 min UV radiation followed by treatment with EMS150 μg/mL concentration. The RNA was extracted and after its PCR amplification the mutant cellulase gene was cloned into suitable host. Thus in the present work best mutant was screened on the basis of Congo Red and Cellulase Assay method. The mutant cellulase gene from an indigenous strain of Aspergillus niger was successfully cloned and coated on macromolecules. The macromolecules coated with hyper-expressed cellulase enzyme from cloned mutant cellulase gene can be employed in almost every industry for improved, faster and cost effective degradation of cellulosic biomaterial that would be helpful for the environment and economy worldwide and would be new era of growth and development.

CELL 73

Opportunities to improve biomass pretreatments revealed by molecular dynamics simulations of xylan and xylan-cellulose complexes

Micholas D. Smith²,¹, micholasdsmith@gmail.com, Rajeev Kumar⁶, Preenaa Moyer³, Nicole Labbé³, Charles Cai⁶, Loukas Petridis⁴, Jeremy Smith⁵. (1) Center for Molecular Biophysics, University of Tennessee/ORNL, Knoxville, Tennessee, United States (2) The University of Tennessee Knoxville, Knoxville, Tennessee, United States (3) Univ of Tennessee, Knoxville, Tennessee, United States (4) Center for Molecular Biophysics, Oak Ridge National LAboratory, Oak Ridge, Tennessee, United States (5) University of Tennessee/Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (6) UC Riverside/CE-CERT, Riverside, California, United States

The cost-efficient production of renewable materials and fuels from lignocellulosic biomass is a long-standing engineering challenge due to the natural recalcitrance of biomass. In recent years advances in pretreatment technologies have shown promise in overcoming the recalcitrance challenge; however, improvements must still be made to compete with the modern petrochemical fuel and chemical sector. To rationally improve current biomass pretreatment technologies, it is necessary to obtain insights into the fundamental behavior of lignocellulose substituents under common pretreatment conditions. Here we report on the results of molecular simulations of Xylan under three different pretreatments (Ionic liquids, CELF, and hydrothermal) and highlight how the results of these simulations can provide crucial insight into the improvement of various pretreatments.

CELL 74
Nitro-oxidation on raw agricultural residues

Priyanka R. Sharma¹, prsharma195@gmail.com, Sunil Kumar Sharma². (1)
Interdisciplinary Center for Water Research, Indian Institute of Science, Bangalore, India, India (2) R&D, IPI, Mountain Top, Pennsylvania, United States

Nitro-oxidation method comprised of nitric acid-sodium nitrite was performed on raw agricultural biomass (without washing and pretreatment) to generate the carboxycellulose nanofibers. A combination of nitric acid-sodium nitrite during nitro-oxidation can effectively remove the lignin and hemicellulose impurities, and securely generate the carboxycellulose fibers. The effect of amount of sodium nitrite, concentration of nitric acid and the reaction time on generation of nanofibers and its carboxylate content was studied. Additionally, the produced nanofibers from different agricultural residues were introduced for the measurement of residual lignin and hemicellulose content. The preliminary analysis indicates that the carboxycellulose nanofibers extracted from different biomasses possessed length (L) more than 1000 nm and width (W) in the range of 4-10 nm. The increase in the amount of sodium nitrite during Nitro-oxidation elevates the carboxyl content onto the Carboxycellulose nanofibers. However, no significant changes observed in the residual content of lignin onto the Carboxycellulose nanofibers on the increase in the amount of Sodium nitrite.

CELL 75

Comparing physicochemical properties and sorption behaviors of pyrolosis-derived and microwave-mediated biochar

Colten Brickler¹, cb18fd@my.fsu.edu, Yudi Wu¹, Simeng Li², Gang Chen¹, Anandhi Swamy³. (1) Civil and Environmental Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida, United States (2) Civil Engineering, California State Polytechnic University, Pomona, California, United States (3) Biological Systems Engineering, Florida Agricultural and Mechanical University, Tallahassee, Florida, United States

Biochar’s ability to amend and remediate soil has been a growing interest, though the high energy expenses from high-temperature pyrolysis deter the motivation of the product use. Three types of feedstock (i.e., switchgrass, biochar, and live oak leaves) were used to produce biochar via slow pyrolysis at different temperatures and microwave irradiation at various power levels in this study. The resulting biochar was characterized for their physiochemical properties, including surface functionality, elemental composition, recalcitrance, and thermal stability. Through comparison, it was discovered that microwave biochar was more resistant to thermal decomposition, yet more diverse surface functional groups were preserved than pyrolysis biochar. Sorption behaviors of biochar were investigated by isotherm experiments. Microwave biochar exhibited better effectiveness in retaining ammonium nitrogen (NH₄⁺-N), which could be attributed to its larger specific surface area and abundance of hydrophilic groups. The findings in this study aimed at creating a product with similar or better properties as conventional pyrolysis biochar to allow a large reduction in production costs through
microwave utilization. The results suggested that microwaves with increased power output would be needed to expose the feedstock to a temperature high enough to cause significant thermal transformation. Biochar produced through microwave irradiation has the potential to increase nitrogen retention for increased agricultural crop yields.

CELL 76

High-efficiency, energy-saving and “green” route for fabrication of chitin-based materials

Jie Cai, caijie@whu.edu.cn. Wuhan University, Wuhan, Hubei, China

Crystalline polysaccharides, such as cellulose, chitin/chitosan are useful for important and rapidly growing applications ranging from advanced energy storage, green electronics and catalyst or enzyme supports to tissue engineering and biological devices. However, the potential value of chitin in such applications is currently neglected because of its poor swellability, reactivity and solubility in most commonly used solvents. Herein, a high-efficiency, energy-saving and “green” route for the fabrication of chitin-based hydrogels, aerogels, films, fibers and derivatives is described in which chitin is dissolved in an aqueous KOH/urea solution. The structure and properties of these chitin-based materials were characterized. The simplicity of the process and the widely tunable properties of the chitin-based materials make them promising candidates for applications in various fields in the future. The method developed here should contribute to the utilization of seafood waste and, thereby, to the sustainable use of marine resources.

CELL 77

Evaluating the impact of natural fiber welding on the surface area of biopolymer materials

Julia A. Mcfarland¹, m204026@usna.edu, U.S. Naval Academy Attn: Aiello¹, Christian E. Hoffman¹, Tyler Cosby¹, David P. Durkin¹, Paul C. Trulove². (1) Chemistry, United States Naval Academy, Annapolis, Maryland, United States (2) Chemistry, U.S. Naval Academy, Annapolis, Maryland, United States

Ionic liquids (ILs) are highly versatile solvents that can dissolve a wide variety of materials including biopolymers such as cellulose or silk. A process known as Natural Fiber Welding (NFW) applies this unique property of ILs to the partial dissolution and reconstitution of natural fibers. This allows for material property enhancement, such as increased strength, without the complete sacrifice of the native structure. Adjustable parameters such as time, temperature, and type of ILs control the degree of dissolution. Literature, however, only provides limited quantitative data that describes the impact that NFW has on the dissolution and reconstitution processes. A more complete understanding of the NFW process is important, especially as we continue to develop it for future applications of functional biocomposite materials. In this study, we apply
physisorption (Kr and N₂) and microscopy methods to measure changes to the surface area of cellulosic materials due to systematic variations of NFW process variables.

CELL 78

Development of a cellulosic 3D structure “white-colored bamboo”

Tatsuki KUREI¹, q01-sw-makar@st.go.tuat.ac.jp, Rino TSUSHIMA¹, Satoshi NAKABA¹, Ryo FUNADA¹, Yoko OKAHISA², Yoshiki HORIKAWA¹. (1) Tokyo University of Agriculture and Technology, Tokyo, Japan (2) Kyoto Institute of Technology, Kyoto, Japan

Creation of a cellulosic material with maintaining highly-controlled 3D structure was prepared by optimizing chemical treatment. Though alkaline processing and alcoholysis are effective approach to remove the lignin from lignified cell wall, neither chemical treatment is insufficient for bamboo block. However, we found the combination of alkaline processing and alcoholysis followed by repetition of bleaching treatment using sodium chlorite enabled to get rid of non-cellulosic components including hemicellulose and lignin from bamboo’s cell wall of parenchyma as well as that of vascular bundles. Then, multiple structural assessments from anatomical- to nano-level was performed by using X-ray CT (computed tomography), X-ray diffraction and transmission electron microscopy incorporated with TEMPO-mediated oxidation technique. X-ray CT was initially applied to observe the anatomical structure and inner architecture, which revealed that the typical cell arrangement was maintained. Next, X-ray diffraction analysis demonstrated microfibril orientation in the cell wall as well as natural crystalline structure of cellulose were unaltered. Lastly, cellulose nanofiber was obtained by applying TEMPO-mediated oxidation technique to evaluate the microfibril morphology. TEM observation image showed that the normal morphology of cellulose microfibrils was also kept. As abovementioned, multidirectional assessment revealed the "White-Colored Bamboo" maintained its inherent hierarchical structure, which will prompt to produce new functional biomaterials. In addition, we will present a distribution of silica particles on the epidermis even in "White-Colored Bamboo".

CELL 79

Trypsin active paper for sample preparation steps in paper-spray mass spectrometry applications

Laura M. Riedler¹,², riedler@cellulose.tu-darmstadt.de, Uta Schwenke¹,³, Tina Bock¹,³, Gerhard Schwall¹,³, Markus Biesalski¹,². (1) Merck Lab @ TU Darmstadt, Technische Universität Darmstadt, Darmstadt, Germany (2) Macromolecular and Paper Chemistry, Technische Universität Darmstadt, Darmstadt, Germany (3) Science Relations, Merck KGaA, Darmstadt, Germany

Cellulose filter paper are widely used in microfluidic devices, due to their well-known properties like capillary fluid flow, non-toxic chemical nature, good disposability and
availability. For the fabrication of analytical microfluidic assays, cellulose filter paper is modified with hydrophobic components for the formation of microfluidic channels. Further, functional molecules like antigens, enzymes etc. can be incorporated in certain regions of the channel to establish an analytical device. Several strategies for the formation of microfluidic channels, as well as for the incorporation of (bio-) active components onto cellulose filter paper have already been reported.

In the present project, the question rather is: "What can paper do to facilitate sample preparation steps in analytical investigations?" Therefore, the focus is not to detect and indicate specific compounds of the analyte solution, but furthermore to conduct separation processes and/or chemical modifications of specific sample compounds. It is aimed to transfer wet-chemistry sample preparation steps for analytical investigations as “Dried Blood Spots" or “Paper-Spray Mass Spectrometry” to functional papers, forming a new field of application, called “Paper in the Lab". By having sample preparations for e.g. medical samples in mind, a variety of different preparation steps, requiring different functional molecules may have to be conducted. To deal with this diversity of functionalities, another prerequisite is to design the functionalization strategy as modular and versatile as possible.

So far, we already established modular immobilization strategies based on different types of click chemistry. Furthermore, we successfully immobilized trypsin on model paper for Paper-SPray MS analyses under receiving its activity. Therefore, azide functionalization of cellulose fibers, alkyne functionalization of trypsin, followed by the click reaction between the azide-functionalized fibers and the alkyne-functionalized trypsin, as well as the impact of each functionalization step on the tryptic activity, were studied. Hereafter, the immobilization strategy will be applied to additional functionalities for a broader range of analytical applications in future.

**Towards understanding capillary driven transport in paper: Quasi-stationary investigations using a spinning device**
Since the pioneering work by Whiteside et al. in 2007, and others, paper-based microfluidic devices have been increasingly studied owing to their great potential in various fields of application, such as point-of-care diagnostics, environmental monitoring and food quality testing. The interest in using paper as a substrate for such devices is based on the unique porous structure of paper, enabling liquid transport without any external pumping system. Through selective surface modification as e.g. hydrophobization by wax coating, a directed analyte fluid flow towards specific detector systems is possible. While the fluid flow behavior on a macroscopic scale is well investigated and can be described by various numerical models, a more detailed understanding of the fluid flow characteristics on a microscopic scale is crucial for further improvement of these paper-based analytical devices. The dominating effects governing fluid flow can be divided into wetting, swelling, diffusion, evaporation and, last but not least, capillary transport. The latter can be modulated by intrinsic paper parameters such as fiber type, fiber pretreatments or fines content as well as extrinsic parameters such as coatings. Most importantly, such dynamic water-fiber interactions are not accounted for with simple Lucas-Washburn or Darcy kinetics. Hence, it would be desirable to investigate the influence of the above mentioned effects on the dynamics of fluid flow separately from each other.

In our present project, a self-developed spinning device is used to quantify the capillary forces of different paper materials by generating a force equilibrium between the capillary forces driving the fluid flow and the centrifugal forces originating from the spinning device. By analyzing the fluid flow distance until the equilibrium state between these two forces is established, conclusions about the paper intrinsic properties can be drawn. Here, a longer distance points to higher capillary pressure, which allows assumptions about the pore geometry at known fluid properties. These measurements suggest that it is in principle possible to separate capillary imbibition from fiber wetting and swelling, respectively.
The relative gel strengths of gelatin and SeaGel® formulations were investigated. A standard gelatin “Bloom test” was applied to the as formulated gel masses to determine the gel strength for the two different materials. The gel strength was measured at 4°C, 10°C, 25°C, and 37°C. In all cases, the SeaGel® gel mass showed a higher strength than the gelatin, and had less of a dependence on temperature. The higher gel integrity at elevated temperatures could lead to improved handling of the gel mass and therefore better encapsulation performance.

The relative drying rates of films prepared with the SeaGel® formulation and gelatin formulation were also investigated. Films were dried using both TGA and DVS to understand the impact as a function of temperature and humidity. SeaGel® films demonstrated faster drying at all temperature conditions as compared to gelatin. At room temperature, SeaGel® capsules can be dried over 3x faster than gelatin at the same temperature. SeaGel films are also able to tolerate higher temperatures than gelatin. Gelatin films began to show signs of melting at temperatures above 35°C whereas SeaGel® films are stable up to ~80°C. Higher thermal stability can be a benefit in capsule applications where the fill material requires higher temperatures to pump into the capsule shell. The same trend was observed when the films were subjected to
drying in humidity controlled environments. At 0, 25, and 7% relative humidity, SeaGel® films exhibited significantly faster drying capability than gelatin.

Gelatin films also exhibited a case hardening effect wherein at elevated temperatures (>35°C) the drying appears to slow due to a "skin" forming on the surface of the gelatin film. This skin does not allow interior water to escape from the film, leading to the appearance of drying, without actually removing all of the moisture. The remaining interior moisture can then slowly migrate out of the film and cause poor stability performance of the capsules.

Finally, overall capsule physical property testing was conducted. Burst and rupture tests were performed with a texture analyzer to compare the relative capsule strength of the two materials. Gelatin capsules had a higher burst and rupture force compared to SeaGel®. Both materials had disintegration behavior that was equivalent on a relative time scale.

**CELL 82**

**Development of rigid poliurethane foam from kraft lignin and renewable chain extender: Thermal insulation application**

*Lara Tavares¹, lara.btavares@hotmail.com, Suel E. Vidotti². (1) Entropic Solutions, São Caetano do Sul, SP, Brazil (2) Federal University of ABC, Santo André, São Paulo, Brazil*

Lignin is a promising renewable resource and is considered an alternative raw material for the synthesis of sustainable polymers and chemicals. In particular, the development of lignin-based rigid polyurethane (PU) foams is favored by the presence hydroxyls group and aromatic rings in its structure. However, the low reactivity of aromatic hydroxyls and reduced solubility in vegetal oils require a previous modification of lignins structure, in order to synthesize rigid foams with suitable properties such as thermal conductivity, distribution/cell size, and mechanical behaviors. This work aims to develop rigid PU foams from kraft lignin (KL), combined with modified castor oil as chain extender, for a biobased polyols synthesis. Technical kraft lignin (Suzano Papel e Celulose, Brazil) was oxypropilated; propylene oxide was used as reagent to obtain oxypropilated lignin (OKL). In addition, castor oil (CO) was transesterified using glycerol to obtain modified castor oil (MCO). OKL and MCO were charaterized by Fourier-transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and hydroxyl value determination. Afterward, OKL and MCO were mechanically mixed in different ratios and reacted with MDI, forming rigid PU foams. Rigid PU foam containing up to 50 wt% of OKL was obtained. The results show that oxypropilation improved reactivity and solubility in modified castor oil.

**CELL 83**

**Characterization of silk/cellulose biocomposites infused with rGO**
Abneris Morales¹, abneris.morales@yahoo.com, Bailey Blessing¹, Stacy Love², Sean M. O’Malley³, Xiao Hu⁴, David Salas-de la Cruz⁵,². (1) Chemistry, Rutgers University-Camden, Camden, New Jersey, United States (2) Center for Computational and Integrative Biology, Rutgers University-Camden, Camden, New Jersey, United States (3) Physics, Rutgers University-Camden, Camden, New Jersey, United States (4) Physics and Astronomy, Rowan University, Glassboro, New Jersey, United States (5) Chemistry, Rutgers University, Philadelphia, Pennsylvania, United States

In the recent years, biomaterials from renewable sources have shown potential in medicine and materials science alike. They are rapidly expanding class of materials and have been of interest in the recent decades due to their abundance, low cost, biocompatibility, and tunable morphological and physicochemical properties. Cellulose is appealing to the industry due to its crystalline and amorphous polymorphs; while silk is made up of flexible protein fibers, is attractive due to its tunable biodegradation and excellent biocompatibility. When these two natural biomacromolecules are mixed together, their properties can be tuned by changing material composition and fabrication method (i.e. solvent type, coagulation agent and temperature). Reduced graphene oxide (rGO) is an ideal compound to increase molecular interactions and stabilization of these two components. In addition, being strong oxidizing agent, it offers hydrophilicity giving it good solubility properties. In this study, we aim to understand how rGO molecules affect the carbohydrate crystallinity and protein secondary structure formation as well as their physicochemical properties including ionic conductivity. The fabricated biocomposites with rGO were investigated using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), X-Ray Scattering, Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA). The results showed that the addition of rGO stabilizes the morphology and thermal properties of the biocomposites. The results also demonstrated that the cellulose crystallinity and the silk beta sheet content influence the ionic conductivity of the materials.

CELL 84

Crystallization behavior and thermal restoring of superhydrophobic flower-like structures using binary mixtures of cellulose-based polymers and waxes

Cynthia Cordt, cordt@cellulose.tu-darmstadt.de, Andreas Geissler, Markus Biesalski. Macromolecular and Paper Chemistry, Technische Universität Darmstadt, Darmstadt, Germany

In this contribution we present a novel strategy for superhydrophobic coatings based on cellulose polymers, whose functionality can be restored, even after thermal or mechanical impact. Barrier coatings made of renewable raw materials are ideally suited for paper finishing, whereby (super-)hydrophobic coatings are particular important for a number of different paper applications e.g. packaging materials and furthermore for a new class of paper-based construction materials. Nevertheless, this coating is not limited to paper, but can also be transferred to wood, glass or PET, for instance.
Recently, our working group has intensively studied the synthesis and application of cellulose-based hydrophobic nanoparticles e.g. of C18-esters of cellulose or hydroxypropyl cellulose, respectively, which possess auspicious properties. However, the superhydrophobicity is limited due to a change of coating structure from a particulate to a smooth film, for instance by thermal or mechanical impacts. To overcome these limitations, our current studies focus on the combination of such cellulose-based C18-esters with low molecular waxes. By the interaction of both materials we observed flower-like surface morphologies with a roughness on nano- to microscale that causes superhydrophobic properties. These structures crystallize spontaneously during cooling from the molten state ($T_m$: 35-65 °C). Accordingly, if superhydrophobic properties are lost, contact angles above 150° can be thermally restored by a simple reheating process. Currently, we are focusing on gaining a fundamental understanding of this structure forming process: Does the polymer chains act as “structure-guide” to direct the thermally induced formation of flower like structures? Does this lead to a co-crystallization of the material along the given structure? What influence do the polymer properties e.g. molecular weight or C18-ester degree of substitution have on the size of the emerging structures?

Thermally generated flower-like polymer/wax structures lead to superhydrophobic paper surface.

CELL 85

Dual-triggered CMC/dopamine/cystamine hydrogels driven by dynamic metal-ligand and redox for self-healing and agrichemical release

Tianyu Guo$^{1,2}$, Wangxia Wang$^1$, Huining Xiao$^2$, Yongcan Jin$^1$, jinyongcan@njfu.edu.cn.
(1) Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing, China (2) Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada

Expanding the useful lifespan of materials is becoming highly desirable, and self-healing and stimuli-responsive materials may become valuable commodities. In this work, dual-triggered dopamine (DA)/cystamine (CYS) hybrid carboxymethyl cellulose (CMC)-based hydrogels were synthesized. The system introduced a dual stimuli-responsive hydrogel containing CMC chains modified with electron donor dopamine sites and disulfide bonds. In the presence of DA and CYS, a stiff hydrogel consists of CMC chains was
formed, cooperatively stabilized and cross-linked by dynamically restructuring DA/metal-ligand interactions and by CYS. The cyclic and reversible formation and dissociation of the supramolecular donor-acceptor interactions, through dynamic metal–ligand coordination with DA, or via reduction and subsequent oxidation of the CYS sites, led to hydrogels of self-healing and switchable stiffness. Based on this, a facile and versatile method is suggested for directly integrating drugs into CMC-based hydrogels as a surface-mediated agrichemical delivery platform, which is favorable for the long-term sustained release of the drug. The dynamic properties of these dual-triggered hydrogels provide great potential for drug delivery in a wide variety of biomedical applications.

CELL 86

Low-cost synthesis of cellulose-biochar composites for enhanced water and nitrogen use efficiency in agricultural fields

Yudi Wu2, yw17h@my.fsu.edu, Colten Brickler2, Simeng Li1, Gang Chen2. (1) Department of Civil Engineering, California State Polytechnic University Pomona, Pomona, California, United States (2) Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida, United States

Superabsorbent hydrogels have been used to enhance water and nutrient retention in agricultural soils. However, wide applications of these polymeric soil amendments on large farms are plagued by their high costs and environmental footprints. In this study, cost-saving and eco-friendly cellulose-biochar composites were synthesized through rapid mediation of microwave radiation. Urea was incorporated in the composites to produce slow-released fertilizers. The physicochemical properties of these composites, such as surface functionality, thermal stability, crystallinity, and morphology, were characterized using various state-of-the-art analytical techniques. The sorption properties of these novel composites were also investigated by a combination of isotherm experiments and mathematical models. The discoveries in this study demonstrated that microwave irradiation could effectively facilitate structural alteration and optimize cross-linkage of cellulose-biochar composites. As a result, the significantly improved swelling capacity of these composites was able to allow larger storage of water and dissolvable minerals to combat against drought and nutrient deficiency in soils. The slow release of urea into the environment could not only increase nitrogen use efficiency (NUE), but also reduce nitrous oxide emission (N₂O) from agricultural fields. A life-cycle cost analysis based on a large-farm application scenario supported the economic viability of these “green” composites.

CELL 87

Natural rubber nanocomposites with nanocellulose: Suspension rheology and elastomeric properties
Natural rubbers are ideal candidates for green composites and mechanical properties can be adapted by adding different types of microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC) and microfibrillated cellulose with hydrophobic surface modification (mMFC). The influences of morphology and surface functionality of cellulose on the rheological properties and dynamic mechanical performance of natural rubber composites are evaluated. Therefore, the shear viscosity of the natural rubber was dominated importantly by adding fibrillated cellulose even in small amounts of 1 to 7 wt.-%, representing more pronounced shear thinning behaviour and hysteresis at high fiber concentrations. The NFC provides lowest viscosity while surface modification of mMFC slightly increases the viscosity due to formation of a network structure. A specific study on the flow properties of natural rubber composites against frequency revealed the development of shear-induced curing properties depending on the compatibility between the cellulose fillers and the rubber (i.e. immobilization mechanism). In parallel, an increase in crosslinking density was highest for the NFC, while intermediate for the MFC and lowest for the mMFC. The latter was confirmed by thermal analysis considering variations in glass transition temperatures and modelling the curing kinetics at different temperatures and times. The dynamic mechanical analysis on uncured and cured films confirmed a shift in loss modulus and broadening of tan delta peak depending on the filler concentration and restriction of chain mobility and the fiber/matrix interface, as demonstrated by spectroscopic analysis. In particular, mechanical response under creep, frequency testing and temperature testing inferred that the reinforcing capacity and elastomeric properties depends on the fiber dispersion and interaction between both phases. The microscopy of cross-sections indicated better distributive and dispersive mixing of the mMFC up to 7 wt.-% concentrations, in contrast with poor wetting of the matrix at the fiber interface resulting in fiber pull-out for unmodified fibrillated cellulose.

**CELL 88**

Wood-inspired binder enabled vertical ink printing of g-C₃N₄ forest for highly efficient photocatalytic hydrogen evolution

Bo Jiang¹, Zhiqiang Liang², Yongcan Jin¹, jinyongcan@njfu.edu.cn. (1) Nanjing Forestry University, Nanjing, China (2) Institute of Functional Nano and Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices and Joint International Research Laboratory of Carbon-Based Functional Materials and Devices, Soochow University, Suzhou, China

g-C₃N₄, with the advantages of low cost, proper band position, chemical stability, molecular tunability, and nontoxic nature, has drawn growing interest in the photocatalysis area. However, the application of frequently used bulk g-C₃N₄ is limited by its poor absorption, fast charge recombination, and low specific surface area. Herein,
Inspired by wood structure that lignin is a natural binder contributing wood rigidity and strength, we developed a vertical ink printing strategy to build $g$-C$_3$N$_4$ forest for photocatalytic hydrogen evolution by using lignin as a binder. The $g$-C$_3$N$_4$/lignin ink adjusted by F127 shows outstanding self-supporting capacity after direct vertical printing with the storage modulus of $10^5$ Pa. After thermal stabilization (150 °C), lignin can keep the resulted $g$-C$_3$N$_4$ forest intact in water due to its hydrophobic nature. Moreover, the printed forest has porous structure with much higher specific surface area than bulk $g$-C$_3$N$_4$, which significantly increases visible light harvesting capability, and improves separation efficiency of charge carriers. As a result, $g$-C$_3$N$_4$ forest shows much higher hydrogen evolution rate than bulk $g$-C$_3$N$_4$ and has desirable recyclability. This new approach of the facile and scalable direct ink printing opens a new avenue to fabricate highly efficient $g$-C$_3$N$_4$ catalysts.

**CELL 89**

**On the effect of the presence of lignin on feedstock and its effects on the properties of mechanically produced lignin-containing cellulose nanofibrils (LCNF)**

*Maria C. Iglesias*$^{1,2}$, *mci0006@auburn.edu*, *Maria S. Peresin*$^{1,2}$. (1) School of Forestry and Wildlife Science, Auburn University, Auburn, Alabama, United States (2) Forest Products Development Center, Auburn University, Auburn, Alabama, United States

When wood is chemically treated to obtain cellulose pulps, lignin structure, which is well known for its interconnected arrangement based on aromatic units, changes when compared with its native counterpart. When analyzing residual kraft lignin remaining on cellulose pulps, free phenolic hydroxyl groups are generated during the pulping process, which increases the hydrophilicity of lignin, and as a result, its solubility, which allows for the separation of the cellulose fibers from the lignin matrix. It has been hypothesized that during the mechanical production of lignin-containing cellulose nanofibrils (LCNF), free radicals are stabilized due to the aromatic resonant structures of lignin, enabling better repulsion between the fibrils, and as a result, better defibrillation of the samples. This behavior has been reported in the literature, where LCNF showed better defibrillation degrees than its bleached counterpart. Additionally, the chemical composition of the samples, in terms of lignin and hemicelluloses content, plays an important role in their rheological behavior, which is of relevant importance as they affect handling and processing.

In this work, we focused on the effects of lignin during the production of LCNF from kraft softwood cellulose pulps containing different amounts of residual lignin. Mechanoradical formation will be measured by electron paramagnetic resonance (EPR) at different stages of the nanocellulose production. Additionally, the effects of lignin on the rheological behavior of LCNF samples will be analyzed together with their morphology, chemical composition, surface chemistry, and colloidal stability, thermal stability, and interfacial free energies.

**CELL 90**
Efficient production of glucose via acid-catalyzed hydrolysis of cation-modified microcrystalline cellulose

Tingwei Zhang¹, Huining Xiao², Yongcan Jin¹, jinyongcan@njfu.edu.cn. (1) Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing, China (2) Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada

To develop green and sustainable economics, a wide variety of renewable energy technologies have been explored, and the conversion of renewable biomass into valuable compounds is already one of the most promising technology. Cellulose that widely exists in the natural resources has been extensively studied for using as feedstock for the production of glucose, oligosaccharide, as well as bio-based chemicals and fuels. However, the acid-catalyzed hydrolysis of microcrystalline cellulose (MCC) is difficult due to the rigid structure, and such circumstances would hinder the widespread utilization of MCC. To improve the efficiency of MCC hydrolysis, introducing various strategies to partially deconstruct MCC original structure should be useful. In this study, a cation modified MCC (CMCC) has been synthesized using 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTMAC) through microwave irradiation, and it was found that the solubility of CMCC in water was far better than MCC. Furthermore, the hydrolysis of CMCC was tested using dilute hydrochloric acid (1 wt%), and favorable glucose yield was obtained under relatively mild reaction temperature (130 °C). The above results may indicate that the modification treatment makes the access of acidic sites to 1, 4-β-glycosidic bond more easily, and then facilitates the cleavage of 1, 4-β-glycosidic bond. In subsequent studies, we will optimize the synthesis parameter of CMCC to make it more hydrolysable, and investigate the catalytic reactivity of carbon-based solid acids for CMCC hydrolysis.

Addition of water-soluble lignin for enhancing enzymatic saccharification of pretreated lignocellulosic biomasses

Wangxia Wang¹,², Yangsu Zhu¹, Yan Wang¹, Wenjuan Wu¹, Yongcan Jin¹, jinyongcan@njfu.edu.cn. (1) Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing, China (2) School of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng, China

The influence of lignin on the enzymatic digestibility of lignocellulose has been widely investigated. Physical blockage and unproductive enzyme binding were recognized as two mechanisms that inhibit the enzymatic digestibility. Hydrophobic interaction between cellulase and lignin has been considered as the primary driving force that governs cellulase non-productive binding. Certain additives such as PEG can increase the substrate enzymatic digestibility (SED), while kraft lignin (KL) exhibits little or even negative effect. The cellulases are easy to be adsorbed non-productively onto KL due to
its insolubility in water, which results in a low enzymatic sugar conversion. In this work, water-soluble lignin samples, including sulfonated lignin (SL) and kraft lignin fraction which can be dissolved in water at pH 5 (KLWS), was used as additives in the enzymatic hydrolysis to understand their effect on the enzymatic saccharification of green liquor (GL) and acidic bisulfite (AS) pretreated poplar. The results showed that the addition of water-soluble lignin could considerably increase the enzymatic sugar conversion. The SED increments of both GL- and AS-pretreated poplar were more than 25 percentage points when KLWS and SL was charged at 0.1 g and 0.2 g per gram of o.d. substrate, respectively. Excessive addition of SL or KLWS resulted in a drop of the SED. The existence of water-soluble lignin reduces the non-productive adsorption of cellulases onto the substrate lignin, which can be explained by "competitive adsorption mechanism".

CELL 92

**Nanocellulose-based SERS sensor for the detection of explosives**

*Jingjing Wu, Ying Feng, Weibing Wu, wbwu@njfu.edu.cn. Nanjing Forestry University, Nanjing, Jiangsu, China*

Accurate, reliable and rapid detection of explosives in the environment is of great significance for timely detection of hidden explosives, prevention of terrorist crimes, tracking of environmental quality and protection of human health. Surface-enhanced Raman scattering (SERS) technology possesses the advantages of high sensitivity, fast analysis speed, low cost and portability. A new type of three-dimensional (3D) SERS sensor was constructed by loading Au@Ag nanoparticles on the substrate of bacterial cellulose (BC) aerogels with high specific surface area and good porosity. Based on the 3D porous substrate and localized surface plasmon resonance, the composite SERS substrate realized the detection of rhodamine and trinitrotoluene (TNT) at extremely low concentrations. Core-shell Au@Ag nanoparticles were synthesized by encapsulating Au nanorods into Ag nanocuboids to improve the SERS sensitivity and stability. Adjusting the density of BC aerogels and the loading capacity of Au@Ag nanoparticles was used to optimize the structure of SERS substrates. Higher aerogel density and the amount of loaded Au@Ag nanoparticles resulted in dense multi-hotspot distribution. Moreover, Au@Ag nanoparticles were modified with p-aminothiophenol (PATP) to facilitate the formation of Meisenheimer complex between TNT and the SERS substrate, and further improve the affinity to TNT. The limit of detection (LOD) was as low as \(1\times10^{-14}\) mol/L owing to the multi-hotspot structure of SERS substrate and the formation of Meisenheimer complex. This type of SERS substrate shows potential applications in the gas phase detection of trace explosives.
High-wet-strength lignocellulosic paper for heavy metal ion adsorption and oil/water separation

Shan Jiang, Han Tian, Weibing Wu, wbwu@njfu.edu.cn. Nanjing Forestry University, Nanjing, Jiangsu, China

Heavy metal ions and oil are the two harmful substances that cause serious water pollution. It has become a new research hotspot to develop lignocellulose-based adsorbents with both the performances of heavy metal ion adsorption and oil/water separation. In this paper, paper-based lignocellulosic adsorption-separation materials with high wet strength, high adsorption capacity and efficient oil/water separation and recycling performance were prepared from polar chemimechanical pulp by the simple process of papermaking and one-step dip coating. Maleic anhydride and sodium hypophosphate, which can react with the hydroxyl groups of cellulose, were used to increase the wet strength and the carboxyl content of the adsorption-separation papersheets. Both the wet strength and carboxyl content increase upon increasing the beating degree and the dosage of maleic anhydride. The wet strengths reach more than 35% of their dry strengths and the carboxyl contents are in the range of 0 - 0.69 mmol/g. Adsorption kinetic and thermodynamics studies of Cu(II) and Pb(II) explain pseudo-second-order equation and Langmuir model as the best fit. For the papersheets loaded with porous zeolite filler, the theoretical maximum adsorption capacities of Cu(II) and Pb(II) are high up to 56.46 and 126.58 mg/g, respectively. In addition, the functional papersheets with specific micro-nano pore structure and high hydrophilicity show the good underwater oil repellency, and are able to effectively separate the mixture of oil...
and water. The underwater contact angles to various oil substances including chloroform, petroleum ether, toluene, and n-hexane are higher 150°, and the oil/water separation efficiencies are higher than 99%. The membrane fluxes can be tuned in the range of 300-11,000 L/(m² h). The synthetic strategy of multifunctional paper based on polar chemimechanical pulp provides new ideas and methods for the full and high-value utilization of lignocellulose.

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Fluorescently-labelled cellulose nanofibrils for leaching detection

Maria Karlsson², Christian Aulin¹, Andreas B. Fall¹, Tiffany Abitbol¹, tiffany.abitbol@ri.se. (1) RISE Bioeconomy, Stockholm, Sweden (2) Linköping University, Linköping, Sweden

Separate from issues of safety, questions remain surrounding nanocellulose localization, detection, and migration, especially in products such as reinforced papers for food packaging. In this work, we use a straightforward method to produce fluorescent cellulose nanofibrils (CNF) of different qualities with the aim of using this material to quantify potential leaching from nanocellulose-containing papers. To do this, enzymatically pre-treated pulp was labelled with 5-[(4,6-Dichlorotriazin-2-yl)amino]fluorescein hydrochloride (DTAF) in a one-pot reaction followed by extensive purification to remove unbound dye. Microfluidization was employed to generate fluorescent CNF of different qualities by varying the number of passes through the microfluidizer (1, 3 or 10 passes). The degree of DTAF labelling for the CNF was ~2 µmol DTAF/g cellulose, a value that decreased to ~1.5 µmol DTAF/g cellulose after further purification by ultrafiltration. This degree of labelling was enough to impart sensitive and quantitative fluorescence detection but not so much as to significantly alter other material properties, indicating that the fluorescent CNF is a good mimic for unmodified CNF. Fluorescence detection was used to study the CNF leaching from CNF-containing papers using cold-water and hot water-assays based on a standard assay designed for food contact papers. CNF leaching levels of ~1% were obtained, with slightly higher values in the hot water assays, and slightly lower values obtained for the finer quality CNF tested (10 passes in the microfluidizer).

CELL 95

Understanding the structural, thermal and morphological properties of cellulose-keratin biocomposites

Emily McDermott¹, esm111@scarletmail.rutgers.edu, Karleena Rybacki³, Kaylyn Cai⁴, Abneris Morales¹, Stacy Love³, Xiao Hu², David Salas-de la Cruz³. (1) Chemistry, Rutgers University, Pennsauken, New Jersey, United States (2) Physics and Astronomy, Rowan University, Glassboro, New Jersey, United States (3) Computational and Integrative Biology, Rutgers University, Camden, New Jersey, United States (4) Chemical Engineering, Rutgers University, New Brunswick, New Jersey, United States
The regeneration of biocomposite from natural materials is a growing topic of interest recently. Understanding the intermolecular interactions between different components in these composites in relation to their physiochemical properties can lead to new functional materials such as tunable scaffolds for tissue engineering. In this study, we report the structural, thermal and morphological properties of cellulose-keratin biocomposites regenerated using ionic liquids and various coagulation agents. Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and X-Ray Scattering were used to characterize the physiochemical properties and morphology of the composites. The results suggest that keratin and cellulose structures can be manipulated during the formation of the biocomposite materials. Specifically, the beta sheet content in keratin increases with the increase of the ethanol solution concentration while the cellulose crystallinity increases with the increase of the hydrogen peroxide concentration during the coagulation process. Both changes result in an increase in thermal stability of the composite materials. This knowledge about the mechanism of interaction between keratin secondary structures and cellulose crystalline structures fabricated from different methods is very important, which not only leads to advances in tissue engineering, but also to advances in green chemistry, such as development of bio-batteries and filtration membranes for heavy metals.

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Oxidative coupling of methyl furoate to form 5,5′-dicarboxylic-2,2′-bifuran methyl esters

Mingchun YE1, MCYE@UDEL.EDU, Raul F. Lobo2. (1) Chemical Engineering, University of Delaware, Newark, Delaware, United States (2) Dept of Chem Biomol Eng, 332 Colburn Lab, Univ of Delaware, Newark, Delaware, United States

To mitigate the environmental impact of plastic waste and reduce our dependence on fossil fuels, we must find renewable alternatives with desirable combinations of physical and chemical properties. Recent investigations have shown that bifuran-based polyesters could afford such materials: poly (ethylene bifuranoate), for example, has shown attractive UV blocking and gas barrier properties. To scale up the synthesis of bifuran polymers, alternatives for the selective C-C homocoupling of methyl furanoate via the Heck reaction need to be found. In this poster we will investigate and optimize the oxidative coupling of methyl furoate using homogeneous Pd(II) catalysts. We found that the reaction of methyl furoate, palladium acetate and sodium pivalate as catalyst and additives, in dimethylacetamide (DMAc) solvent under mild conditions (60 to 80 °C) generates acceptable yields (~10% in 2 hours) of the product. The reaction kinetics were investigated, and a possible mechanism and rate determine step (RDS) are proposed. We found that the amount of catalyst, the concentration of reactant, and reaction temperature have significant impact on the reaction rate and yield, while oxygen pressure shows no influence, which states that the Reductive elimination is not the RDS. Concentration of sodium pivalate and temperature have an influence on catalyst stability. The transmetalation of two Pd-activated furoates is suggested as the
most likely RDS. Ligands with suitable size and nucleophilicity can be chosen to further increases the reaction rate and catalyst stability.

**CELL 97**

**From native colombian fibers to novel nanostructured materials: Industrial wastewater treatment applications**

_Brenda L. Nagles^1_, brendanagles@gamil.com, _Eduart Gutiérrez Pineda^2_, _Cristian Blanco-Tirado^3_, _Marianny Y. Combariza^4_. (1) Santander, Unidades Tecnologicas de Santander, Bucaramanga, Colombia (2) Universidad Industrial de Santander (UIS), Bucaramanga, Colombia (3) Chemistry, Universidad Industrial de Santander, Bucaramanga, Colombia (4) Escuela de Química, Universidad Industrial de Santander, Bucaramanga, Santander, Colombia

Cellulose-based nanomaterials are often prepared of native cellulose by direct dilution, which involves tedious processes and solvent recovery problems. In this work, we developed a novel class of hydrogels based on nanostructured cellulose prepared via a cellulose nanofiber (NFC) gelation process from fique fibers (_Furcrae spp_) oxidized with TEMPO. This oxidation process was used to generate negatively charged surfaces by adding carboxylate groups COO⁻. The degree of oxidation and the COO⁻ concentration were evaluated by conductimetric titrations. Different TEMPO-oxidized NFC’s with different concentration of COO⁻ were evaluated using TEM, SEM, FTIR, and DSC. As a result of the strong interactions between the COO⁻ groups and the transition metals (M²⁺), these NFC’s were employed as matrixes for nucleation and growing of F₃O₄ and MnO₂ metallic nanoparticles (NPs). Morphological and spectroscopic properties of the obtained nanocomposites in form of hydrogels, films, and xerogels were measured by SEM, FTIR, DSC, and XPS. We are using NFC/NPs M²⁺ nanocomposites to oxidize pollutants in industrial wastewaters.

**CELL 98**

**Development of a nafion-free proton transport cellulose membrane for the proton exchange membrane fuel cell**

_Bhawan Sandhu^2_, bhawansandhu2020@gmail.com, _Christine Kong^2_, christinekong12@gmail.com, _Likun Wang^1_, _Aniket Raut^1_, _Rebecca Isseroff^1_, lawrencescienceresearch@gmail.com, _Sunil Sharma^3_, _Priyanka R. Sharma^3_, _Miriam Rafailovich^1_. (1) Dept. of Materials Science and Engineering, Stony Brook University, Stony Brook, New York, United States (2) Garcia Summer Scholars Program, Stony Brook University, Stony Brook, New York, United States (3) Chemistry, Stony Brook University, Stony Brook, New York, United States

Proton Exchange Membrane Fuel Cells (PEMFCs) provide a method of producing clean energy through the oxidation and reduction of hydrogen and oxygen gas, with H₂O emitted as the only by-product. The electrons of the oxidized hydrogen ions travel
through a wire to perform work, while the hydrogen ions (protons) migrate to the cathode through a membrane that is impermeable to electrons. Currently the most commonly used proton transport membranes are made of Nafion, a fluorinated ion conducting polymer. However, Nafion’s limitations include its high cost, sensitivity to hydration, and its degradation at higher temperatures. As an alternative to Nafion, this research has created a fuel cell membrane using inexpensive and widely available cellulose filter paper as a scaffold to support Resorcinol bis(diphenylphosphate) (RDP), an oligomeric phosphate ester flame retardant which possesses high heat stability. The combination of RDP on cellulose filter papers, when tested on the fuel cell, enabled significant power output. To further enhance proton conduction, cellulose filters were treated with phosphoric acid, citric acid, and sulfuric acid, respectively, before the application of RDP, and then tested on a hydrogen fuel cell at temperatures ranging from 30°C to 90°C; amplified power output was exhibited even at higher temperatures. The interrelationship between RDP and the cellulose filter was examined by scanning electron microscopy, displaying the RDP distribution among the cellulose fibers. Ion exchange was conducted on each type of treated membrane. This work represents an easily fabricated yet novel approach for creating a new generation of cost-effective, thermally stable proton-conducting membranes for PEMFCs.

CELL 99

Novel organosolv pretreatment method for lignin isolation enhanced by oxygen

Jing Li¹, lijing1987@gmail.com, Xinsheng Chai². (1) School of Environmental and Natural Resources, Zhejiang University of Science and Technology, Hangzhou, Zhejiang, China (2) South China University of Technology, Key Lab of Pulp and Paper Engineering, Guangzhou, Guangzhou, China

Potential safety hazard of ethanol pulping process due to high temperature and pressure (200°C, 2Mpa) limited its industrial application. A novel crude lignin seperation process by low-temperature/pressure (<90°C, 0.6Mpa) ethanol system enhanced by oxygen (LtPEO) was investigated. With the same process conditions, enhancement by oxygen can greatly improve the lignin yield. Lignin yield will achieve the maximium, 50.8%, at process temperature of 80°C, but decrease with the increase of ethanol concentration. Fourier transform infrared spectroscopy analysis showed that yield non-conjugate carbonyl group was highly strengthened compared to orignial lignin. Kinetic analysis proved that the delingnification process includes two stages: bulk stage within 10mins, and residual stage. Scan electronic microscopy results showed that the invalid lignin precipitation still exists on the cooked wheat straw after separation from liquid fraction.
Effect of chemical modification of CNF on the properties of PVP/CNF hydrogel

Hye Jung Youn\textsuperscript{1}, page94@snu.ac.kr, Wanhee Im\textsuperscript{1}, Hak Lae Lee\textsuperscript{2}, Shin Young Park\textsuperscript{1}, Simyub Yook\textsuperscript{1}, Sooim Goo\textsuperscript{1}. (1) Seoul National University, Seoul, Korea (the Republic of) (2) Forestry, Seoul National University, Seoul, Korea (the Republic of)

Cellulose nanofiber-based hydrogels or aerogels have been studied for diverse application including tissue engineering, wound dressing media, air or water purification. In this study, cellulose nanofibrils (CNF) was incorporated into polyvinylpyrrolidone (PVP) hydrogels for temporary wound dressing. PVP hydrogels are prepared by electron beam irradiation which is environmentally friendly, simple process, but the mechanical properties of the products should be improved. Therefore, three types of CNF (untreated CNF, carboxymethylated CNF, and quaternized CNF) with different morphology and surface charge property were prepared by chemical pretreatment and their effect on the properties of PVP/CNF hydrogels were investigated. PVP was added to CNF suspension with different concentrations, then irradiated by electron beam. The gel content of PVP/CNF was not affected by the types and addition level of CNF. However, the transparency of the hydrogel was affected by morphology of CNF. When PVP/CNF hydrogel was immersed in phosphate buffered saline (PBS) solution, swelling degree and storage modulus was increased by the addition of CNF. The surface charge...
of CNF had a greater impact on the swelling degree and storage modulus of hydrogel than untreated CNF and carboxymethylated CNF. The cationic CNF could reinforce the PVP hydrogels after immersion in PBS solution. The stronger PVP/CNF hydrogel can be prepared by incorporation of CNF with proper properties.

CELL 101

**Cellulose sulfate nanofibers for ammonium removal and water purification applications**

*Ken Johnson¹, ken.johnson@stonybrook.edu, William Borges¹, WBorges20@roslynschools.org, Priyanka R. Sharma², Sunil Sharma³, Hao-Yen Jefferson Chang¹, Min Liu¹, Benjamin S. Hsiao¹. (1) Stony Brook University, Port Jefferson Station, New York, United States (2) Chemistry, Stony Brook University, Chittorgarh, Rajasthan, India (3) CHEMISTRY, STONY BROOK UNIVERSITY, NEWYork, New York, United States*

Ammonium concentrations at or above 20 ppm in water pose a significant threat to the environment and global health. Locally, excretions from marine organisms and people cause ammonium water contamination. Industrial practices convert ammonium to nitrogen gas using a lengthy nitrification-denitrification process. We propose a material which may remove ammonium from the very first step. Jute fibers are functionalized using a one-step reaction using chlorosulfonic acid and are further homogenized to yield cellulose sulfate nanofibers. Ammonium solutions ranging from 5 – 250 ppm were tested with the cellulose sulfate to determine adsorption capacity. Samples were characterized using FTIR, contact angle, SEM-EDS, and zeta potential. The zeta potential of cellulose sulfate showed little change as a function of pH, indicating cellulose sulfate is more stable for real wastewater applications, relative to carboxylated cellulose. After remediation studies, ammonium loaded cellulose sulfate was tested for reusability using sodium chloride regeneration, which showed a direct relationship to functionality. The nanostructured cellulose sulfate microfibers were tested for column filtration. An influent solution of 10 ppm ammonium solution was passed through the column and effluent samples measured at greater than 90% removal.

CELL 102

**Controlling barrier properties of composites using nonspherical particles**

*Asad Abbas, asad.alchemist@gmail.com, Vikram Singh. Chemical Engineering, Indian Institute of Technology, Delhi, New Delhi, Delhi, India*

**Abstract**

The limited barrier properties of polymeric films have led to the development of polymer composites made up of polymer matrix doped with impermeable particles. The polymer composite with embedded impermeable non-spherical fillers creates long tortuous paths for diffusion and hence has shown to decrease the diffusivity by several degrees as
compared to the pure membranes [1]. The properties of such composites depend on a number of factors such as the uniform dispersion of the fillers, filler aspect ratio, loading and orientation within the polymer matrix. The effect of these factors has been widely studied using experiments, models and simulations. While factors like filler loading and filler aspect ratio (size and geometry) are well controlled in the experimental studies, factors like orientation distribution of the particles and dispersion which are dependent on the process conditions of mixing, polymerization, and stability of suspensions are not well controlled. As a result, the understanding of the influence of particle orientation on the permeability of the membrane is still lacking. There has been no experimental study so far where the permeability of a suspension of thin-disk particles with well-defined orientation been verified with models. In this work, we will be interested in tuning the orientation of thin disk particles of different sizes and aspect ratios with the help of an external magnetic field [2]. We plan to coat the thin disk particles with superparamagnetic particles. The coated thin disk particles will then be homogeneously mixed with the polymer matrix. The homogeneous suspension of coated thin disk particles will then be oriented using the external magnetic field. The orientation distribution and the position of the particles in the membrane will be experimentally correlated with the permeability of the membrane.

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Valorization of industrial hemp hurds for antimicrobial lignin-containing cellulose nanofibers

Preeti Tyagi\textsuperscript{1}, ptyagi2@ncsu.edu, Joseph Gutierrez\textsuperscript{1}, Ved Nathani\textsuperscript{1}, Reny Mathew\textsuperscript{2}, Hasan Jameel\textsuperscript{1}, Orlando Rojas\textsuperscript{3}, Lucian A. Lucia\textsuperscript{1}, Lokendra Pal\textsuperscript{1}. (1) Forest Biomaterials, North carolina State University, Raleigh, North Carolina, United States (2) Department of Plant pathology, North carolina State University, Raleigh, North Carolina, United States (3) Department of Bioproducts and Biosystems, Aalto University, Helsinki, Finland

Antimicrobial activity is among the most studied properties of hemp although it has been the subject of numerous contradictions and anecdotal information. Nevertheless, most of the studies on antimicrobial activity have been focused on the extractives obtained from polar and non-polar solvent extraction using petroleum ether, acetone, methanol, ethanol, etc. Very few studies have shown the antimicrobial property of hemp hurds themselves. Considering the experimental and anecdotal findings, the current work examined the antimicrobial activity of unprocessed hemp hurds powder, processed hemp hurds cellulose nanofibers (CNF), and their extractives. The morphological and chemical characterizations of CNF were carried out using SEM, EDX and ToF-SIMS. The chemical characterization of hemp hurds for the presence of antimicrobial active compounds was carried out using GC-MS. The CNF films and extractives were tested against \textit{E. coli} for antimicrobial activity. The extractives treated-paper discs showed a significant reduction in bacterial growth and resulted in a zone of bacterial inhibition according to the disk diffusion assay whose results were confirmed by conducting a
colony-forming assay. Thus, hemp extractives and CNF as antibacterial coatings have great potential for valorizing industrial hemp waste for value-added products.

CELL 104

Use of steam explosion to produce microfibrillated cellulose from *Posidonia oceanica* waste

**Malek Khadraoui**\(^1,2\), malek.khadraoui@grenoble-inp.fr, **Ramzi Khiari**\(^3,1,4\), **Nicolas Brosse**\(^5\), **Latifa Bergaoui**\(^2\), **Evelyne Mauret**\(^1\). (1) Univ. Grenoble Alpes, CNRS, Grenoble INP, LGP2, F-38000 Grenoble, France, Grenoble, France (2) National Institute of Applied Science and Technology, BP 676, 1080, Tunis Cedex, Tunisia, Tunis, Tunisia (3) University of Monastir, Faculty of Sciences, UR13 ES 63 - Research Unity of Applied Chemistry & Environment, 5000 Monastir, Tunisia, Monastir, Tunisia (4) Higher Institute of Technological Studies of KsarHellal, Department of Textile-Tunisia, KsarHellal, Tunisia (5) Fac of Science Technologies, University of Lorraine, Vandoruve, France

*Posidonia oceanica* (leaves and balls) is the dominant seagrass in the Mediterranean Sea. This biomass has great potential for use as a novel lignocellulosic material on an industrial scale. In this approach, the valorisation of this marine biomass was carried out by preparing a bio-based and renewable material namely: microfibrillated cellulose (MFC). First, the fibres were isolated by a delignification-bleaching process, followed by refining and Tempo-mediated oxidation to facilitate the further nanofibrillation. In this study, Tempo-oxidized MFC were produced using an energy efficient process: the steam explosion (SE). The prepared MFC were compared to the Tempo-oxidized MFC produced by grinding (Masuko Supermasscolloider). Then, the efficiency of the combination of Tempo-mediated oxidation and steam explosion was discussed. To this purpose, the produced MFC were characterized by several techniques such as optical microscopy, atomic force microscopy, transmission electron microscopy, MorFi analysis, tensile test, and turbidity. The steam explosion process allows producing MFC with a width between 5 and 12 nm, close to those obtained by grinding. The degree of polymerization and crystallinity showed that the steam explosion degrades the fibers less than the supermasscolloider grinder. To better understand the microfibrillation effect of the SE, refined fibres (chemically untreated) were exploded. These results prove the potential of steam explosion, as an ecofriendly process and good alternative for the production of microfibrillated cellulose.
Effect of surface modification of interaction and self-assembly of cellulose nanocrystals

**Mohit Garg, mohit.garg@liu.se, Mathieu Linares, Igor V. Zozoulenko.** Laboratory of Organic Electronics, ITN, Linköping University, Norrköping, Sweden

Cellulose is one of the major components of the plant cell wall, present in both crystalline and amorphous domains. Controlled acid hydrolysis breaks the amorphous domains and render various functional groups on their surface. In this work, we used molecular dynamics simulations to study the strength of interaction between the native cellulose nanocrystals (NCNC) and the surface modified cellulose nanocrystals (CNCs) by calculating the potential of mean force (PMF) between them and then their self-assembly in the bundle arrangement. We took two types of CNCs, the sulfonated CNCs
(SCNCs) and the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidized CNC (TCNC) with two types of molecular counter ions namely, Na⁺ and Ca²⁺. We found that PMF between the CNCs decreases when we modify the surface of CNCs. Although, the PMF between the SCNCs and TCNCs is similar for the same degree of surface substitution but the counter ions have a great impact on the PMF. The presence of divalent counterions between the CNCs produces a higher PMF compared to the monovalent counterions. Our results indicated that the Ca²⁺ ion can act as a bridge between the two CNCs which can result in better aggregation or even gelation in cellulose nanocrystals.

Next, we studied the self-assembly of the CNCs in the bundle form, a level of structure hierarchy present in the plant cell wall and studied how that changes when we modify the surface of CNCs. We studied various features of these bundles, e.g., the degree of twist, bound water inside the bundle and the number of hydrogen bonds between the CNCs in the bundle. Our calculations provide a deeper insight into the interactions and self-assembly of cellulose nanocrystals which can be used in understanding the rheological, mechanical and morphological properties of CNCs.

**CELL 106**

**Guidance of corneal epithelial cells migration by co-operative effects of stretched bacterial cellulose/gelatin and DC electric fields**

*Li Wang*¹, 337413587@qq.com, *Zhijun Shi*¹, zhizhijun@hust.edu.cn, *Min Zhao*³, *Guang Yang*², yang_sunny@yahoo.com. (1) Huazhong University of Science and Technology, Wuhan, HUBEI, China (2) Huazhong University Of Science & Technology, Wuhan, China (3) University of california uc davis, Sacramento, California, United States

Corneal epithelia cells in the eye are guided by the ordered fibre arrays and a naturally occurring DC electric field (EF). But little is known about the mechanisms and guidances of cell migration by nanotopography or by an EF. Here, we used bacterial cellulose (BC), which is one of the most common fibrous materials in nature, to mimic similar ordered fiber alignment with natural tissue by stretching. The tensile strength of the unstretched BC/Gelatin film is 137.95MPa and it can be enhanced from 286.26 to 832.32Mpa as the strain was increased from 20% to 40%. And we examined cell migration on stretched BC/Gelatin (40%) with a physiological EF (150mv/mm) separately and in combination. Corneal epithelia cells aligned parallel to the fiber alignment and the migration speed of cells on stretched BC/Gelatin were enhanced compared to cells on unstretched BC/Gelatin. When the direction of an EF was parallel to fiber alignment, cathodal electrotaxis along fiber alignment was enhanced compared to that on unstretched BC/Gelatin. Therefore, the migration of corneal epithelia cells can be enhanced by co-operative of stretched BC/Gelatin and DC electric fields, which can be exploited in tissue engineering.
Bio-based industries make use of biomass sources and sustainable supply chains. As such, they lower dependency on crude oil imports and contribute to raw material security. With 90% of Europe’s chemical industry feedstocks for non-energy using coming from fossil fuel resources, access to alternatives is an important strategic issue. By replacing fossil-fuel based products with bio-based products which tend to have a smaller carbon footprint, bio-based industries can make a critical contribution to Europe’s climate goals.

SElectiveLi will provide proof of concept on the laboratory scale to demonstrate the potential for converting low cost lignosulfonate feedstocks (by-product from paper and pulp industry) into high value biosustainable chemicals.

SELECTIVELI will produce four main lignosulfonate-derived products; Aldehyde fraction -vanillin and syringaldehyde, special chemicals of value-added nature (benzoquinone derivatives, stilbenes and acetovanillone), a mixed phenolic fraction for further downstream processing of intermediate monomer building blocks to yield epoxies and formaldehyde resins as well as diphenolic species analogous to bisphenol A and a fraction of partially degraded lignosulfonates which can potentially serve as tailor-made surfactants or dispersants.
Cellulose nanocrystal surface modification with nucleophiles to improve dispersibility

Krista Bullard, KristaBullard@gatech.edu, Will R. Gutekusnt. Georgia Institute of Technology, Atlanta, Georgia, United States

As environmental concerns increase, the interest in using cellulose and cellulose derivatives for the creation of new functional materials also grows larger. Cellulose nanocrystals (CNCs) possess extraordinary physical and mechanical properties, but there is a lack of robust methods to modify the CNC surface for integration into polymer composites and other applications. To increase the utility of these renewable particles, a versatile strategy to functionalize CNCs using classical nucleophilic substitution reactions has been developed. Nucleophiles containing thiols, amines, carboxylic acids, and phosphines can be attached to CNCs with high surface coverage to dramatically change the interfacial properties. These materials were characterized through Fourier transform infrared spectroscopy (FTIR), solid-state $^{13}$C NMR, elemental analysis, and thermogravimetric analysis (TGA) to quantify the degree of functionalization and thermal stability. In addition, atomic force microscopy (AFM) and dynamic light scattering (DLS) analysis showed minimal change in the average size of the CNCs after surface modifications. The versatility of the method enabled the addition of long alkyl chains with four distinct chemistries that greatly improve the hydrophobicity of the CNCs and results in the ability of the particles to disperse in nonpolar polymer films.
Preparation of Au nanoparticles/cellulose nanocrystals composites and their SERS performance

Qing Zhang, Heli Feng, Weibing Wu, wbwu@njfu.edu.cn. Nanjing Forestry University, Nanjing, Jiangsu, China

Nano-biosensor technology based on surface enhanced Raman scattering (SERS) is a potential sensitive and reliable method for early detection of tumors. The unique morphology, template structure, modifiability and biocompatibility of cellulose nanocrystals (CNC) make them excellent supporters for constructing multifunctional SERS nanocomposite biosensors. Carboxylated cellulose nanocrystals (CNC-COOH) were converted to thiolated cellulose nanocrystals (CNC-SH) via EDC/NHS reaction. CNC-SH with mercapto contents in the range of 0.05 - 0.2 mmol/g were obtained by adjusting the dosage of cysteamine. SERS nano-biosensors of CNC loaded with Au nanospheres (AuNSs@CNC) were constructed by both self-assembly and in-situ synthesis methods. Uniform AuNSs with the sizes of 10, 30 and 60 nm were deposited on the surface of CNC-SH via Au-S and the loading density and spacing were further regulated by mercapto contents. For the in-situ synthesis method, the loading of AuNSs on CNC was also controlled by changing the mercapto contents of CNC-SH and the growth conditions. The results show that the size and spacing of AuNSs on CNC determine the SERS sensitivity of the composite substrate. With the decrease of gap distance between the loaded AuNSs, the SERS signal increases gradually. The enhanced SERS sensitivity can be ascribed to the formation of hot spots. The optimum size of AuNSs is about 30 nm. This type SERS probe based on AuNSs@CNC nanocomposite shows potential applications in early diagnosis and treatment of cancer tissue.

Bacterial cellulose synthesis at solid-gas-liquid interface and its biomedical applications
Bacterial cellulose is a nano-size cellulose synthesized by *Gluconacetobacter xylinus* during growth and movement. Due to its good mechanical property, good biocompatibility and non-toxicity to many kinds of cells, and abundant hydrogen bond in BC for its chemical modification, which led to extensive research and application of BC in biomedicine, such as wound repair, artificial blood vessel, drug delivery carrier, artificial intervertebral disc, nerve interface research, etc. *Gluconacetobacter xylinus* is a kind of aerobic bacteria, which preferentially synthesizes a BC film at the gas-liquid interface. In patterned bacterial cellulose synthesis, BC can only be synthesized at the solid-liquid interface after the microstructure template is covered with the bacterial liquid, the difference of patterned BC depth in surface is low, which limits its further application. In this study, we referred to the "solid-gas-liquid" three-phase interface formed on the interface of superhydrophobic nanomaterials in aqueous solution to solve the problem of providing sufficient oxygen between ordered microstructure template and bacterial culture medium (Figure 1), which got many micro-size fibers (Figure 2). We analyzed characteristics of BC formation at different microstructure array interfaces and explored potential applications in cell capture and circulating tumor cell monitoring.

**Figure 1.** Diagram of BC synthesized by *Gluconacetobacter xylinus* at microstructural solid-gas-liquid interface.
Figure 2. Patterned BC synthesized by *Gluconacetobacter xylinus* at microstructural solid-gas-liquid interface.

CELL 111

**Pectin and nanocellulose from soybean hulls as partial substituents in methylene diphenyl diisocyanate adhesive formulations**

*Javier A. Hernandez*2, *jah0189@auburn.edu*, *Bhawna Soni*1, *Maria C. Iglesias*2, *R. G. Richey*3, *Charles E. Frazier*1, *Maria S. Peresin*2. (1) Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States (2) School of Forestry and Wildlife Science, Auburn University, Auburn, Alabama, United States (3) Harbert College of Business, Auburn University, Auburn, Alabama, United States

The society is demanding formaldehyde-free adhesives due to the proven health risks associated to their emissions. The industry is actively seeking alternatives such as methylene diphenyl diisocyanate (pMDI), nevertheless this adhesive presents a significant lack of tack. Tack is the property of adhesives to form a bond with a surface upon contact, in other words is the initial adhesive strength. An increase in the adhesive tack will decrease the risk of delamination of the wood composite and related manufacturing complications. We propose to use pectin and nanocellulose fibers (CNF) isolated from soybean hulls for the formulation of emulsions with pMDI. Isolated from any lignocellulosic feedstock using mechanical treatment, nanofibrillated cellulose (CNF) displays several benefits based on their nanosized dimensions, such as mechanical strength and high aspect ratio. Meanwhile the pectin is a heteropolysaccharide that is usually isolated from apple or citrus peel although it can be found in other sources. Pectin serves as gelling and stabilizing polymer in diverse specialty products in a wide range of industry applications.

In this work, pectin and CNF from soybean hulls where isolated and used as additives for pMDI. A rheology-based method for measuring tack was used. Addition of CNF improves the stability of emulsions of pMDI, while pectin also positively affected the pMDI tack. Properties such as internal bond, wet modulus of elasticity and modulus of rupture, and thickness swelling were measured. Techno-economic analysis of the newly developed formulations will be discussed.

CELL 112

**Formulation of cellular structured hydrogels for tissue engineering applications by stereolithography**

*Prutha Joshi*, *ppj0001@auburn.edu*, *Yuyang Wang*, *Joseph Naro*, *Steven Breaux*, *Maria L. Auad*. Chemical Engineering/CPAC, Auburn University, Auburn, Alabama, United States
Hydrogels are evolving in the arena of tissue engineering as matrices for repairing or regenerating tissues and organs. 3D printing of tissue/organ structures has numerous benefits such as design flexibility and use of specific cell lines; however, it needs further enhancements in different areas such as the development of new bio-inks and the commercialization of the 3D printed products. Hydrogels, due to their porous structural similarity to soft tissue, are considered as potential candidates for tissue-engineered scaffolds. The cellular structure of hydrogels can mimic the tissue structure present in the human body.

In this study, we developed bio-inks based on poly(ethylene glycol) dimethacrylate (PEGDA) hydrogels to obtain a cellular structure by stereolithography 3D manufacturing. These new biomaterials allow the fabrication of porous structure and define the cellular macroscopic shape of the hydrogel for tissue engineering.

**CELL 113**

**Catalytic access to alkylation cyclohexanoles**

Kristian Alt, kralt@uni-mainz.de, Siegfried R. Waldvogel. Department of Chemistry, Johannes Gutenberg University, Mainz, Germany

In the last century, the global demand for energy and fine chemicals rose rapidly due to the industrialization of developing countries and increasing world population. The primary feedstock to produce organic chemicals or polymers is covered by using fossil resources. To decrease the need for fossil resources, it is essential to find alternative raw materials. One promising feedstock is using renewable organic biomass to obtain a broad variety of low molecular, aromatic or saturated fine chemicals.

A classical approach to obtain cyclohexanones from bio-based feedstock such as Lignin was investigated. The reaction took place under mild reaction conditions with Raney nickel as a catalyst and without the use of external H₂. To obtain cyclohexanones in a more sustainable way an electrochemical approach was established. Thereby, the electrocatalytic hydrogenation took place at nickel based electrodes at ambient temperatures. The electrocatalytic hydrogenation was studied regarding current density, charge quantity, temperature, and used electrolyte.
Alkaline thermostable recombinant laccase from *Coprinopsis cinerea* uses syringyl-type phenols as mediators and effectively oxidizes lignin

Jussi Kontro, Christina Lyra, Riku Maltari, Joona Mikkilä, Mika Kähkönen, Miia Mäkelä, Kristiina Hildén, **Paula Nousiainen**, paula.nousiainen@helsinki.fi, Jussi Sipila. University of Helsinki, Helsinki, Finland

Laccases are multi-copper oxidases that use molecular oxygen as the electron acceptor to oxidize both phenolic and, indirectly also non-phenolic substrates by mechanisms involving radicals. Due to their eco-friendliness and broad substrate specificity, laccases span a wide range of biotechnological applications. Here we present research performed in EU Horizon 2020-project FALCON, Fuel and Chemicals from Lignin through Enzymatic and Chemical Conversion. FALCON aims to valorize this lignin waste stream by enzymatic and mild chemical conversion to produce fuels, such as low sulfur marine fuel, fuel additives and chemical building blocks. We have heterologously expressed laccase from the litter-degrading basidiomycete *Coprinopsis cinerea* (CcLcc9) in methylotrophic *Pichia pastoris* yeast. The recombinant CcLcc9 oxidized 2,6-dimethoxyphenol in neutral pH range and showed thermostability. The oxidation of non-phenolic compounds by CcLcc9 was tested with low molecular weight mediators, such as syringyl-type plant phenols, which have shown potential as natural co-oxidants for lignocellulosic materials. The results show that syringyl nitrile and methyl syringate efficiently mediate the oxidation of veratryl alcohol to veratraldehyde. In addition, in the presence of these mediators CcLcc9 is able to oxidize lignin fractionated from steam-exploded poplar wood by hot ethanol. The depolymerization of lignin by CcLcc9 enzyme combined with formic acid treatment harbors a great potential for the sustainable processes of circular economy and modern biorefineries.
Solubilization of lignin and impact of hydrogen bonding in aprotic/protic solvents systems

Jessica Emond¹, Bin Yao¹, Erin Tiede¹, Lindsey Bottom¹, Lacy Lilleboe¹, Audrey LaVallie¹, Surojit Gupta³, Evguenii Kozliak², evguenii.kozliak@und.edu, Alena Kubatova². (1) Chemistry, University of North Dakota, Grand forks, North Dakota, United States (2) Chemistry Department, University of North Dakota, Grand Forks, North Dakota, United States (3) Mechanical Engineering, University of North Dakota, Grand forks, North Dakota, United States

Lignin is an abundant organic polymer occurring within plant cell walls and has significant potential as a renewable feedstock for various chemical applications. Yet, due to its complexity, recalcitrance and structural diversity its applications are limited, thus demanding efforts on towards lignin fractionation. In this work we have investigated alkali (kraft) lignin fractionation in single organic solvents and their mixtures with water in various ratios. The lignin solubility was evaluated by gravimetry while the molecular weight (MW) was assessed using GPC confirmed by thermal carbon analysis (TCA), which distinguishes thermally evolving monomers and polymers for each other. The optimal solvent systems proved to be aprotic polar solvents with 25-75% water, with the addition of water increasing the solubility up to ten-fold. By contrast, solvent systems containing alcohols, either with or without water, displayed poor recoveries of lignin. The observed trends were consistent with Hansen parameters of these solvent systems. The fractions with higher water content featured lower MW. Detailed characterization of both solid and liquid fractions was accomplished using thermal desorption-pyrolysis-gas chromatography-mass spectrometry.

Renewable carbon fiber for supercapacitor applications

John Hinkle¹, Archana Bansode¹, Thomas J. Elder², Andrew J. Adamczyk³, Maria L. Auad¹, mla0001@auburn.edu. (1) Auburn University, Auburn, Alabama, United States (2) USDA Forest Service, Pineville, Louisiana, United States (3) Chemical Engineering, Auburn University, Auburn Univ, Alabama, United States

Lignin is one of the most common forms of biomass, third only to cellulose and chitin. A majority of this material is burned during the pulp and paper process. It possesses the highest concentration of aromatics groups out of other natural macromolecules, which allows it to be converted into valuable products. One such product is graphitic carbon. By heating lignin to high temperatures under an inert atmosphere, the material can be converted to graphitic carbon. The lignin was dissolved into DMF along with polyethylene oxide for electrospinning. By applying a constant voltage as well as a constant volumetric flow rate, the lignin-based solution was converted to develop the lignin fibers. These fibers underwent a
calcification process to convert the lignin fibers to carbon nanofibers with the intent of having graphitic carbon fiber. The material was then tested to determine the electrochemical properties of the material.

CELL 117

Nanocellulose membranes in diagnostics

Andrew Piper, andrewpiper89@gmail.com, Lars Wagberg, Mahiar Hamedi. KTH Fibre Polymer Techn, Stockholm, Sweden

Nanocellulosic materials and composites have found applications in a wide variety of fields, one of which is in the field of medical diagnostics. This presentation will outline ongoing work in the Wågberg and Hamedi labs, at KTH Royal Institute of Technology, to use nanocellulose membranes for a variety of applications in the field of point of care diagnostics. These include using CNT (Carbon Nano Tube)-CNF (Cellulose Nano Fibril) composites as electrodes for electrochemical sensing applications; using the transparency of nanocelluloses to make colourimetric sensors; using antibody coupled CNF for complex media scrubbing and specific analyte capture and subsequent release for further analysis. Finally, there is the use of nanocellulose membranes as capillary force driven filters for point of care diagnostics. The ability to tune the pore size of nanocellulose membranes allows us to make membranes with a controlled pore size. These can be utilised in lateral flow devices that are driven purely by capillary forces which makes them ideally suited for point of care diagnostic tests where pump free filtering is still required. This research also yields fundamental information as to the effective pore size of nanocellulose membranes in the wet state.

CELL 118

Operation of proton exchange membrane (PEM) fuel cells using natural cellulose fiber membranes

Aniket Raut¹, aniket.raut@stonybrook.edu, Likun Wang¹, Miriam Rafailovich¹, Sunil Sharma², Rebecca Isseroff³. (1) Material Sciences and Chemical Engineering, Stony Brook University, Stony Brook, New York, United States (2) CHEMISTRY, STONY BROOK UNIVERSITY, NEwYork , New York, United States (3) Dept. of Materials Science and Engineering, Stony Brook University, West Hempstead, New York, United States

Proton exchange membranes (PEMs), such as Nafion, are still one of the reasons for the high cost of PEMFCs. Among the alternatives, cellulose, a low cost and biodegradable material, has been considered in the form of its derivatives, such as cellulose acetate, bacterial cellulose or nanocellulose, as the PEM in fuel cells. However, its use involves more chemical synthesis steps. Here, we use low-cost 1.5-micron cellulose filter paper as the scaffold and prepare membranes for PEMFCs by
simply impregnating it with a 10% Nafion solution or immersing it in resorcinol bis (diphenyl phosphate) (RDP). The prepared membranes are primarily composed of cellulose, with cellulose to Nafion or RDP ratio of 2:1 or 1:1. The membrane electrode assemblies (MEAs) incorporating the as-prepared membranes exhibit a maximum output power of 23 mW cm\(^{-2}\) at 80 °C for the cellulose/Nafion membrane or 10 mW cm\(^{-2}\) at 60 °C for the cellulose/RDP membrane with only 0.1 mg cm\(^{-2}\) Platinum catalyst loading on the anode and cathode, when operated in air. The stability results of the membranes after 100 hours of continuous operation indicate a loss of only 10% in power for the cellulose/Nafion membrane and 20% for the cellulose/RDP membrane. It is revealed by FTIR spectroscopy that both the Nafion polymer and RDP were hydrogen-bonded to the cellulose fibers, facilitating proton conduction and stabilizing them against further dissolution.

**CELL 119**

**Synthesis of a novel flame-retardant hydrogel for skin protection using xanthan gum and resorcinol bis(diphenyl phosphate)-coated starch**

Yuan Xue\(^1\), Mingkang Li\(^2\), mingkang.li@stonybrook.edu, Bole Pan\(^3\), bole.pan@stonybrook.edu, Lisa Quinto\(^1\), Jalaj Metha\(^4\), Lauren Steifel\(^5\), Miriam Rafailovich\(^6\). (1) Materials Science and Chemical Engineering Department, Stony Brook University, Stony Brook, New York, United States (2) Shanghai Star-river Bilingual School, Shanghai, China (3) Guangzhou Tianhe Foreign Language School, Guangzhou, China (4) Hauppauge High School, Hauppauge, New York, United States (5) Yeshiva University High School for Girls, Holliswood, New York, United States

Firefighters continually endanger their lives in order to rescue others. This can leave them with severe burns; in 2017 alone, 2,835 U.S. firefighters suffered from burn-related injuries. In this research, a flame retardant hydrogel was synthesized using biodegradable, non-toxic cellulose based materials: xanthan gum (XG) and resorcinol bis(diphenyl phosphate) (RDP) and starch. RDP was first coated onto the xanthan gum and starch surface. Fourier-transform Infrared Spectroscopy confirmed the hydrogen bonding between RDP and XG/starch. To evaluate the protection of FR hydrogel, sheepskin was embedded in aluminum pans, covered with hydrogel, and burned continuously for 150s. Temperature change of the sheepskin was recorded during burning test. Results showed the formation of a uniform char layer from the FR hydrogel which protect the underlying gel layer and skin. The FR hydrogel sample outperformed its pure XG gel control sample by 29% in terms of the final temperature. The FR hydrogel helped to remain the skin temperature below 45 °C for over 50 seconds and below 55 °C for 114 seconds upon direct burning with a propane torch. TGA tests showed that the FR hydrogel had more residue after test which is in agreement to the char formation during the burning test. Data from the viscosity tests revealed that all samples displayed shear-thinning behavior. Thermal protective performance (TPP) tests were also done to evaluate heat transmission through the FR hydro gel when exposed to a continuous heat source, and result compared to the Stoll Curve which represent the
heat level for causing second-degree burn. The TPP test result showed that the FR hydrogel provided a prolonged protection time comparing to the control sample

**CELL 120**

**Incorporation of iron on nanocellulose for arsenic removal from water**

Madani Khan¹, madani.khan@stonybrook.edu, Wenjing Yang¹, Jenny Gao¹, Benjamin S. Hsiao², Dale G. Drueckhammer². (1) SUNY Stony Brook University, Jackson Heights, New York, United States (2) Stony Brook University, Stony Brook, New York, United States

The availability of safe drinking water is still a scarcity in many parts of the world, especially in sub-Saharan African countries. Therefore, the need for a cheap, simple, and environmentally-friendly method is essential for the removal of many contaminants, especially for hard to remove species such as arsenic. Previously, copper component has been used to remove anionic arsenate from water selectively. However, the cost of copper is about four times higher than iron. In this work, nanocellulose was extracted from jute, and its hydroxyl group at C-6 was carboxylated. Subsequently, iron oxide was incorporated into the carboxylated nanocellulose system to create a positive charge source. The resulting absorbent system was found to effectively remove negatively charged toxins, such as arsenic from drinking water. Additional characterization also involved the kinetic, absorptivity, and reusability tests for this particular absorbent system.

**CELL 121**

**Multimodal imaging of plant protoplasts with regenerating cell walls**

Mohammad Irfan¹, mi260@scarletmail.rutgers.edu, Dharanidaran Jayachandran¹, Hyun Huh², Wellington Muchero⁴, Matthew Lang⁵, Eric Lam³, Sang-Hyuk Lee², Shishir P. Chundawat¹. (1) Chemical and Biochemical Engineering, Rutgers University, Piscataway, New Jersey, United States (2) Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey, United States (3) Department of Plant Biology, Rutgers University, New Brunswick, New Jersey, United States (4) Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (5) Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee, United States

Cell walls are one of the most important constituent of plant cells composed predominantly of complex polysaccharides. One such critical wall polysaccharide component is composed of b-1,4-linked glucose units that form a highly layered mesh of cellulose microcrystalline fibers (CMF). Single cellulose chains are processively synthesized and assembled into the CMF matrix by plasma membrane localized cellulose synthase enzyme complexes (CSC). Each CSC are composed of six trimers of individual cellulose synthase (CESA) units in a rosette-like arrangement that produce an
elementary CMF. In order to study in planta cellulose synthesis by CSC, here, we are developing a multimodal microscopy based platform to characterize single plant protoplast cells with regenerating cell walls. We have successfully optimized various parameters for cellulose biosynthesis and cell wall regeneration in protoplasts of model Arabidopsis system and a relevant bioenergy plant (i.e., Poplar). We are transiently expressing CESA constructs fused with photoactivable fluorescent proteins in plant protoplasts for super resolution microscopic analysis of the cell wall regeneration and cellulose biosynthesis process. Ultimately, this work will help advance our mechanistic and holistic understanding of in vivo cell wall synthesis using multimodal imaging methods that would accelerate the development of improved transgenic crops for bioenergy and bioproducts relevant applications.

CELL 122

Catalytic degradation of hard- and softwood lignin using vanadate and molybdate catalyst systems

Lucia Penin¹, Heiko Lange², Federica Sabuzi³, Matteo Gigli⁴, matteo.gigli@unive.it, Pierluca Galloni³, Valeria Conte⁵, Valentin Santos¹, Claudia Crestini⁶, Juan C. Parajó¹. (1) Chemical Engineering Department, University of Vigo, Ourense, Spain (2) Department of Pharmacy, University of Naples ‘Federico II’, Naples, Italy (3) Department of Chemical Science and Technologies, University of Rome ‘Tor Vergata’, Rome, Italy (4) Department of Molecular Sciences and Nanosystems, University of Venice Ca’ Foscari, Venice, Italy (5) Sc. Tec. Chimiche, Univ. Roma Tor Vergata, Rome, Italy (6) Department of Molecular Science and Nanosystems, Università Ca’ Foscari, Venezia, Italy

Lignocellulosic materials represent a widespread, low cost and renewable bioresource suitable as raw material for the sustainable production of fuels, chemicals and materials. In search for an efficient catalyst system that would allow degradation of lignins towards aromatic platform chemicals for the chemical industry, we investigated green catalyst systems on the basis of vanadate and molybdate. Both hardwood lignin, in form of Eucalyptus, and softwood lignin, in forma of Pine, each isolated both as organosolv and ionosolv lignins, were subjected to various conditions during initial screening. Decomposition products were analysed by GC-MS, re-isolated lignins were analysed for structural changes eventually introduced into the backbone by ³¹P NMR. Hardwood and softwood required different catalyst systems. As most efficient system for Eucalyptus ionosolv lignin was identified a vanadate system leading to 33% decomposition. 64% decomposition were found for ionosolv pine lignin using a molybdate system.

CELL 123

Bio-based thermosets prepared using aza-michael addition of furan and isosorbide building blocks
The Aza-Michael addition reaction of (meth)acrylates with amines can be used for the preparation of thermosets for coating applications because fast reaction kinetics allow for rapid cure at a low temperature. Furan-based building blocks have been investigated as alternatives to incumbent phenolic systems and have been found to possess good mechanical and barrier properties. Multifunctional furan-based amine cross-linkers and Isosorbide Methacrylate (IM) were used to create thermosets utilizing the Aza-Michael addition reaction. The system can be cured at low temperatures in a relatively short period of time while yielding good thermal and mechanical properties due to high functionality of the amine cross-linkers and high reactivity of IM. In this investigation, the cure behavior of these new systems was investigated using spectroscopic techniques. The relative reactivity of primary and secondary amine was evaluated and formulations were obtained that resulted in IM conversion greater than 90%. Furthermore, furan-based epoxy was also introduced into the formulation to react with secondary amine moieties to add crosslinking to the system with improved glass transition temperature and modulus. It is found that unreacted secondary amines in such networks react freely with epoxy monomers providing additional control of network structure and composition. The Aza-Michael addition scheme for network formation provides an effective platform to design hybrid systems incorporating bio-based building blocks that express specific behavioral characteristics.

**CELL 124**

**Sustainable microwave assisted extraction of bioactive compounds from agricultural residues**

Alfonso Jimenez, alfjimenez@ua.es, Marina Ramos, Ana Cristina Mellinas, Ignacio Solaberrieta, Carlos Pelegrin, Yaiza Flores, Maria del Carmen Garrigós. Analytical Chemistry, University of Alicante, San Vicente del Raspeig, Alicante, Spain

The NANOBIOPOL research group in the University of Alicante (Spain) has developed high expertise and know-how in the use of microwave assisted extraction for the valorization of agricultural residues from different origins. Our group has optimized green extraction methods based on microwave assisted extraction (MAE) to isolate and purify valuable chemicals with different functionalities. These chemicals have been obtained from a broad range of agricultural residues as well as other natural sources common in the Mediterranean region.

Microwave-assisted extraction (MAE) is growing as a valid extraction technique due to the time saving, high efficiency, selectivity, green solvent use and low energy consumption, compared to conventional extraction procedures. Agricultural residues have been increasingly exploited to isolate and purify bioactive compounds, and recent
studies have reported on the antioxidant potential of by-products of fruits. Within the scope of four different H2020 European Projects and other national research programmes, our research group has optimized MAE protocols in different agro-food by-products as to evaluate its potential to extract different polysaccharides and functional compounds (pigments, antimicrobials, antioxidants, natural fragrances, reinforcing agents), either within a cascade sequential approach, or in parallel. The extraction was optimized according to multilevel factorial designs and response surface methodologies, keeping subsequent scale-up processes in mind to get isolated and highly pure chemicals with specific functionalities. These studies showed the potential of MAE to selectively and sequentially extract natural pigments (lemon, pomegranate), pectins (lemon, pomegranate, cocoa), polyphenols and essential oils with antimicrobial and/or antioxidant performance (lemon, mushroom, pomegranate, aromatic herbs, cocoa, A. vera), glucans (mushroom) or cellulose and xylan reinforcing fibers with antioxidant properties (almond, pomegranate). These chemicals can be further added to polymer and biopolymer matrices to obtain multifunctional formulations opening a broad range of functionalities. Apart from the end-users involved in the different consortia, these extracts have a wide potential interest as additives in nutraceuticals, cleaning products, chemicals, bioplastics, construction, automotive, packaging or biomedical applications, as a green cost-effective alternative to traditional ones.

**CELL 125**

**Fabrication and characterization of bacterial nanocellulose-based functional materials for biomedical applications**

**Guang Yang**, gyang-hust@hust.edu.cn. College of Life Science Technology, Huazhong University of Science Technology, Wuhan Hubei, China

Bacterial nanocellulose (BNC) is naturally produced by several bacterial genera in the form of a hydrogel at the air-medium interface. It is an unbranched polymer comprised of repeated glucose units, which are linked together through β-(1-4) glycosidic linkages and form nanofibrils. These linear glucan chains form highly regular intra- and intermolecular hydrogen bonds, which stabilize its structure. BNC is an environment-friendly material and possesses unique features such as high mechanical properties, biodegradability, and biocompatibility, owing to its unique nano-size (20-100 nm) fibrous structure. The presence of free hydroxyl (-OH) groups on its surface allows its surface modification by different chemical and physical methods to bless it with unique functional properties, thus can find potential applications in medical field such as skin tissue repair materials, artificial blood vessels, intervertebral disc replacement materials, controlled-release drug carrier, injectable embolization agent, electroactive hydrogel, and so on. Furthermore, we are adopting engineered *Gluconacetobacter xylinum* and utilizing the assembly and arrangement of cellulose fibers to achieve highly specific three-dimensional micro-patterns, which will provide highly sophisticated multi-level tissue engineering scaffolds to induce directed cell adhesion and aggregation for applications in regenerative medicines.
Antiplasticization behavior of biobased additives on the structure, properties, and solution spinning of regenerated cellulose fibers

Manik Biswas, mbiswas2@ncsu.edu, Ericka Ford. Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina, United States

Cellulosic fibers, characterized by poor processable biorenewable polymers due to strong inter- and intramolecular hydrogen bond, are produced comprising low molar mass species by lowering their second order transition and improve their poor structural properties. Recent global environmental awareness, sustainability trends in textiles and high rate of depletion of petroleum resources pave the way to use toward natural and/or biodegradable antiplasticizer with low toxicity and high compatibility with the matrix as a replacement of traditional petrochemical based antiplasticizer along with the use of biorenewable polymers. This study focuses to a method for the production of cellulosic fibers according to wet spinning method, in which cellulosic fiber forming polymer and a specified biobased antiplasticizer dissolved in a suitable solvent and spun through a spinneret nozzle into a coagulation bath at room temperature. The as spun fiber subsequently dried with hot air flow and drawn at elevated temperature and wound up eventually. The biobased antiplasticizer comprised cellulosic fiber exhibited high...
modulus, high tensile strength and toughness compared to pristine fibers which are desirable industrial fiber properties for high performance industrial applications.

CELL 127

**Development of environmentally friendly flame retardant solution for cellulose based materials**

Yuan Xue, **Conor Kimmey**, conor.kimmey@stonybrook.edu, Xianghao Zuo, Miriam Rafailovich. Materials Science and Chemical Engineering Department, Stony Brook University, Stony Brook, New York, United States

In 2019 alone, there have been over 5,000 wildfires in California, which have consumed over 160,000 acres of land. Wildfires are a threat not only to vegetation and property, but also to local residents and firefighters. Current methods in fighting the wildfires are mostly reactive, rather than preventive. Moreover, the chemicals used for quenching the fire and their impacts on land field and human health have always been in debate. Since the target materials (wood, leaves, clothing for firefighter) are all cellulose based, we developed a novel environmentally friendly flame retardant solution that targets cellulose based organic materials, and could be applied periodically to prevent wildfires and enhance the protection of clothing. The flame retardant solution consists of ammonium polyphosphate (APP), resorcinol bis(diphenyl phosphate) (RDP), and lactide monomer (LM). The flame retardant solution was applied to samples of leaves and cotton clothing, then burned. Each sample successfully self-extinguished immediately after being ignited and showed significant flame retardant performance. The leaf samples were analyzed by limited oxygen index (LOI), showing an improvement when using the flame retardant solution. The burn tests of the cotton clothing were analyzed by forward looking infrared (FLIR) thermal imaging and showed significantly lower temperatures during burning when the flame retardant solution was applied. It is proposed that the flame retardant is effective due to the synergistic effects of APP/RDP/LM bonding with cellulose that promote the formation of a protective char layer.

CELL 128

**Use of fractionated lignin and its methacrylic derivatives in the synthesis of polymer materials**

Marta Goliszek¹, Claudia Crestini², Simone Cailotto², Matteo Gigli³, Beata Podkosciełna¹, Ayumu Tagami⁴, Olena Sevastyanova⁵, olena@kth.se. (1) Department of Polymer Chemistry, Maria Curie-Sklodowska University, Lublin, Poland (2) Department of Molecular Science and Nanosystems, Università Ca' Foscari, Venezia, Italy (3) Department of Molecular Sciences and Nanosystems, University of Venice Ca' Foscari, Venice, Italy (4) Research Laboratory, Nippon Paper Industries Co., Tokyo, Japan (5) Wallenberg Wood Science Center, KTH - Royal Institute of Technology, Stockholm, Sweden
Currently, lignins are considered as important aromatic renewable resource and promising alternative feedstock for the production of biobased polymers. Due to a highly functional character of lignin, rich in hydroxyl groups, it can be a great candidate for various chemical modifications. On the other side, one of the main problems hindering the use of lignin in industrial applications, is its high dispersity and structural diversity which is dependent on the lignin origin and extraction process. Thus, fractionation into low-molecular weight fractions and their thorough chemical characterization is a necessary step for any future uses. Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful, rapid and reliable analytical tool for detailed structural elucidation of lignin. This work investigates the impact of fractionation and functionalization process on the structural and thermal properties of lignin. Two kraft lignin samples of different origins, softwood (Norwegian spruce) and hardwood (Eucalyptus grandis), isolated from a pulping process according to the Lignoboost technology, were used in this study. They were fractionated with organic solvents, ethyl acetate followed by methanol, into materials characterized by low polydispersity, different molecular weights and functionalities (contents of carboxylic, phenolic and aliphatic hydroxyl groups). After the fractionation, lignin samples reacted with methacryloyl chloride, forming methacrylic esters. Structural characterization of initial lignins as well as lignin fractions before and after methacrylation were thoroughly investigated by 31P NMR technique. 2D heteronuclear single-quantum coherence (HSQC) NMR was used to determine different interlinkages in lignin samples. Thermal properties were studied by the means of thermogravimetric analysis (TGA). Lignins with low polydispersity, specified molecular weights and contents of reactive double bonds are attractive precursor for a large variety of polymeric biomaterials. The use of natural polymer, lignin, in polymeric materials can contribute to more efficient utilization of biomass and promote sustainability for the existing plastic industry.

**CELL 129**

**Fundamentals of cellulose nanocrystals (CNCs) in common organic solvents**

*Allen Chang*, *Alice Zheng*, *alzheng@umass.edu*, *Kenneth R. Carter*. (1) Polymer Science and Engineering, UMass Amherst, Amherst, Massachusetts, United States (2) Biology, UMass Amherst, Amherst, Massachusetts, United States

Cellulose Nanocrystals (CNCs) are examined in a selection of common organic solvents. In general, these are all poor solvents for CNCs – save for acetone – which lead to poor dispersions. However, we investigate conditions that allow for single phase dispersions of CNC in solvent, as well as their sedimenting 2-phase counterparts. Certain properties of CNCs such as casted film clarity, solid state ordering, and morphology are examined for CNC dispersions in different solvents. We show that there is dependence of these properties on the dispersing solvent as well as the concentration of the dispersions. For example, an acetone/CNC dispersion casts semi-transparent, hard films whereas toluene/CNC dispersions cast opaque white, easily sheared, powdery coatings. Apart from DMSO and DMF, no other common organic solvents have been studied in this fashion. The results of this work will significantly
impact the potential modification chemistries available to cellulose scientists. As more aspects of CNC in organic solvent dispersions become clearer, we will be better able to perform non-aqueous chemical modifications on CNC surfaces.

CELL 130

Bacterial cellulose modification using quaternary ammonium salts

Angelica Stefany S. Sandoval Miranda, asmiranda.sandoval@gmail.com, Julio R. Pinzon, Cristian Blanco-Tirado, Marianny Y. Combariza. Escuela de Química, Universidad Industrial de Santander, Bucaramanga, Santander, Colombia

Bacterial cellulose (BC) is a biopolymer of D-glucopyranose that can be produced by microorganisms like Gluconacetobacter xylinus using sugars from residual biomass. This study shows that is possible to obtain BC from cocoa’s biomass. BC is an interesting raw material for many applications due to its malleability, permeability to liquids and gases, resistance, biocompatibility as well as its high degree of crystallinity and low immunogenicity. These properties can be modulated by modifying the hydroxyl groups in the C2, C3 or C6 of cellulose surface to produce functionalized nanocellulose. Our results show that it is possible to obtain cationic cellulose by reacting quaternary ammonium salts with the polymer surface. Firstly, TEMPO nanocellulose was prepared and modified by using an uronium salt (TBTU) as a coupling agent in a “one-pot” reaction. Then, cationization of nanocellulose was accomplished by N-methylation with CH₃Cl. By studying morphological (FE-SEM), structural (FTIR spectroscopy, X-ray diffraction, conductivity, ζ-potential), thermal (TGA) and emulsifying properties of cationic-nanocellulose we show that modified nano BC can be an alternative to replace conventional surfactants due to its emulsifying activity.
Time-dependency and structural alignment of cellulose nanocrystal suspensions in shear- rheometry coupled with polarized light visualizations

Mina Fazilati¹, mina.fazilati@chalmers.se, Roland Kadar¹, Tiina Nypelo². (1) Chalmers University of Technology, Gothenburg, Sweden (2) Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Tulln, Sweden

The rheology of high aspect ratio particle suspensions, such as cellulose nanocrystals (CNC), depends to a great extent on the size distribution, the orientation, and the morphology of the rods under shear flow. The CNC suspensions additionally experience a time-dependent flow characteristic, thixotropy. Here, we elucidate time-dependent properties of CNC suspension in 4-8 wt% CNC concentration by four tests that support thixotropy quantification: creep test, complex viscosity, hysteresis flow curve, thixotropy recovery. CNC suspensions exhibit aging and rejuvenation in varying imposed shear stresses in time, and viscosity bifurcation is observed when the viscosity is plotted as a function of time. Combining rheological thixotropy with microscopic visualization of
micro-phase transitions provides a completely new aspect in designing the structure of materials from CNC flow.

CELL 132

**Eucalyptus nitens** lignins by ionic liquid-based biorefinery methods

*Lucia Penin¹, Heiko Lange², heiko.lange@unina.it, Claudia Crestini³, Valentin Santos¹, Juan C. Parajó¹.* (1) Chemical Engineering Department, University of Vigo, Ourense, Spain (2) Department of Pharmacy, University of Naples ‘Federico II’, Naples, Italy (3) Department of Molecular Science and Nanosystems, Università Ca’ Foscari, Venezia, Italy

Lignocellulosic materials represent a widespread, low cost and renewable bioresource suitable as a raw material for the sustainable production of fuels, chemicals and materials. In quantitative terms, woods are the most important type of lignocellulosic materials. Considered as feedstocks for the industry, woods show important comparative advantages over other lignocellulosic materials of agricultural origin, including large availability, non-seasonal character, favorable composition (defined by their contents of polysaccharides and polyphenols, ash, sulfur and nitrogen), and ability to grow in lands unsuitable for agriculture, thus avoiding direct and indirect competition with the food chain.

*Eucalyptus* spp. are fast growing hardwoods with favorable features to be valorized by sustainable conversion technologies. *Eucalyptus* is the most widely planted type of hardwoods, and can be produced at relatively low cost. Although the most important *Eucalyptus* species in terms of world plantations are *E. grandis*, *E. urophylla*, *E. camaldulensis* and *E. globulus*, growing attention is being paid to *E. nitens* owing to their decreased susceptibility to *Gonipterus* plagues and to its ability to resist a wide range of environmental conditions unsuitable for other *Eucalyptus* species.

Ionic liquids (ILs), eventually representing an environmentally beneficial alternative to common solvents, have been exploited in fractionation of lignocellulosic materials. The most suited ones for *Eucalyptus* wood fractionation bear the methylimidazolium cation. In an attempt to extend the knowledge regarding the effects of IL-based fractionation of *E. nitens*, the fractionation of *E. nitens* wood was performed by consecutive stages of aqueous processing to achieve the selective solubilization of hemicelluloses, and a solid phase with increased contents of cellulose and lignin; and the delignification of this latter. Isolated lignins were characterized by $^{31}$P NMR, HSQC, $^{13}$C NMR and GPC to obtain key information defining their potential as substrates for further chemical conversion into value-added products.

CELL 133

Carbohydrate polymers based value-added co-products from sorghum bran, bagasse and biomass
Three different types of sorghum are currently being developed by plant breeders, grain sorghum (bred for high yield of kernels), sweet sorghum (bred for high yields of sugar in the stems) and forage/biomass sorghum (bred for high yield of total biomass). The alkali soluble arabinoxyylans (Hemicellulose B) and insoluble fibrous cellulose rich fractions from sorghum bran, sorghum bagasse and biomass sorghum were isolated by alkaline treatment, characterized and their functionalities were studied. The monosaccharide composition of the Hemi. B fraction from sorghum bran showed a highly branched structure but the Hemi. B fractions from sorghum bagasse and biomass sorghum were less branched. The Hemi. B from all these three sorghum sources appear to have useful properties as emulsifiers and soluble dietary fibers. Like corn fiber gum, these polysaccharides are unique in their ability to make low viscosity solutions, even at high concentrations and they show shear thinning behavior. Cellulose rich fractions prepared from the residues remaining after Hemi. B isolation were also characterized and their water holding capacity was determined. The cellulose rich fractions from all these sorghum sources have high water holding capacity (22.76 to 35.27 g water/g cellulose rich fraction). The new insoluble fibers from these sorghum sources are expected to have unique applications as non-caloric food bulking agents and may be useful in replacing fat with healthy fiber and water without changing taste. The new insoluble fibers may also improve mouth feel of foods such as bakery products, dairy products, meats, dressings, mac and cheese etc. Understanding the functional properties of Hemi. B and cellulose rich fraction will be beneficial for their commercialization and for identifying new applications in food industries.

CELL 134

Bio-based latex nanoparticles via RAFT emulsion polymerization for modification of biofibre surfaces

Alexandros Efraim E. Alexakis¹,², aleale@kth.se, Eva E. Malmstrom³. (1) Fibre and Polymer Technology, Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden (2) Fibre and Polymer Technology, Division of Coating Technology, KTH Royal Institute of Technology, Stockholm, Sweden (3) Dept of Fibre and polymer technology, KTH Royal Institute of Technology, Stockholm, Sweden

Cellulose, being a biopolymer with superior properties, and its derivatives have earned its place in the spotlight during the past decades. A lot of research has been performed in an effort to compatibilize it with synthetic polymers. However, in order for compatibilization to be successful, modification of the cellulose surface may be necessary. One possible way to accomplish that is to utilize nanoparticles. Such nanoparticles, can be synthesized through RAFT-mediated surfactant free emulsion polymerization by employing the process of polymerization induced self-assembly (PISA) in water. Many synthetic monomers, such as methacrylates, acrylates and styrenes have been explored for this, resulting in nanosized latex particles with a variety
of properties and shapes. For instance, latex nanoparticles with a cationic corona and PMMA core have been successfully employed in the stabilization of cellulose nanofibrils (CNFs). However, only a few cases of bio-based alternatives can be found that include hemicelluloses, fatty acids, etc. In the current study, monosaccharide-based monomers were used to synthesize bio-based macroRAFT agents with varying degrees of polymerization. Thereafter, the macroRAFTs were chain extended with a hydrophobic core in water and by using the PISA process, latex nanoparticles were formed. Finally, the resulting nanoparticles were characterized and their adsorption to nanocellulose surfaces was investigated.

CELL 135

Structural characterization during the production of carboxymethylated cellulose nanofibrils

Christian Aulin, Andreas B. Fall, andreas.fall@ri.se, Niklas Nordgren, Ruben Alvarez-Asencio, Tomas Larsson, Jasna Stevanic Smrdovic, Tiffany Abitbol. Bioeconomy, RISE, Research Institutes of Sweden, Stockholm, Sweden

The effect on the molecular and particle structure/morphology of carboxymethylated cellulose nanofibril (CM-CNf) is presented. An established functionalization route, carboxymethylation, was used to modify bleach cellulose pulp fibers to a degree of substitution (D.S.) ranging from 0.05 to 0.60, followed by high-pressure homogenization to produced CM-CNf gels. A significant impact of increasing D.S. was found already on the pulp fibers, prior homogenization, on the fiber morphology (SEM) and molecular structure (WAXS and NMR). The following homogenization accelerated these effects. Disrupted nanofibrils structure was observed by AFM, where increasing D.S. showed increasingly CMC-like treads protruding out from the fibril surface as well as completely liberated single chain polymers, verifying the WAXS/NMR results. The nanofibril yield, the colloidal, rheological and optical properties of the gels were also studied and found to depend on D.S.

Understanding how modifications and process conditions affects the properties of CM-CNf, especially that it partly dissolve, open up the possibility to design CNFs with unique and tunable properties, making them potentialy interesting for a vaste varity of applications, for example in high-value application within the fields of hygiene, biomedical or as component in inks for printed electronics.

CELL 136

Alkali hydrolysis of sulfated cellulose nanocrystals: Optimization of reaction conditions toward tailored surface charge

Jacobs H. Jordan, jacobshjordan@gmail.com, Michael W. Easson, Brian D. Condon. Agricultural Research Service, US Department of Agriculture, New Orleans, Louisiana, United States
Cellulose nanocrystals (CNCs) are a biorenewable resource, which may be chemically modified to impart specific properties. Modified CNCs have found use in imaging applications, as rheology modifiers, polymer reinforcements, barrier and/or optical films, and nanocomposites. However, the physical properties are dependent upon the degree and type of functionalization of the surface charge groups imparted during preparation. In the case of CNCs produced from sulfuric acid hydrolysis, the sulfated surface groups may be partially removed prior to further functionalization. This gives more available hydroxyls yet renders the CNCs less colloidally stable based on ζ-potential measurements (Fig 1). Furthermore, conditions vary significantly, and there is no consensus for the optimal conditions for partial removal of sulfate functionality or conditions developed to give specific surface charge. In the following, alkali hydrolysis of sulfate half-esters was quantified by conductometric titration of the strong acid groups, and using a design of experiments (DOE), optimal conditions were determined to produce CNCs with tailored surface charge (Fig 2).
Plot of ζ-potential (mV) versus –OSO₃⁻ functionalization (mmol kg⁻¹). Error indicated by the size of the spheres; color bar represents hydrolysis reaction temperature (°C), while the numbers represent time (hours) and molar concentration of NaOH, (e.g., 3 h, 1.0 mol L⁻¹ is [3, 1.0]. t = 0 masked for clarity.

Plot of temperature (°C) versus NaOH concentration (as equiv. NaOH per µmol –OSO₃⁻); output (z-axis) – OSO₃⁻ functionalization (mmol kg⁻¹). (t = 6 h).

CELL 137

Dual-functional epoxy-methacrylate monomers from bio-based feedstocks and their respective epoxy-functional thermoplastics

Kayla Sweet¹, sweetk4@students.rowan.edu, Alexander Bassett¹, Robert O’Dea², Amy E. Honnig¹, Claire M. Breyta¹, Julia H. Reilly¹, John J. LaScala³, Thomas H. Epps², Joseph F. Stanzione¹. (1) Department of Chemical Engineering, Rowan University, Glassboro, New Jersey, United States (2) Department of Chemical & Biomolecular
Dual-functional monomers consist of two distinct functional groups that enable chemical versatility. Glycidyl methacrylate (GMA) is the sole commercially available epoxy-methacrylate monomer. GMA can be polymerized to form poly(GMA), an epoxy-functional thermoplastic with highly versatile and tunable chemical, mechanical, and thermal properties. In an effort to produce bio-based, aromatic complements to GMA, the asymmetric phenolic diols vanillyl alcohol (VA), syringyl alcohol (SA), gastrodigenin (GD), and tyrosol were identified. VA, SA, and GD are derived from lignin, whereas tyrosol can be extracted from olive mill wastewater. Each diol was selectively epoxidized at the aromatic hydroxyl group followed by esterification at the aliphatic hydroxyl group to prepare dual functional monomers vanillyl alcohol epoxy-methacrylate (VAEM), syringyl alcohol epoxy-methacrylate (SAEM), gastrodigenin epoxy-methacrylate (GDEM), and tyrosol epoxy-methacrylate (TEM). VAEM, SAEM, GDEM, and TEM were polymerized to form bio-based epoxy-functional poly(GMA) alternatives. The molecular weight distributions and thermal properties of each polymer were evaluated, as were the surface characteristics of flow-coated thin films from these polymers. Most of the newly prepared epoxy-functional thermoplastics exhibited increased thermal stability relative to poly(GMA) while retaining similar glass transition temperatures and surface energies; thus, these materials could be substituted for poly(GMA) and be useful in higher-temperature applications.

**CELL 138**

Investigating structural changes in softwood lignin induced by ball milling

Ioanna Sapouna\(^1\), sapouna@kth.se, Lauren McKee\(^{1,2}\), Martin Lawoko\(^1\). (1) Fibre and Polymer Technology, Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden (2) Chemistry, Division of Glycoscience, KTH Royal Institute of Technology, Stockholm, Sweden

Approximately 30% of softwoods remains severely unutilized. This is the amount of lignin in softwoods, which due to its heterogeneity is mainly used for the production of energy by combustion. However, interest in this material is increasing, with a variety of new applications developing, from component in thermosets and thermoplastics, to antioxidant and carbon fibres. The applications of lignin are highly dependent on its structure. Many protocols regarding analytical lignin extraction utilize ball milling, in order to make the fibres more accessible and use milder extracting conditions. At the same time, it is hypothesized that the structure of native lignin is altered, through both fragmentation and the formation of new bonds during the milling. The high energy introduced during the process, both thermal and mechanical, as well as the aromatic structure of this material, work in favour of this hypothesis. Lignin polymerization occurs via radical coupling and depending on the type of the bond, rearomatization, formation...
of intermediates and other mechanisms, proceed the formation of the final structure. The severe ball milling conditions may favour the formation of radicals through homolytic cleavage reactions. Subsequent re-coupling reactions could lead to an inaccurate perception of native lignin structure. This study focuses on the effect of ball milling interval duration and conduction under inert atmosphere, on the structure of lignin. Warm water and mild alkali extraction followed by enzymatic hydrolysis of the cellulose and hemicelluloses were parts of the method developed for the mild extraction of lignin. With this approach, the structural differences induced by the extraction methods will be reported. Analytical techniques include 1D and 2D NMR analyses.

**CELL 139**

**Promise of bioplastics from lignin**

Li-Yang Liu, liyang.liu@alumni.ubc.ca, Kim Bessler, kimmarie.bessler@gmail.com, Scott Renneckar. Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

The most seemingly straightforward application of lignin is to utilize it in degradable bioplastics taking advantage of its natural characteristics such as UV absorption, biodegradability, and stiffness. Industrial technical lignins such as kraft lignin is an emerging feedstock for this type of large-scale opportunity. To utilize these lignin resources, chemical modification, especially esterification, has a crucial role in tailoring its properties for applications requiring specific solubility and thermal properties. Further, traditional modification routes can cause severe environmental issues. Also, blending lignin derivatives above the 25 - 40% threshold level will make severe impacts on the mechanical properties of lignin-based bioplastics. In this study, the first objective was to develop a simple greener route to obtain a series of esterified lignin derivatives with controlled thermal properties and absolute molar mass. HSQC NMR, $^{13}$C NMR, gel permeation chromatography combined with multi-angle light scattering and viscometer detectors, and rheology were used to characterize these lignin derivatives thoroughly. Further, these well-characterized lignin derivatives were blended with degradable plastics, polybutylene adipate terephthalate (PBAT), up to a 40% substitution level; injection molded samples were subsequently mechanically tested. The structure-property relationships were discussed by combining the fundamental characters of lignin with the mechanical strength of lignin-PBAT blends. Within the further understanding of the structure of the lignin and thermal rheology of the derivatives, we were able to process and prepare near 100% lignin derivatives bioplastic materials with specific shapes. The brittleness of these resulting materials can be potentially conquered with appropriate plasticizers.

**CELL 140**

**Mixing up lignin fractions: Tailoring thermal properties for ultralight nanofibrous lignin sponges**
Over 30 t/day of softwood kraft lignin is recovered by the LignoForce™ system in Canada. A continuous supply of softwood lignin means there are many potential opportunities to replace petroleum based materials and chemicals with lignin based products. Moreover, developing applications of renewable materials with lignin should be combined with green and sustainable processes, where waste is minimized and toxic chemicals are avoided. In this study, LignoForce™ lignin was fractioned into two parts and the resulting lignin had varying thermo-rheological behavior. These two fractionated lignins were combined together in specific ratios and transformed into nanofibers by electrospinning. The electrospun materials were disrupted by agitating the mats in water and the materials were transformed into ultralight 3D sponges. Using only this combination of two fractions, morphology of lignin nanofibers was tailored by heat treatment resulting in lignin sponges with high flexibility and significant shape recovery properties. Various microscale structures of lignin fibers impacted the properties of lignin based sponge materials such as resilience, compressive strength, and electrical conductivity for the carbonized samples. By exploiting lignin’s sensitivity to heat, and tailoring the thermal properties of the lignin through fractionation, the work provides an interesting path to form lignin derived functional materials without any toxic chemical additives.

CELL 141

Bio-nanofiber derived 3D porous nanocarbons for green electronics

Luting Zhu1, Sharollzhu@gmail.com, Yuki Yoshida2, Kojiro Uetani2, Masaya Nogi2, Hirotaka Koga2. (1) Graduate School of Engineering, Osaka University, Osaka, Japan (2) The Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan

3D porous nanocarbons have shown great promise for environmental protection, electrochemical energy storage and conversion, and advanced sensing to achieve green innovation. Because 3D porous structures could provide largely expanded working volume, multiplexed conduction networks, 3D interfacing, or intercalation with other system components (e.g., electrolytes and reactants). Recently, the drive to actively use defective sites in 3D porous carbon materials has been accelerated in electrochemical applications. The defective sites have been confirmed to play important roles in electrocatalytic reactions and improving electrocapacitive properties. Nanocellulose and nanochitin, the most abundant natural polymers from forest and sea, would have great potential as precursors for 3D porous nanocarbons with defective structures toward green electronics because of their attracting properties such as excellent mechanical strength, high specific surface areas, renewability and biodegradability. Here we report bio-nanofiber (nanocellulose and nanochitin) derived 3D porous nanocarbons via freeze drying and carbonization at different temperatures to impart controllable electronic properties and defective structures. With the proper carbonizing
temperature, these nanocarbon materials could act as high-performance supercapacitor electrodes and photo-sensors. Of special note is that the nanochitin-derived 3D porous nanocarbons provided higher capacitance and photo sensitivity than nanocellulose-derived nanocarbons, possibly due to nitrogen doping from intrinsic chitin structure. Our strategy will open new doors for bio-nanofiber based green electronics.

CELL 142

Time-resolved structural transition during nanocellulose gel formation using an in situ SAXS/flow-focusing technique

Tomas Rosen²,¹, trosen@kth.se, Ruifu Wang², HongRui He², Chengbo Zhan², Shirish Chodankar³, Benjamin S. Hsiao². (1) Treeseach, KTH Royal Institute of Technology, Stockholm, Sweden (2) Chemistry, Stony Brook University, Stony Brook, New York, United States (3) National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, United States

In situ X-ray characterization of mixing processes can pose some engineering challenges especially when the process leads to a dramatic change in viscoelasticity of the material. One notable challenge is to create a well-defined mixing system without the residual material sticking on walls, which often leads to unreliable measurements of the time-resolved data. Furthermore, in order to minimize radiation damage, it is desired to not irradiate the same material during the mixing process. In this work, we present a flow-focusing mixing system for in-situ structural characterization during mixing using a scanning SAXS technique. In this system, the focused core material detaches from the walls and forms a plug flow with no shear, allowing for easy conversion of spatial coordinates to mixing time. Additionally, radiation damage can be neglected as the material is continuously flowing through the beam. Using this system, we studied dispersed cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC) mixed with a NaCl solution, which results in gel formation. The structural changes during this process reveals new information regarding how the positive ions screen the charges of CNC and result in the loss of structure through Brownian motion. For CNF, the structural changes can be attributed to the formation of a connected network with segmental aggregates, which in turn leads to reduced Brownian motion and a more oriented structure. This work not only captures the timescales of nanocellulose gelation, but also provides new insight into the development of new processes of making continuous nanostructured bio-based materials. The demonstrated technique can serve as a powerful tool for time-resolved investigation of any structural change occurring during mixing, especially relevant to soft matter.

CELL 143

Dehydrating polymer desiccants via centrifugation

Alexandra Pine¹, Srivatsan Raghavan², Cheng-Chi Wu², Dimitris I. Collias³, Brian J. Love¹,⁴,⁵, bjlove@umich.edu. (1) Materials Science and Engineering, Univ of Michigan,
Experiments evaluated centrifugation as a technique to achieve drying of a sodium acrylate-based superabsorbent polymer (SAP) saturated from both deionized (DI) water and a simulated urine solution. It was hypothesized that drying procedures for saturated desiccants using mechanical methods might be more economical than evaporation. A commercial, mid-grade, multi-welled centrifuge capable of loading up to 12 specimens was used at ambient temperature and speeds as high as 4000 rpm (2400 g). To perform the centrifugation extraction, a separate mesh construction was used to contain each sample saturated with either DI water or a simulated urine solution while the fluid was driven from the sample under controlled spinning conditions. We will present the efficiency of fluid extraction from saturated desiccants while varying both the time of the spin cycle between 2 and 20 minutes and the centripetal velocity between 1000 and 4000 rpm. Gravimetric determinations following centrifugation found that between 30 and 60% of the fluid were extracted. The ionic strength of the simulated urine solution was much higher than that of water, which reduced fluid saturation volumes of the urine solution in the SAP. We extracted at most ~31% of the simulated urine solutions and ~60% of the DI water. This demonstration compared the mechanical energy used relative to that required for evaporation. The modest amount of fluid extracted could be enhanced if the pore size of the meshes was larger to allow for more facilitated transport through them. Centrifugation can extract the fluid content from saturated desiccants, and the efficiency is a function of the centripetal g force, the mesh pore size, and longer time which is directly proportional to energy expended.

CELL 144

Data analysis pipeline for scanning micro–diffraction measurements on plant tissues

Jiliang Liu\textsuperscript{1}, ligerliu@gmail.com, Lin Yang\textsuperscript{2}. (1) NSLS–II, Brookhaven National Laboratory, Port Jefferson, New York, United States (2) National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York, United States

Recent developments at synchrotron facilities have enabled routine scanning diffraction measurements on biological tissues using micron–size X-ray beams. These measurements produce thousands of scattering patterns per scan. Extracting the rich structural information contained in the scattering data calls for a generic data processing pipeline that can be configured to perform sample-specific data analysis. We demonstrate such a pipeline using data collected from plant tissues. The typical data flow starts from the conversion of scattering data into intensity maps with reciprocal coordinates that are independent of the experimental configuration. This is
accomplished using py4xs, which also performs common preprocessing such as gap-filling in the detector data. Sample-specific functions are then used to distill the intensity maps into attributes that are informative of the underlying structure. For plant tissues, we have developed to functions that calculate cellulose crystallinity, fiber size and microfibril angle by fitting both SAXS and WAXS data, from data collected in either powder diffraction or fiber diffraction geometry. The extracted features are then assembled into false-color maps to reveal structural variations that are invisible in optical images. Tomographic reconstruction from 2D projections collected from different angles is also possible.

CELL 145

Isosorbide-based low viscosity resins for additive manufacturing applications

Xi Chu\textsuperscript{1}, xichu1007@gmail.com, Heather Berensmann\textsuperscript{1}, John J. LaScala\textsuperscript{3}, Giuseppe R. Palmese\textsuperscript{2}. (1) Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States (2) Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States (3) Army research Laboratory, Aberdeen Proving Ground, Maryland, United States

Additive manufacturing is currently at the forefront of the seemingly impending industrial revolution as researchers are investigating new ways to improve and optimize the manufacturing of machine/tooling components. Widely understood as Industrialized 3-D printing, additive manufacturing provides the promise of manufacturing entire machines and machine parts such as jet engines, hearing aids and gas turbines. According to studies conducted by the Fraunhofer Additive Manufacturing Alliance, approximately 150 companies currently operate in this services market; an interesting prospect as market researchers forecast a 300% growth in additive manufacturing niches over the next decade. Although currently used for rapid prototyping, additive manufacturing is expected to grow past conventional production methods as it is projected to be 50% cheaper and 400% faster in the next five years. This work aims to show the synthesis and characterization of isosorbide based low viscosity crosslinkers that can potentially be integrated into additive manufacturing resins. Isosorbide based crosslinkers have the potential to impart high thermal properties ($T_G \approx 220$ °C) and high modulus (> 4 GPa) on bio-based polymers for additive manufacturing.

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Electron microscopy of cellulosics: Historical perspectives and technical challenges

Yu Ogawa, ogawa@cermav.cnrs.fr. Cermav, CNRS, Grenoble, France

Transmission electron microscopy (TEM) has played a significant role in the characterization of cellulosic materials, especially “nanocelluloses”, from visualizing nanoscale morphologies to investigating crystal structures. In this contribution, I will
present a historical perspective on the contributions of TEM in the ultrastructural characterization of cellulose and related materials.\[1\] I will also discuss the state-of-the-art techniques such as microED and technical challenges we are facing today for better understanding of cellulosic structures.\[2\]

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Lignin/PEDOT Electrodes for Energy Storage Applications

**Ujwala Ail**\(^1\), ujwala.ail@liu.se, **Jaywant Phopase**\(^2\), **Fatima Nadia Ajjan**\(^1\), **Magnus Berggren**\(^3\), **Xavier Crispin**\(^1\). (1) Dept. of Science and Technology, Linköping University, Norrköping, Sweden (2) Linköping University, Linköping, Sweden (3) Linkoping University, Norrkoping, Sweden

One of the most debated topics in the energy world today is about the extent to which carbon-free renewable energy can be used in our day-to-day life. Since the two most popular sources of renewable energies; namely the solar and wind power are intermittent, they cannot match with the energy demand of human activity. Hence large-scale batteries are emerging as integral components of the energy solutions for the future to enable constant power delivery on the electrical grid. The current technologies for large scale electrical energy storage rely on raw materials that have limited abundance or expensive to manufacture. On this regard, we report the development of a safe and sustainable bio-based battery components using materials that are abundant and recyclable. Lignin being one of the most abundant biopolymers, qualifies to be one of the potential candidates, as it has quinone-aromatic chemical groups that can be employed to store and deliver electrical charges by reversible Faradaic reactions. But lignin is also an electrical insulating material. To enable those Faradaic reactions, we composite lignin with a conducting polymer and obtain a nanocomposite that is conducting electricity and thus provide electrons and ions to lignin. More specifically, we report the preparation and optimization of the composite electrode materials of lignosulfonate (LS) (lignin) and the conducting polymer (poly 3, 4-ethylenedioxythiophene; PEDOT) for energy storage application. Scaled-up synthesis route in aqueous media for low-cost environmentally friendly technology to make large volume batteries will be discussed. The results of the battery concept incorporating this lignin/PEDOT based-positrode and a bio-based negatrode; PACA (poly(1-amino-5-chloroanthraquinone)/PEDOT in a water-based electrolyte along with cellulose based separator will be presented.

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Thermal properties of treated date palm fibers

**Helanka J. Perera**\(^1\), hperera@hct.ac.ae, **Basmah Abdulleh Mohammed Alattas**\(^2\). (1) Math's & Natural Science, Abu Dhabi Women's, Higher Colleges of Technology, Abu
Recently, great interest was paid to natural fibers while developing new technologies by considering the environmental aspect. These new technologies are going to lead us proper utilization of the available natural resources and on waste management. Applications of natural fibers in industries have taken great attention on the last few years as an alternative to the glass or carbon fibers. Date palm fibers (DPF) are good substitutes for synthetic reinforced fibers. The properties of the DPF composite depends on the interfacial bonding between fibers and polymer matrix. This interfacial bonding can be increased by treating the natural fibers with different silane coupling agents: such as fluoro and nonfluoro silanes. After modifying, the final properties of treated fibers are very important, while it used on different applications. Thermal property is one of the main property gives an idea of the stability of the material with temperature fluctuation. During this study, raw DPF undergoing different surface modifications with the help of fluoro- and nonfluoro silane. Modified DPF’s are going to be characterized using thermal gravimetric analysis (TGA) to know the thermal stability of treated fibers. Scanning electron microscope (SEM) helps to understand the morphological of the fibers after modification.

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**Sunflower oil enriched with lycopene from pink guava (Psidium guajava L.) through a green process with Waring blender and Ultraturrax**

Mariana Villegas², Carlos Molina³, Angelica Serpa³, Jorge A. Velasquez³, Piedad Gañan Rojo⁴, Robin Zuluaga Gallego⁴, Catalina Gomez Hoyos¹, catalina.gomezh@upb.edu.co. (1) ENGINEERING, Universidad Pontificia Bolivariana, Medellin, Colombia (2) Ingeniería, Universidad Pontificia Bolivariana, Medellín, Antioquia, Colombia (3) Universidad Pontificia Bolivariana, Medellin Antioquia, Colombia (4) New Materials Research Group, Pontificia Bolivariana University, Medellín, ANT, Colombia
Lycopene is the most efficient singlet oxygen quencher of carotenoids, with health benefits associated to its consumption. However, its low bioavailability limits its potential in food and nutraceutical applications. Also, it is mostly isolated from tomatoes, neglecting the potential of other sources, such as pink guava (*Psidium guajava L.*), in Colombia, this fruit is characterized by a low level of technification.

The aim of this investigation was to produce sunflower oil (SFO) enriched with lycopene from Colombian pink guavas (*Psidium guajava L.*) (PG) by means of a green method, allowing its use in the formulation of emulsions for nutraceutical and food applications. For this purpose, PG were characterized by several methods; proximate analysis for protein, fat, carbohydrate, ash, moisture, and vitamin C content were performed according to the methods described by the Association of Official Analytical Chemists. While Fourier-Transformed Infrared spectroscopy, optical microscopy and UV-vis spectroscopy were used to characterize lycopene present in pink guava. Subsequently, SFO was enriched with lycopene by a green method involving a two-step process. First, a homogeneous mixture of SFO and PG (1:1) was prepared using mechanical treatments, whether Waring blender or a sequence of Waring blender followed by an Ultraturrax process, to form a homogeneous mixture of SFO and PG paste. Second, the SFO enriched with lycopene was separated by centrifugation. Lycopene was extracted using a mixture of hexane, acetone and ethanol (2:1:1) for its quantification in both PG SFO mixture an in the SFO enriched with lycopene after centrifugation by means of UV-vis spectroscopy. Results showed that using vegetable oil as a solvent, increased the obtained lycopene concentration nearly 36 %, compared to an oil-free isolation. This is because lycopene has a greater chemical affinity with oil than with the mixture of hexane, acetone and ethanol. In addition, mechanical treatments favored the breakdown of the cell wall and therefore the release of lycopene. The mechanical treatment Waring blender/Ultraturrax increased lycopene concentration around 10 % respect to only using the Waring blender. While the combination of oil with Waring blender/Ultraturrax increased around 42 % the amount lycopene extracted. Therefore, the combination of mechanical treatments and SF allows a higher valorization of PG and allowing new raw materials for the food and nutraceutical industry.

**CELL 150**

**Functionalization of ethyl cellulose by hydroxyl-yne click chemistry**

Bowen Li, Juan Yu, yujuannjfu@njfu.edu.cn, Yimin Fan. Nanjing Forestry University, Nanjing, China

Hydroxyl group is one of the most important functional group in cellulose and cellulose derivative. Here, we reported a simple modification method based on hydroxyl-yne click chemistry to functionalize cellulose with novel properties. 1-Phenyl-2-propyn-1-one was attached onto the backbone of ethyl cellulose with the help of 4-dimethylaminopyridine (DMAP) under room temperature. The chemical structure of prepared ethyl cellulose phenyl propyl ketene ether (ECPPK) was confirmed by $^1$HNMR and FTIR which showed the existence of aromatic rings in ECPPK. Furthermore, the ECPPK film showed excellent UV-properties (range from 200–400 nm) and fluorescence properties under.
Figure 1. UV-visible transmittance of ECPPK film: insert photographs: ECPPK and EC films under white light and UV irradiation)

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Putting cellulose from bacteria and plants to work

Richard A. Gross¹, grossr@rpi.edu, Anna-Christina Amason¹, James F. Nowak², Johnson Samuel². (1) 4005B Biotechnology Bldg, Rensselaer Polytechnic Institute, Troy, New York, United States (2) Department of Mechanical Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States

The first part of this presentation will describe a general strategy for introducing remarkable changes in organization of the bacterial cellulose (BC) nanoscale 3-D matrix and, consequently, functional properties of bacterial cellulose (BC). We found that BC producing cells were induced by a well-defined atomized droplet nutrient delivery (ADND) system to form pellicles with a regular layered morphology that persists throughout the mat depth. In contrast, the morphology of mats formed by conventional static medium nutrient delivery (SMND) is irregular with no distinguishable pattern. We will also report on other details of the structures formed and the corresponding mat properties. The second topic will be on methods to prepare and modify cellulose nanocrystals (CNCs) from plant sources. A single step one-pot procedure that combines concurrent cellulose acid hydrolysis and organic acid catalyzed Fischer esterification was one approach used to build in a wide range of CNC surface functionalization. The
second approach focused on compatibilizing CNC's with PLA. Since PMMA and PLA are miscible in the melt, grafting of MMA from CNCs in aqueous media was carried out using ceric ammonium nitrate (CAN). By using CAN, a high grafting efficiency (77%) was achieved which increased the PMMA content on CNC surfaces. After PMMA grafting in water, modified CNCs are predispersed in a PMMA network. Miscibility between PMMA grafts and PLLA as well as the predispersion of CNCs played a key role in the dispersion of CNCs in PLLA and the formation of composites with an increase in the heat deflection temperature (HDT) from about 70°C to above 130 °C.

Proposed mechanisms for BC fibril formation in (A) SMND processing (dense, random morphology) and (B) ADND processing (porous, layered morphology).

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Cellulose-NaOH solutions: Influence of non-dissolved fibers on solution gelation and properties of all-cellulose composites

Oona Korhonen², Khaled Labidi²,³,⁴, Tatiana Budtova²,¹, Tatiana.Budtova@mines-paristech.fr. (1) CEMEF/Mines ParisTech, Sophia Antipolis, France (2) School of
The dissolution of cellulose in 6-9 wt% NaOH-water is known to be hampered by cellulose high molecular weight and concentration. These solutions are also geling with time and temperature increase. Incomplete dissolution leads to the presence of non-dissolved fibers or their fragments. How does the residual solid cellulose influence the gelation and the properties of materials prepared from such system? In this work, pulps from wood (birch) and alfa (Stipa tenacissima) were dissolved in 8 wt% NaOH-water. First, we studied the dissolution limit (residual solid cellulose content) of the dissolving pulp of various degree of polymerization. Then, the rheological properties of cellulose solutions in the presence of non-dissolved entities were investigated focusing on the gelation kinetics. Finally, all-cellulose composites were prepared using dissolved pulps as continuous phase and either softwood or alfa fibers as reinforcement. Morphology, density, crystallinity, cellulose I content and mechanical properties of the composites were studied and correlated with the presence of non-dissolved cellulose originating from the incomplete dissolution of the pulp.

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Sustainable polymers and fibers from lignin

Maria L. Auad, auad@auburn.edu, John Hinkle, Archana Bansode. Auburn University, Auburn, Alabama, United States

The exponential growth of the worldwide population requires increasing amounts of water, food, and energy, for this reason, technological solutions are required to secure sustainable supplied.

During this talk, I will discuss how the polymer industry is currently facing challenges in direct response to this reality and how researchers and scientists can respond developing sustainable engineering products, design energy-efficient processes, and develop efficient supply chain and enterprise.

I will organize my talk into two sections. In the first one, I will emphasized the current challenges in the industry and a few sustainable technological solutions that are becoming relevant. During the second part, I will discuss new opportunities in the bioenergy arena to produce sustainable chemicals and fibers from fast pyrolysis lignin based bio-oil and lignin.

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Segmentation and kink-formation mechanisms of TEMPO-oxidized cellulose fibrils during sonication in water to form TEMPO-CNCs

Yaxin Zhou, Akira Isogai, aisogai@mail.ecc.u-tokyo.ac.jp. Univ Tokyo, Tokyo, Japan
TEMPO-mediated oxidation of wood cellulose fibers under suitable conditions and subsequent mechanical disintegration of the oxidized cellulose fibers in water give versatile nanocelluloses, i.e., cellulose nanonetworks, nanofibers, and nanocrystals, depending on mechanical disintegration conditions. In particular, TEMPO-CNCs prepared from wood cellulose fiber were obtained from TEMPO-oxidized wood cellulose fiber and microcrystalline cellulose by sonication in water for 60-120 min. The TEMPO-CNCs prepared from wood cellulose fiber were obtained in high yields of >90%, and had needle-like morphologies, high sodium carboxylate contents of 1-1.7 mmol/g, homogeneous widths of ~3 nm, and aspect ratios of <100. When TEMPO-CNCs were prepared from microcrystalline cellulose, their yields and average widths were ~70% and 3-5 nm, respectively. These characteristics of TEMPO-CNCs are different from those of conventional CNCs prepared with 65% sulfuric acid. Changes in average lengths, widths, and molar masses of TEMPO-oxidized wood cellulose fiber and microcrystalline cellulose to TEMPO-CNCs were studied in terms of cavitation-induced segmentation and kink-formation mechanisms. CNCs prepared from wood cellulose fiber with 65% sulfuric acid at 70 degree C for 10 min followed by sonication in water (Acid-CNCs) were used as references. TEMPO-CNCs prepared from wood cellulose fiber decreased in average length from 290 to 220 nm as the sonication time was increased from 60 to 120 min, and correspondingly they decreased in weight-average molar mass (DPw) from 670 to 540. TEMPO-CNCs prepared from microcrystalline cellulose decreased in average length from 300 to 200 nm with sonication time from 10 to 120 min, but they have almost constant DPw values of 240-300 irrespective of sonication time. These differences between TEMPO-CNCs prepared from wood cellulose fiber and microcrystalline cellulose were hypothesized to be caused by distribution of disordered regions periodically present along the longitudinal direction of wood cellulose microfibril and aggregation behavior of cellulose microfibrils present in microcrystalline cellulose and Acid-CNCs formed during acid hydrolysis.

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Regio- and chemoselective synthesis of glycosaminoglycan analogs from simple precursors

Chengzhe Gao\textsuperscript{1}, Kevin J. Edgar\textsuperscript{2}, kjedgar@vt.edu. (1) Chemistry, Virginia Tech, Blacksburg, Virginia, United States (2) Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States

Glycosaminoglycans (GAGs) are perhaps the most complex polymers in nature, and are certainly among the most bioactive, crucial polymers in nature. Their interactions with proteins, in particular, drive a myriad of processes essential to vertebrate life, including blood clotting, development of the central nervous system, cell interactions and motility, and interactions with numerous pathogens. The associated interactions seem, at least in some cases, to be exquisitely specific and dependent on polysaccharide structure. However, due to the extreme complexity of GAG chemical synthesis (typically by lengthy, expensive, ultralow-yield total synthesis building from individual monosaccharides), the mechanisms of these interactions are poorly
understood. Even more challenging, though highly attractive, is the concept of being able to manipulate these interactions to address physiological malfunctions. We describe here methodologies for synthesis of complex GAG analogs from simple, inexpensive, readily available polysaccharide derivatives. The efficient methods developed have high regio- and chemoselectivity. These new probes should be valuable for interrogating mechanisms of the important protein-GAG interactions.

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Topochemical engineering of porous cellulose-based hybrid functional materials for applications in photocatalysis and skin tissue engineering

Pedro Fardim\textsuperscript{1,2}, pedro.fardim@kuleuven.be, Liji Sobhanadha\textsuperscript{2}, Giriprasath Ramanathan\textsuperscript{1,3}, Grace F. Jeyakumara\textsuperscript{3}, Vimala D. Mohana\textsuperscript{3}, Uma T. Sivagnanama\textsuperscript{2}. (1) Bio&Chemical Systems Technology, Reactor Engineering and Safety, Department of Chemical Engineering, KU Leuven, Leuven, Belgium (2) Laboratory of Fibre and Cellulose Technology, Abo Akademi University, Abo, Finland (3) Biological Materials Lab, CSIR-Central Leather Research Institute (CLRI), Chennai, India

Cellulose is a highly abundant biopolymer and cellulose-based hybrid materials have a great potential to boost new initiatives in bio-based economy. Porous cellulose materials such as bioaerogels and bilayered materials can be applied as support for bio- and photocatalysts and for wound healing applications. Topochemical engineering is a method to design fractionation (disassembly) and fabrication (assembly) of functional materials. In this work, we present topochemical fabrication of porous cellulose-based materials using hybridization with layered double hydroxides (LDH), bioactive latex, pharmaceuticals and collagen. We present the synthesis and characterization of hybrid aerogel microspheres containing NiFe-LDH for applications in heterogenous photocatalysis for esterification of cellulose fibre surfaces using grafting of ethyl acrylate. The reaction medium is water, the catalyst can be easily removed by filtration and the resulting functional fibre is hydrophobic. We also present the topochemical fabrication of a bilayer matrix by electrospinning of a biohybrid cellulose acetate nanofibres containing bioactive latex or Ciprofloxacin over highly interconnected collagen 3D matrix. The bilayer matrix exhibited nanofibrous and 3D porous structure with properties such as high porosity, swelling, and stability required by a biomaterial for desired soft tissue engineering applications. Furthermore, the \textit{in vitro} biological and fluorescence properties of the matrix were tested against NIH 3T3 fibroblast and Human keratinocyte (HaCaT) cell lines and showed good cell adhesion and proliferation over the bilayer matrix.

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Novel fully biobased polymers from hemicelluloses-derived building blocks

Nejib Kasmi\textsuperscript{1}, Rienier Dieden\textsuperscript{1}, Denielson Da Silva Perez\textsuperscript{2}, Youssef Habibi\textsuperscript{1}, Youssef.Habibi@list.lu. (1) Materials Research and Technology Department,
Hemicelluloses are considered as the most abundant family of plant-based polysaccharides after cellulose. This family has recently stood out as a highly promising source for the production of biobased chemicals. Wide range of downstream processes, including catalysis, chemoenzymatic processes, etc are being used to break down this attractive source into reactive building blocks. Polyols as well as diacids all are among the relevant examples of hemicelluloses-derived monomers that are prepared. These building blocks are mostly used for the synthesis of polymers such as polyesters, polyurethanes, polycarbonates etc.

The present work deals with successful synthesis of new fully biobased polyesters and non-isocyanates polyurethanes using building blocks derived from hemicellulose sugars. The structural features were confirmed by 1H NMR and FTIR spectroscopies and ToF-MS and their thermal properties were investigated by DSC and TGA. This oral presentation will spotlight our findings.

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Biointeractive cellulose based nanomaterials with antibacterial properties

Monica K. Ek¹, monicaek@kth.se, Jonatan Henschen³, Josefin Illergard², Dongfang K. Li⁴, Lars Wagberg². (1) Fibre and Polymer Technology, KTH, Stockholm, Sweden (2) Fiber and Polymer Technology, KTH, Stockholm, Sweden (3) Finecell Sweden AB, Stockholm, Sweden

Nanocellulose is a material which can be extracted from wood, with interesting properties and wide range of possible applications. A novel method to produce nanocellulose as well as the possibility of using polyelectrolyte adsorption to alter the interaction with bacteria of nanocellulose based materials will be presented. Nanocellulose can be produced by a novel concurrent esterification and hydrolysis of wood pulp fibers in molten oxalic acid dihydrate. The resulting mixture can then be fibrillated to nanocellulose. The resulting nanocellulose obtained with a high yield had a high surface charge, and contained particles with a morphology similar to both cellulose nanocrystals and cellulose nanofibrils. The material was used to prepare both Pickering emulsions and thin films.

To investigate the antimicrobial effect of different nanocellulose-based materials, i.e. films and aerogels were treated with environmentally friendly alternatives to traditional biocides to prevent microbial growth. By using the multilayer technique, i.e. altering the surface charge of the material, by polyelectrolyte adsorption of polyvinyl amine and polyacrylic acid it is possible to modify cellulose based materials. and to prepare materials with both high and low bacterial adhesion as well as materials with either contact active or non-adhesive antibacterial properties, both of which are sustainable alternatives to the currently used antibacterial materials. Nanocellulose is a material which in the near future will probably be used in a wide range of applications. In order to improve the usability of nanocelluloses it will be necessary to use novel production
methods. By modifying the bacterial adhesion to materials prepared from nanocellulose, many new medical and health applications emerge.

**CELL 159**

*Surface modified cellulose nanocrystals: Investigating cellulose in electronics*

**Allen Chang**, allenchang@umass.edu, **Kenneth R. Carter**. Polymer Science and Engineering, UMass Amherst, Amherst, Massachusetts, United States

Cellulose nanocrystals (CNCs) are surface modified to allow for cross coupling grafting of conjugated polymers. Conjugated polyfluorenes are coupled to surface active sites via Yamamoto chemistry, thus imparting some semiconducting properties in the inherently electrically inactive cellulosic material. With graft lengths well within the effective conjugation length ($6 < n < 22$, $M_w \sim 4500$ Da), it is expected that the grafted polymers are able to exhibit electrical functionality. The overall polymer loading is shown to be about 15 wt% of the composite material. As we fabricate devices with these composite CNC/polymer active layer materials, short circuiting becomes a challenge due to the non-uniform film processing of these composite materials. Early turn-on voltages (< 4 V) and high current flows (~ 500 mA) can be attributed to electrodes directly contacting each other through a conductive pathway. By changing the architecture of the active layer, we demonstrate that the presence of CNCs do not absolutely disrupt the emission of light from emissive polymers. Furthermore, we combat the short circuiting phenomenon by employing extra transport layers. The resulting device demonstrates emission from the polymers grafted from the surfaces of CNCs.

**CELL 160**

*Directed cellulose nanocrystal supramolecular functionalization*

**Emilie Ressouche**

1. emilie.ressouche@aalto.fi, **Johanna Majoinen**

2. **Marco Beaumont**

3. **Samuel Girmay**

4. **Jarkko Etula**

5. **Blaise Tardy**

6. **Olli T. Ikkala**

7. **Orlando Rojas**

(1) Department of Applied Physics, Aalto University, Espoo, Finland (2) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (3) Department of Chemistry and Materials Science, Aalto University, Espoo, Finland

Cellulose nanocrystals (CNC) are getting a spreading interest in material science, due to their renewable origin, their optical properties in suspensions and in films, and their outstanding mechanical properties at the nanocrystal scale. Due to the multiple hydroxyl groups at the surface of CNCs, their modification has been extensively developed, in order to improve their colloidal stability, their compatibility in hydrophobic media, or their surface properties and reactivity towards further modifications. More recently, the surface of CNCs has been modified with supramolecular Ureidopyrimidinone (UPy) groups, resulting in light-healable composite materials. End-functionalization of CNC remains however more subtle and delicate, and
requires specific chemical reactions to the reducing end carbonyl functional groups. Moreover, the characterization of end-functionalized CNCs remains tedious, due to the low proportion of end groups compared to surface hydroxyl moieties. So far, few studies report successful and effective end-functionalization of CNCs, with accurate characterization techniques, leading to all-cellulose materials. Herein we present selective functionalization of cellulose nanocrystal reducing ends by UPy. CNC functionalization occurred in 3 steps, in order to promote the grafting of UPy selectively at the reducing ends. UPy modified CNCs can demonstrate unique material properties with controlled supramolecular interactions.

**CELL 161**

**Relationship between morphology, elasticity, and conductivity of cellulose-silk biocomposites fabricated from ionic liquids and various coagulation agents**

*Bailey Blessing*¹, bvb9@camden.rutgers.edu, Cory Trout², Karleena Rybacki³, Abneris Morales⁴, Stacy Love⁵, Sean M. O'Malley², Xiao Hu⁵, David Salas-de la Cruz⁶. (1) Chemistry, Rutgers University Camden, Camden, New Jersey, United States (2) Physics, Rutgers University Camden, Camden, New Jersey, United States (3) Rutgers University, Camden, New Jersey, United States (4) Rutgers University, Camden, New Jersey, United States (5) Physics and Astronomy, Rowan University, Glassboro, New Jersey, United States (6) Chemistry, Rutgers University, Philadelphia, Pennsylvania, United States

The study of biomaterials includes aspects of medicine, biology, chemistry, engineering, environmental science and materials science. Biomaterials are likely to revolutionize modern materials science, yet there are still many open questions regarding their processability and our ability to predict their properties, especially for materials made from multiple biopolymer components. The focus of this research is to understand the interactions between Avicel cellulose and *Bombyx mori* silk biocomposites, and how these interactions affect the cellulose crystallite formation and protein secondary structures, which directly affect ionic conductivity. Various characterization methods were employed to study the morphological, thermal, and mechanical properties of the biocomposite films including Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), X-Ray Scattering, Dielectric Relaxation Spectroscopy (DRS), and Atomic Force Microscopy (AFM). With systematic variation of the cellulose/silk percent ratio, ionic liquid type and coagulation agent, we provided evidence to suggest a direct relationship between morphology and ionic conductivity. In particular, the results show that the ionic conductivity is dependent on material content, cellulose crystallinity and protein beta sheet content.

**CELL 162**

**Organic inkjet-printed devices on conductive nanopaper**
Organic electronics is proving to be a suitable technology for the fabrication of electronic devices on conformable, flexible and transparent substrates, presently relying on plastic substrates. In this context, the growing production volume of flexible electronic devices and the very slow degradation of plastics is expecting to lead the near future on the use of more environmental substrates which should be bio-based and biodegradable. Cellulose-based green electronics is a novel platform with unique virtues including easy recycling/disposal and cost efficiency. Derived from abundant and renewable raw materials, and thanks to their outstanding physico-chemical and mechanical properties, cellulose nanofibers (CNFs) are rapidly emerging as one of the most promising future components for the production of sustainable, biodegradable, and eco-friendly electronics. Their combination with conductive polymers to obtain conductive nanopapers allows moving their functionality from substrates to active components of the device.

In this work, a route for the inkjet-printing of organic diodes is outlined. The proposed strategy is based on the use of conductive nanopapers as both substrates and bottom electrodes onto which insulator and organic semiconducting layers are deposited to fabricate novel diode structures. A leaky dielectric between the electrode and the semiconductor is responsible for the creation of an energy barrier that allows the current to flow just in one direction and gives the asymmetric current-voltage characteristic typical of a diode. Different combinations of CNPs and insulating polymers have been tested. Rectification ratios of up to 1.2*10^3 at |3 V| and a current density up to approximately 6.5 µAcm^2 were recorded. Finally, an NO_2 gas sensor based on the diode is presented as a proof-of-concept of the potentiality of our approach for versatile, low-temperature, and disposable sensing applications.
Modification of cellulose surfaces through strongly adsorbed polymer layers: Way to cellulose hydrophobization

Wenyang Xu¹, wxu@abo.fi, Oliver Werzer², Roland Resel³, Torbjorn Pettersson⁴, Eero Kontturi⁵, eero.kontturi@aalto.fi. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Department of Pharmaceutical Technology, University of Graz, Graz, Austria (3) Institute of Solid State Physics, Graz University of Technology, Graz, Austria (4) Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Surface modification is a fundamental necessity regarding material applications concerning cellulose. Surface modification by chemical reactions has suffered from accessibility issues, harsh reaction conditions and poor control over the substitution.[1]
A preliminary work[2] demonstrated that the surface of cellulose nanopapers could be exclusively modified by facile adsorption of hydrophobic polymers from aprotic solvents, thereby omitting chemical reactions. However, the surface coverages were fairly meagre and the adsorbed layers were weakly attached. In the present study, a surface adsorption from a molten state of polymer on a cellulose surface was established, inducing the formation of a strongly adsorbed polymer layer, i.e., a so-called Guiselin layer.[3] As a proof-of-concept, a steady Guiselin layer of polystyrene (PS) was studied on the model films of cellulose. A thicker film of PS was coated on cellulose, followed by annealing above the glass transition temperature, which induced a strongly adsorbed Guiselin layer of PS on cellulose. A subsequent leaching of the excess polymer by a good solvent finalized the procedure. As a result, a polystyrene film with nanoscale dimensions was irreversibly adsorbed on cellulose changing the physio-chemical properties of the cellulose surface into a hydrophobic exterior. Moreover, this method supplies a new route for surface modification of lignocellulosic materials with direct polymer melt coating, beneficial for developing functionalities in lignocellulosic materials.

CELL 164

Characterization of nanopaper capacitors and humidity sensors for green sensor networks

Takaaki Kasuga, tkasuga@eco.sanken.osaka-u.ac.jp, Hitomi Yagyu, Kojiro Uetani, Hirotaka Koga, Masaya Nogi. ISIR, Osaka University, Osaka, Japan

Wireless sensor networks composed of internet of things (IoT) devices are beginning to play a key role in a wide range of areas, including urban management, food production, and climate forecasting. In the era of mass production and mass consumption of sensor devices, there is a need for biodegradable sensor devices. Nanopaper fabricated by drying of a water dispersion of cellulose nanofiber is a promising substrate for the biodegradable electronic devices thanks to the high surface smoothness, heat resistance, flexibility, high dielectric constant, and biodegradability. In this study, a nanopaper sensor device that combines humidity sensing, wireless information transmission, and degradability has been fabricated using wood-derived nanopaper as the substrate and dielectric layers. The nanopaper shows excellent suitability for capacitor dielectric layers due to its high dielectric constant, insulating and lamination properties. Nanopaper capacitor shows not only high-performance dielectric layers for capacitors but also suitability as humidity sensors. A wireless transmission circuit consists of the nanopaper capacitor, printed Ag conductive lines, and chip transistor can transmit radio signals in the megahertz band, and the relative humidity change can be output as a change in the radio signal owing to the humidity sensitivity of the nanopaper capacitor. In addition, it was confirmed that more than 95% of the total volume of the nanopaper sensor device degraded in soil after 40 days. Our results show that nanopaper sensor device has the potential to the realization of the green sensor networks.
Fully biodegradable nanogenerators based on functional nanocellulose

zhijun shi, shizhijun@hust.edu.cn, Guang Yang. College of Life Science Technology, Huazhong University of Science Technology, Wuhan Hubei, China

Nanocellulose has gained a lot of attention for applications in biomedical and functional energy related field because they are abundant, lightweight, biodegradable and biocompatible. Herein, we present a series of fully biodegradable nanogenerators based on functional nanocellulose hydrogel, fibers and membrane. The mechanism of electricity production involved triboelectric, electromagnetic and so on. The nanocellulose based nanogenerators showed excellent mechanical stability and electricity generate performance. Biodegradation experiments show that all the nanocellulose based nanogenerators could be degraded completely into water in two months, and can be degraded completely by cellulase in four hours. The nanocellulose based nanogenerators provide promising green wearable and implantable devices for body monitoring, energy harvesting et al., and meanwhile, can be dissolve with no adverse effect to environment.
Uncover the circular polarization potentials of cellulose nanocrystals

Jiawei Tao¹, Wei Fan¹, Ziyi Zhao¹, Di Lu¹, Yan Xu², yanxu@jlu.edu.cn. (1) State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, China (2) Chemistry, Jilin University, Changchun, Jilin, China

Circularly polarized light is central to information technology. A key challenge lies on developing a general route for circularly polarized light generation with tailorable chiroptical activity using sustainable materials suitable for scale-up. This study describes the intrinsic circular polarization ability of cellulose nanocrystal-based films leading to photonic bandgap-based selective reflection and transmission of circularly polarized light, and selective transmission of circularly polarized luminescence of specific handedness. Such circular polarization ability can be manipulated by meso-structure change. The potential of cellulose nanocrystal-based chiral photonic films for optical encryption and anti-counterfeit labels is illustrated. The evaporation-induced self-assembly coupled with renewable cellulose nanocrystals opens new venues for technological advances and enables a powerful approach for circularly polarized materials development.

Polymer-assisted modulation of photonic bandgap in cellulose nanocrystal nanocomposite towards adaptive materials

Jiaqi Guo¹,²,³, xinshangren8687@hotmail.com, Claas-Hendrik Stamp¹, Dejin Jiao¹,²,³, Guido Creusen¹,²,³, Daniel Hoenders¹,²,³, Andreas Walther¹,²,³. (1) Institute for Macromolecular Chemistry, Freiburg University, Freiburg, Germany (2) Freiburg Materials Research Center, Freiburg University, Freiburg 79104, Germany (3) Freiburg Center for Interactive Materials and Bioinspired Technologies, Freiburg University, Freiburg, Germany

Cellulose nanocrystals (CNCs), typically isolated by strong sulfuric acid hydrolysis of lignocellulosic biomass, are renewable, sustainable nanomaterials. CNCs are self-twisted, highly crystalline, rod-shaped with the dimension of 5-30 nm in diameter and 100-300 nm in length. CNCs have a fascinating property that they can organize in aqueous suspension at a critical concentration into chiral nematic liquid crystals. The resulting chiral nematic structure forms a layered structure during drying into a thin solid film. The cholesteric order with helical dimensions in the visible wavelength leads to a photonic band gap (PBG) in the visible region and can act as a 1-D photonic structure. In this communication, Inspired by nature, we develop a facile, waterborne self-assembly pathway to mimic the multiscale cuticle structure of the crustacean armor by
combining cellulose nanocrystals (CNCs) with various soft polymers (synthetic linear polymer, synthetic star polymer, biopolymer). We will present iridescent CNC nanocomposites with cholesteric liquid-crystal structure, in which different helical pitches and PBGs can be realized by varying the CNC/polymer ratio. After this deep understanding, we will show the adaptivity of such bioinspired CNC nanocomposites, which triggered via external stimuli including humidity, salt solution or electrical field. Our developed CNC nanocomposites would open avenues toward combining photonic properties, multilayer structures, and mechanical robustness. This will be important for developing CNC-based photonic devices and for targeting advanced, high-performance, bioinspired and ordered nanocomposites based on renewable CNCs.

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Optical materials based on cholesteric liquid crystals of cellulose nanocrystals

Yuanyuan Cao¹,², yuanyuan.cao@qmi.ubc.ca, Mark J. Maclachlan¹,². (1) Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver, British Columbia, Canada (2) Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada

Hierarchical structured materials are ubiquitous in nature (e.g. bone, silk and wood). These remarkable self-organized structures exhibit a high degree of sophistication with excellent properties optimized by millions of years of evolution, making them great targets for materials chemists. Among them, the Bouligand structure, which is a continuously twisting lamellar structure found in various kinds of plants, crab shells and insects, endows creatures with iridescent colors due to its specific circular polarized light reflection property. Cellulose nanocrystals (CNCs) are a highly crystalline form of cellulose. Above a critical concentration, CNCs self-assemble into the cholesteric liquid crystal, which shows an analogous supramolecular structure and similar optical properties to the Bouligand structure. Therefore, artificial materials constructed from CNC liquid crystals will provide a feasible route to mimic Bouligand structures, producing materials with diverse optical properties.

We have explored the unique optical properties of CNC assemblies and their applications as smart devices. We have discovered a new micelle-assisted self-assembly strategy to prepare freestanding films of CNCs that display circularly polarized reflection across the visible spectrum. This simple approach distorts the chiral nematic domains of CNCs with variations of helical pitch and orientation, leading to broadband polarization. Furthermore, a novel pressure responsive chiral photonic aerogel using CNCs was designed. This aerogel exhibits color change from scattering white to photonic iridescent under pressure due to the structural transition from a porous aerogel to a planar film. Benefitting from the color variation mechanism of the aerogel, a CNC-based solvent-sensitive ink that shows quick color response to different solvents was further produced. These materials could be important components in further applications such as sensors, probes and other artificial detectors.
Optical consequences of distortions in cellulose nanocrystal films

Bruno Frka-Petesic, bf284@cam.ac.uk, Gen Kamita, Giulia Guidetti, Silvia Vignolini. Chemistry, University of Cambridge, Cambridge, United Kingdom

Cellulose nanocrystals (CNCs) are chiral colloidal nanorods able to spontaneously self-assemble into a cholesteric phase above a critical concentration. Dish-casting the suspension allows forming solid films that retain the cholesteric order, enabling the left-circular polarized reflection of specific wavelengths typically in the visible range. The vertical compression of the sample experienced upon drying can induce important distortions and thus strongly influence the final structure of the film and its optical response.[1]

In this talk, we present a simple affine deformation model of the vertical contraction of the cholesteric domains, from the kinetic arrest till complete solvent evaporation, which allows us to predict some structural and optical consequences in the films.[2,3] At the individual domain scale, a shear distortion of the cholesteric order is predicted in tilted domains. Using a Fourier analysis we show that this must lead to the generation of higher order diffraction peaks and the reflection of right-circular polarized light (RCP) in addition to the expected left-circular polarized light (LCP). Experimental observations were performed using SEM, polarized optical microscopy and angular-resolved optical spectroscopy and all support our structural and optical predictions.
Rationalising the cholesteric phase of cellulose nanocrystals in terms of entropic effects

Massimiliano Chiappini¹, m.chiappini@uu.nl, Simone Dussi², Bruno Frka-Petesic³, Silvia Vignolini⁴, Marjolein Dijkstra¹. (1) Utrecht University, Utrecht, Netherlands (2) Wageningen University, Wageningen, Netherlands (3) Chemistry, University of Cambridge, Cambridge, United Kingdom (4) Cambridge University, Cambridge, United Kingdom

The origin of the cholesteric phase of cellulose nanocrystals (CNCs) is still a matter of debate in the liquid crystal community. The identification of the fundamental ingredients responsible for chiral symmetry breaking in these systems is hindered by uncertainties on the microscopic details of CNCs, usually dependent on their biological source, extraction method and processing. As a consequence, the subtle interplay of various agents, including steric and Coulombic interactions, has not yet been elucidated. We explore the possibility that the cholesteric phase of CNCs could be rationalised in terms of entropic effects alone. We focus on cotton-based CNCs and develop a simple hard-particle model on the basis of novel electron microscopy images and recent all-atoms molecular dynamics simulations. To investigate the effect of thermodynamic and microscopic parameters on the stability and macroscopic properties of cholesteric phases of CNCs, we employ density functional theory calculations and Monte Carlo simulations.

We find that our simple model for CNCs stabilises the cholesteric phase with a pitch length well within the range of experimentally measured values. Our findings show that the effect of surface charge of cotton-based CNCs can be captured in terms of an effective particle shape, and thus that the cholesteric phase of CNCs can be rationalised in terms of entropic effects alone.
Cellulose derivatives and nanocrystals and their liquid crystalline properties: exploitation for engineering materials

Susete N. Fernandes¹, sm.fernandes@fct.unl.pt, Paul Grey¹,², Diogo V. Saraiva¹, Ricardo Chagas¹, Pedro L. Almeida¹,³, Pedro E. Silva¹, Luis Pereira¹,², Maria H. Godinho¹. (1) i3N/CENIMAT, Department of Materials Science, NOVA School of Science and Technology, NOVA University of Lisbon, 2829-516 Caparica, Portugal (2) CEMOP-UNINOVA, 2829-516 Caparica, Portugal (3) Área Departamental de Física, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, 1959-007 Lisboa, Portugal

Cellulose, the most abundant naturally-occurring polymer, can be found in plants in the form of a bundle of nanofibrils, where elongated crystalline domains are parted from disordered regions. If one removes the disordered regions by acid hydrolysis, cellulose nanocrystals (CNCs) are obtained. In the form of stable aqueous suspension, cellulose nanocrystals self-assemble into a liquid crystalline (LC) phase giving rise to structures with tuneable structural coloration and originate an array of biomimetic materials. The chemical versatility of cellulose also leads to a well-known variety of derivatives that can originate LC phases. This feature will impart distinct and interesting properties to the final product but is less exploited in the production of new materials. In this small overview, the use of cellulose nanocrystals and cellulose derivatives on engineering materials are shown in which LC properties have an important role. For instance, all-cellulosic composite systems of hydroxipropylcellulose and CNCs can give rise to biomimetic diffraction gratings with anisotropic mechanical properties and the same cellulose derivative can be used to produce a cellulose liquid crystal motor. Multi-photoresponsive surfaces with opposite wettability can be produced from the thermotropic cellulose derivative acetoxypropylcellulose. While films obtained from an isotropic suspension of CNC can be used as gate dielectric and substrate on field effect transistors, if originated from the LC suspension, the structurally colored films can be used as micrometric circularly polarized light sensors. If these colorful films present microgaps in its cross-section and are infiltrated with a nematic liquid crystal a system capable of presenting tunable reflection of left- and right-handed circularly polarized light is achieved. These examples can open new horizons for the application of these renewable materials.

Understanding the structural diversity in chitins as a versatile template for optical biomimetics
Adrian Pui Ting Ho\textsuperscript{1}, Mustafa Emre Karacar\textsuperscript{2}, Berk Emre Aydemir\textsuperscript{2}, Ahu G. Dumanli\textsuperscript{1}, agd33@cam.ac.uk. (1) Department of Materials, University of Manchester, Manchester, United Kingdom (2) Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey

Chitin is the 2nd most abundant biopolymer, produced by crustacean, insects, and fungi. With such diverse occurrence in nature, chitin assembled in many different nanostructures that leads to a number of striking optical effects such as antireflective arrays \cite{1} in some insects and photonic bandgap structures that give rise to strong iridescence in beetles \cite{2} and some fungi \cite{3} or even gyroid structures in some butterflies \cite{4}.

We are interested to understand the helicoidal organization of chitin and studied \textit{Penaeus setiferus} (King Prawn/Shrimp) which conforms into a chiral nematic structure with variable pitch values between 200 nm and a few microns. \textit{P.setiferus} uses such helicoidal structure mainly to form a strong mechanical network as a part of the exoskeleton and the optical appearance of the shrimp seems to do not reveal the interesting chiral optics. However, when the proteins and Ca-minerals were removed from the shrimp exoskeleton, the residual chitin show quite remarkable iridescent appearance with strong circular polarization, Fig1. This helicoidal framework is highly porous and provides an exciting template for exploring chiral photonics using different deposition methods. With the goal of transferring this intricate network, the iridescent chitin shell is used in this study to decorate with Au nanoparticles using wet chemical methods. Our studies show that the helicoidal organization of the iridescent shrimp shells can be conformed and transferred into higher refractive index materials with a distinctive macroscopic combination of optical effects that causing circular dichroism. The interplay between the plasmonic states of Au and the chiral photonic structure of shrimp shell is characterized using optical microscopy, UV-Vis-NIR visible spectroscopy, and high-resolution SEM and TEM techniques.

![Image of shrimp shells with LCP and RCP polarization](image-url)
Fig 1. Optical microscope image of the photonic chitin film obtained after removal of proteins and calcium minerals from *Penaeus setiferus*, in left handed circular polarization (LCP) and Right handed circular polarization (RCP)

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Cellulose building blocks design for scattering engineering

*Han Yang*, hy342@cam.ac.uk, *Gianni Jacucci*, *Silvia Vignolini*. University of Cambridge, Cambridge, United Kingdom

Inspired by the optimised performances of the random networks found in *Cyphochilus* beetles, here we developed highly scattering materials using only cellulose. Extremely short scattering mean free path about 1.2 μm can be achieved in the fabricated films by optimizing the dimension of rod-shaped cellulose nanoparticles (CNPs) as cellulose building blocks and adjusting porosity via modifying the filtration and freeze-drying conditions. Our developed materials reproduce with high fidelity the 3D disordered nanostructures network of the white beetles (Figure 1). By adjusting the dimension and filling fraction of the CNPs, a typical biomimetic 9 μm cellulose based film exhibits a reflectance of 75-82% in the entire of visible range. Additionally, our developed CNPs can be directly used as highly scattering elements as colour enhancers. The biorenewable and biocompatible characters of the system combined with its good mechanical properties, allow the use of our highly scattering material for applications in paints, LEDs and solar cell devices, but also in food and pharmaceutical with minimal impact on the environment and human health.

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Saccharide autofluorescence: Its origins and applications

*Marcus Johns*, marcus.johns@bristol.ac.uk, *Stephen J. Eichhorn*. Aerospace Engineering, University of Bristol, Bristol, United Kingdom

Saccharides are ubiquitous in nature with a variety of applications including structural components (cellulose and chitin); energy storage (starch and glycogen); the immune system (antigens); and modulating cell responses (glycosaminoglycans). This has led to their exploitation in various areas including drug delivery; rheology modifiers; bioplastics and composites; and tissue engineering scaffolds. For the latter application, various research groups have reported problems with background autofluorescence despite saccharides lacking conventional chemical groups associated with fluorescent emission. Current theories for this attribute it to clustering triggered, or aggregate induced, emission whereby intermolecular interaction between saccharide chains stabilises the overlap of free electron pairs associated with oxygen present in the polymer. This enables efficient n→π* transitions, resulting in autofluorescence under UV excitation.
Here we use multi-channel spectral confocal microscopy to demonstrate that cellulose nanomaterials fluoresce upon gelation. This enables their use as model systems to probe the impact of hydrogen bonding, known to induce hypsochromic shifts in n $\rightarrow \pi^*$ systems, by variation of the gel pH. We also confirm that modification of the cellulose nanomaterial surface chemistry affects the fluorescent spectra, Figure 1.a). In addition, we take advantage of the autofluorescent properties of saccharides to probe a variety of applications, including dispersion of polysaccharides in composites, Figure 1.b).

Figure 1. a) Fluorescent spectra for cellulose nanomaterials with different surface modifications. b) Fluorescent map of octadecylamine modified cellulose microfibrils dispersed in polypropylene–polyethylene matrix.

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Synthesis of biobased building blocks from eugenol: Chemical platform approach for polymer synthesis

Sylvain Caillol, sylvain.caillol@enscm.fr. Institut Charles Gerhardt, Montpellier, France

We propose a platform approach for the synthesis of various building blocks from eugenol in one or two-steps syntheses. Eugenol, which is a natural phenol, is issued either from clove oil or lignin. Eugenol is non-toxic, exhibits anti-bacterial properties and is particularly suitable for the addition of aromatic renewable resources in polymers and materials. Various routes were used for the synthesis of di- and poly-functional building blocks used thereafter in polymer syntheses. Epoxidation was used to obtain both polyepoxide networks and flame-retardants additives. Alder-Ene reaction was used to obtain high thermally stable aromatic networks. Various (meth)acrylate monomers we
also synthesized for radical aqueous emulsion polymerization. Reactive latex were obtained.

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Renewable, tunable polymers from lignin and 5-hydroxymethylfurfural

Thomas J. Schwartz\(^{1,2}\), thomas.schwartz@maine.edu. (1) Chemical and Biomedical Engineering, University of Maine, Orono, Maine, United States (2) Forest Bioproducts Research Institute, University of Maine, Orono, Maine, United States

Modern petroleum-derived polymers have found extensive use as thermoplastic engineering materials, but their synthesis and disposal remains environmentally challenging. Moreover, the shale gas boom has put pressure on the markets for appropriate monomer feedstocks. Consequently, biobased polymers have been targeted as replacements by utilizing biomass-derived, renewable feedstocks. An added benefit to this approach is that the final products are often degradable, leading to decreases in landfilled waste. However, only poly(lactic acid) (PLA) has yet found broad commercial success as a thermoplastic. PLA has mostly been used in the disposable packaging market because it is similar in certain respects to polystyrene and
polyethylene terephthalate. It has not found broader acceptance because its chemical structure yields a low glass transition temperature ($T_g$) of only 60 °C, and it is susceptible to hydrolytic degradation.

In this work, we demonstrate the production of an alternative polymer with tunable functionality, opening the door to a class of materials that share polymerization chemistry but lead to a range of physical properties. 5-hydroxymethylfurfural (HMF), obtained from cellulose dehydration, is used as a platform chemical which can be coupled with phenols obtained via lignin pyrolysis. The HMF undergoes etherification with the phenols, and the phenolic side chain is retained in the final polymer. The HMF-ether is then rearranged to yield a delta-hexalactone functionalized with the same pendant group as was present on the HMF ether. This functionalized lactone is subjected to ring-opening transesterification polymerization, leading to materials with $T_g$ that depend on the identity of the side chain and should be degradable according to the same enzymatic mechanisms that lead to PLA degradation.

**CELL 177**

**Green process for the direct functionalization of lignin for use in thermosets**

Dean C. Webster, dean.webster@ndsu.edu, Eric Krall, Alexander Hart. Dept 2760, North Dakota State University, Fargo, North Dakota, United States

While lignin is the most abundant aromatic biopolymer, effectively using lignin in materials has proven challenging. Approaches to degrade lignin into small molecules usually leads to a mixture of many compounds that are difficult to separate with no single compound in high yield. Partial degradation of lignin can convert solid lignin to a liquid material can be carried out, but it may be challenging to obtain reproducible distributions of oligomers. Functionalization of lignin has been carried out to introduce functional groups that can be used in curing reactions to form thermosets, however, solvents are usually used to dissolve the lignin which then have to be removed, creating waste. We have discovered a process for functionalizing lignin that involves dissolving the lignin into diluent molecules that contain hydroxyl groups and then functionalizing the mixture of lignin and diluent, resulting in a mixture of functionalized lignin and functionalized diluent. Solvent does not have to be removed in the process and the mixture can be used directly to form thermosets. Diluents such as glycerol, 1,4-butanediol and 1,3-propanediol have been explored. Functional groups explored have included methacrylate and acetoacetate and thermosets have been made by curing with these functional groups. This approach provides a novel way of utilizing lignin directly in the preparation of thermoset materials.

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**Advanced chemical modification of lignin fractions: Towards new bio-based thermosets**
Iuliana Ribca\textsuperscript{3,2}, ribca@kth.se, Marcus Jawerth\textsuperscript{3,2}, Martin Lawoko\textsuperscript{1,2}, Mats K. Johansson\textsuperscript{3,2}. (1) Fibre and Polymer Technology (FPT), KTH Royal Insitute of Technology, Jakobsberg, Järfälla, Sweden (2) WWSC Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden (3) Fibre and Polymer Technology, Division of Coating Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Lignin is the third main component of biomass with unique structure and complex reactivity. The characteristic aromatic structure of lignin represents a potential environmentally friendly alternative for replacing petrochemical-based feedstocks. However, the heterogeneity and polydispersity combined with batch variations of technical lignin limits its utilization in high-value applications where precise molecular size, composition and functionality are required. A promising, sustainable and simple approach, a solvent fractionation developed in our lab, was used for improving homogeneity and purity of lignin for further chemical modification. This work is focused on the design of reaction protocols to form bio-based thermoset resin structures. The ethanol soluble fractions were chemically modified by adding an allyl ether functionality, selectively on phenolic hydroxyls group. The content of free phenolic hydroxyl groups is an important factor in lignin functionalization. Consequently, the allylated lignin was thermally cured through thiol-ene reaction. The different polyfunctional linkers: bi-, tri- and tetra-functional aliphatic thiols was selected to cure the modified lignin. The effect of different crosslinkers on the final mechanical properties and morphological structure of thermosets was investigated to reveal details on the structure-property relations for these systems.

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Lignin-based epoxy-resins: understanding the influence of Lignin homo cross-linking during amination reaction to control final elastic properties of the bio-hybrid material

Markus A. Biesalski, biesalski@tu-darmstadt.de, Simon Trosien. TU Darmstadt, Darmstadt, Germany

Replacing petrochemicals by sustainable feedstocks is becoming more and more of general interest for a growing market biogenic plastics. Although a number of interesting demonstrators with respect of using Lignin as a biogenic source already exist, taking a closer look, still a number of challenges exist which need to be addressed in order to place in particular this polymer into real-life applications. One way is to use Lignin in epoxy-resins, however, reactivity of crude lignin in such resins is limited and so are the mechano-elastic properties. To improve the reactivity of lignin, the introduction of amines via Mannich reaction is a commonly used strategy. During this functionalization reaction, intra- as well as intermolecular lignin-lignin crosslinking occurs, which can vastly change the elastic properties of the lignin, and therefore, the properties of the resulting polymeric resin. Therefore, the molecular structure of the amine that is used for such a lignin functionalization may be of great importance. However, the relationship
between the molecular structure of the amine and the elastic properties of the lignin-
based polymer that is generated thereof, has not been investigated in detail. We
investigated this relationship and found that the molecular flexibility of the amines plays
a predominant role: i.e., the use of more flexible amines results in more elastic resins
and the use of less flexible amines gives more rigid ones. In addition to the macroscopic
analysis of the materials by 3-point flexural tests, the elastic modules of the resins were
determined spatially resolved by AFM. Thus, we could demonstrate that the intrinsic
elasticities of the lignin domains are the main reason for this tendency, and our findings
may be useful for a successful design and control of the mechanical properties of Lignin
based epoxy-resins.

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Developing 100% bio based epoxy resin using lignin as bisphenol-A replacement

Saeid Nikafshar, Jiarun Wang, Mojgan Nejad, nejad@msu.edu. Forestry, Michigan State University, East Lansing, Michigan, United States

Lignin has been considered as bisphenol-A replacement by number of studies during
the last three decades. In this study, we developed two different methods to reliably
measure the reactivity of sixteen different technical lignins with a biobased
epichlorohydrin (ECH) and tried to understand how lignin properties can affect its
reaction with ECH. First, we characterized lignin samples by measuring their physical,
chemical and thermal properties using advanced analytical techniques such as 31P NMR, DSC, TGA, GPC and ICP. Then we used a modified version of ASTM D1652 to
determine the amount of unreacted ECH (or epoxy content) with an auto-titrator and H NMR. One of the major problems was insolubility of epoxidized-lignin in most organic
solvents commonly used for titration and NMR analysis (dichloromethane and DMSO respectively). We were able to solve this issue by using DMF as solvent to dissolve
lignin initially and using design of experiment to properly optimize the reaction
parameters to ensure the solubility of epoxidized lignins in these two solvents. Then the
epoxidized lignin made with biobased epichlorohydrin were used along with a biobased
hardener (Cardolite NX-2003) to formulate a biobased epoxy resin for coating
application. Our preliminary results showed that the developed resins had strong
adhesion to metals.

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Synthesis and characterization of a thermosetting epoxy resin from lignin
derivatives

Kelli Hambleton1, hambletok3@students.rowan.edu, Joseph F. Stanzione2, John J. LaScala3. (1) Chemical Engineering, Rowan University, Turnersville, New Jersey,
United States (2) Department of Chemical Engineering, Rowan University, Glassboro,
New Jersey, United States (3) Army Research Laboratory, Aberdeen Proving Ground,
Maryland, United States
Bisphenol-A (BPA) has been extensively used for decades in plastics. However, the adverse health effects of BPA have surfaced in recent years, forcing the industry to look for alternatives. Bisguaiacol, a bio-based alternative to BPA, has been synthesized using vanillyl alcohol and guaiacol via an electrophilic aromatic condensation. Purification provides both bisguaiacol and a vanillyl alcohol oligomer coproduct with a consistent number average molecular weight of about 700 Da across multiple reaction volume scales. This coproduct has been well characterized and transformed into an epoxy that is suitable for use in thermosetting resin development. We present the synthesis of bisguaiacol, characterization of the coproduct, utilization of coproduct as a monomer in thermosetting systems, and successive structure-property relationships. By utilizing the coproduct strategically, the overall production of bisguaiacol has the potential to become more economically feasible.

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Unraveling the relationship between structure and material properties in lignin-derived epoxy resins

Claudio Gioia1, cgioia@kth.se, Martino Colonna1, Ayumu Tagami2, Lilian Medina4, Olena Sevastyanova2, Lars Berglund4, Martin Lawoko4. (1) University of Bologna, Bologna, Bologna, Italy (2) KTH, Stockholm, Sweden (3) Fibre Wood Tech/Wood Chem Pulp Tech, Stockholm, Sweden (4) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Although currently, from an industrial point of view, technical lignin is considered a sub-product which is employed to recover energy by combustion, the valorization of its unique chemical structure is recipient of many efforts from the scientific community. Kraft technology for industrial production of unbleached cellulosic Kraft pulp, produces 70 Mtons/year of lignin-rich byproducts. Such an incredibly abundant source of natural aromatic structures is still poorly exploited in material science due to its variability of structures, chemical composition and polydispersity. The possibility to refine technical lignins into low molar mass fractions presenting high functionality and reproducibility opens new exciting developments in material science. Here we report the relationship between thermo-mechanical properties and chemical structures of well-characterized lignin-based epoxy resins. For this purpose, technical lignins from eucalyptus and spruce, obtained from the Kraft process were used. The choice of lignins was based on the expected differences in molecular structure. The lignins were then refined by solvent fractionation. Subsequent to the refining, three fractions with comparable molecular weights were selected to reduce effects of molar mass on the properties of the final thermoset resins. Consequently, any differences in thermomechanical properties are expected to correlate with molecular structure differences between the lignins. The understanding of the effect of specific structures on the final materials, deliver to the scientific community the unprecedented possibility to design and tune the properties of lignin-based resins.
ForMAX: Multiscale structural characterization of fibrous materials

Kim Nygard, kim.nygard@maxiv.lu.se. MAX IV Laboratory, Lund University, Lund, Sweden

ForMAX is a new initiative at the MAX IV Laboratory, co-funded by industrial partners and private foundations, with the objective to advance research and development of new materials and specialty chemicals from the forest. The ForMAX instrument will combine small- and wide-angle x-ray scattering (SWAXS), scanning SWAXS imaging, and full-field microtomography for multi-scale structural characterization of hierarchical materials from sub-nm to mm length scales, with sufficient temporal resolution to facilitate in-situ studies of material processing. A special focus will be on fibrous materials. The ForMAX beamline is in construction phase and we expect first light in 2021.

Structural characterization of cellulose in plant tissues using X-ray microbeam scattering and scanning imaging
Lin Yang, lyang@bnl.gov. National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York, United States

X-ray scattering and powder diffraction (commonly known as SAXS and XRD) has been long used for characterizing cellulose structures in plants. Generally speaking, the data at wide scattering angles correspond to the crystal form in the cellulose fibrils, while the small-angle data reveal the organization of fibrils. With the unprecedented source brightness achieved at the new synchrotrons and the emergence of new types of x-ray optics, it has become routine to achieve x-ray beam sizes of a few microns or smaller. Together with advances in detector technology, it is therefore possible to perform scattering measurements in a spatially resolved manner, to probe the cellulose structure locally, and to use the information extracted from the scattering data as a contrast mechanism for imaging. At the Life Science X-ray Scattering (LiX) beamline at NSLS-II, we have been developing instrumentation and software for these experiments. We will report our progress, with examples from user research.

A poplar section imaged using x-ray scattering as the contrast mechanism. The false color is based on the nominal crystalinity index extracted from the scattering data. The pixel size is 10 microns.

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Cryo-electron microscopy and tomography of functionalized cellulose nanocrystals

Nonappa Nonappa, nonappa@aalto.fi, Peter Engelhardt. Applied Physics, Aalto University, Espoo, Espoo, Finland

Because of their unique material properties, there is an ever-increasing interest in utilizing naturally abundant and sustainable nanocelluloses in functional nanomaterials. Among nanocelluloses, cellulose nanocrystals (CNCs) with their rigid rod-like structure allow construction of structurally and functionally diverse superstructures, including hybrids and composites. Despite tremendous progress in developing the synthetic
methods for CNCs from various sources, the determination of their three-dimensional (3D) structures remains a challenge. Conventional and cryogenic transmission electron microscopy (cryo-TEM) methods have been utilized to image CNC-based nanomaterials. However, traditional TEM imaging produces two-dimensional (2D) projections of inherently three-dimensional (3D) objects. Moreover, due to the superimposed nature, often limited structural details are extracted solely based on 2D images. Therefore, electron tomographic (ET) and single-particle reconstruction (SPR) methods have been developed to obtain 3D structures. The success of the 3D reconstruction relies on the quality of acquired data, which in turn depends on the specimen preparation method. One of the critical steps is the preservation of the specimen close to its native state under imaging conditions. We have carried out the high-resolution cryo-TEM 3D reconstruction of surface-functionalized cellulose nanocrystals and in their hybrid assemblies. Further, we have compared cryo-ET with other specimen preparation methods, including negative staining and critical point drying. Finally, we have utilized the SPR to gain insights into the high-resolution individual cellulose nanocrystals.

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Scanning electron diffraction as a tool to study the local crystallinity of cellulose

Tom Willhammar, tom.willhammar@mmk.su.se. Stockholm University, Stockholm, Sweden

Cellulose is a crucial constituent of the structure of all living plants. It possesses a complex structure including chirality. Its fascinating structural features combined with its impressive properties in terms of specific strength and stiffness has triggered the engineering of cellulose-based materials with tailored mechanical and optical properties.

The developments of pixelated STEM detectors as well as hybrid pixel detectors have enabled the collection of scanning electron diffraction (SED) data. This type of systems allow for very rapid acquisition of 2D SED maps using a very low beam dose (∼6 e/Å²). This is crucial for obtaining data from a beam sensitive material such as cellulose. A high-level optical system allows for the formation of a pencil beam with the size of 1-5 nm while keeping a small convergence angle. The resulting SED data can be analysed in various ways to produce maps revealing the crystalline microstructure of cellulose nanofibers (CNFs) and cellulose nanocrystals (CNCs).

SED data can be used to study the local crystallographic ordering within CNFs and how it is evolving along the fibers. CNFs has been extensively studied by AFM and electron microscopy imaging and twisting domains have been investigated based on morphological studies. SED data now makes it possible to study the evolution of the crystallographic structure through the twisting sections of the CNFs.

One advantage of SED data over conventional electron diffraction is that the small probe sized enables the study of the local microstructure not just along the cellulose
nanofibers but also in its transverse direction. This enables the comparison of local ordering of polysaccharide chains within CNFs extracted from tunicate and CNCs of bacterial origin revealing the difference in local crystalline structure.

CELL 187

Atomistic simulation studies of cellulose microfibril aggregates

Antti Paajanen¹, antti.paajanen@vtt.fi, Sara Ceccherini², Yogesh Sonavane³, Thaddeus Maloney², Sami Paavilainen³, Jukka A. Ketoja¹. (1) VTT Technical Research Centre of Finland Ltd, Espoo, Finland (2) Aalto University, Espoo, Finland (3) Tampere University, Tampere, Finland (4) Cellulosic Technologies UG, Leinfelden-Echterdingen, Germany

Many important issues in cellulose utilization are traceable to the interactions between cellulose microfibrils and their aggregates. This includes, among others, the production of cellulose nanomaterials, and the processes of cellulose dissolution and hornification. One way to probe these interactions is through atomistic simulations. Their computational cost is low enough for simulating structures of relevant size, while retaining a relatively detailed description of intra and intermolecular forces. Here, we present an overview of the atomistic simulation studies that we have carried out over the last five years, and discuss our experiences on the possibilities and limitations of the approach.

In the first published work, we used molecular dynamics simulations and the umbrella sampling technique to study the aggregation and deaggregation energetics of native and carboxylated microfibrils. Our work describes in detail how surface carboxylation affects the interaction between neighboring microfibrils, and reveals a surprising variability in the electrostatic contributions that constitute the average interaction. This leads us to believe that local variations in surface charge distribution could cause molecular-level failures along fibril-fibril interfaces, and thus explain the heterogeneity observed in the disintegration behavior of TEMPO-oxidised pulp at intermediate functionalization levels.

In the second published work, we used molecular dynamics simulations to study the structure of microfibril bundles and their relationship to the bound water of the cell wall. We compared the atomistic models against several experimentally known features of native cellulose, and found reasonable correspondence for the mass fraction of non-freezing and freezing bound water, the fraction of water-accessible hydroxyl groups, the specific surface area, and the conformational disorder of surface and surface-bound chains. Moreover, the simulations suggest interesting links between molecular-level disorder, supramolecular assembly and bound water.

More recently, we have extended our models to include adsorbed hemicelluloses, and we intend to use them, among others, in simulations related to cellulose dissolution and
moisture behavior. Lastly, we briefly discuss our experiences on the use of reactive force field methods to study the pyrolytic degradation of cellulose.

**CELL 188**

**New developments and strategies for high resolution characterization of secondary plant cell walls by atomic force microscopy**

*Tobias Keplinger, tkeplinger@ethz.ch, Maria Adobes Vidal. ETH Zurich-Wood Materials Science, Zürich, Switzerland*

Since more than 100 years the hierarchical organization and architecture of secondary plant cell walls has been under debate. Thus, its structure has been investigated using numerous microscopic and spectroscopic techniques. Despite all these efforts, no conclusive picture exists on the exact arrangement of the cell wall constituents and the corresponding nano-mechanial properties.

Open points span from discrepancies between individual species, over the distribution of cellulose fibrils to the interaction between cellulose and matrix components. Conflicting observations mainly arise from differences in sample preparation processes including embedding, staining, dehydration, microtome or freeze fracture, which can cause important alterations of the complex polymeric nature of the cell wall.

Within the last 15 years, Atomic Force Microscopy (AFM), equipped with force spectroscopy modes, emerged as key method for the detailed characterization of plant cell walls at the nanoscale. The increasing interest is due to the non-damaging character of the technique and the requirement of minimal sample preparation, which minimizes the introduction of artefacts. In addition, recent developments in the field of force-distance curve mapping allow for simultaneous mapping of topographical, compositional and mechanical properties with nanometer resolution, providing new insight into the structure-function relationships of lignocellulosic materials.

Here, we address the most relevant experimental challenges and strategies in AFM to elucidate the nanostructure of secondary wood cell walls. Specific focus will be given to AFM-based force measurements and the related difficulties to deliver quantitative data on the mechanics at the nanoscale evidenced by the large discrepancy of mechanical values obtained by AFM in comparison to conventional Nanoindentation (NI). In addition we will highlight a new methodology, based on the visualization of the wood fibres in liquid medium, which allows the analysis of delignification processes. This strategy boosts our understanding on the three dimensional arrangement of the cellulose fibrils within secondary cell walls.

**CELL 189**

**Post-mortem nanomechanical property mapping of natural fiber welded interfaces**
As interest in ionic liquids has grown over the past few decades, so has the number of potential applications. Among these is Natural Fiber Welding (NFW), where the biopolymer matrix of natural fibers, such as cellulose, is disrupted by interactions with the ionic liquid. The degree of disruption (welding) can be altered through the manipulation of treatment factors such as time and temperature. The degree of welding has also been shown to significantly affect the material properties. While many studies have been dedicated towards the effect of variable NFW treatment on the material properties, the reported data is characteristic of the bulk material. The kinetic mechanisms and subsequent material property changes dominating at the dynamic solid/liquid interface has proven difficult to understand quantitatively. In this study we use Peak Force Quantitative Nanomechanical Mapping (PFQNM) atomic force microscopy (AFM) to analyze the unique interfaces produced during NFW. Through variation of parameters affecting the degree of welding, the post-mortem modulus and adhesion interfacial data are used to elucidate some of the micro-scale dissolution processes during NFW.

CELL 190

Diffusion in wood cell walls by conductivity, x-ray fluorescence, and nanoindentation mechanical spectroscopy

Joseph E. Jakes², Christopher G. Hunt², Christopher.g.hunt@usda.gov, Samuel I. Zelinka², Peter Ciesielski¹. (1) National Renewable Energy Lab, Golden, Colorado, United States (2) USDA Forest Products Laboratory, Madison, Wisconsin, United States

We show moisture-dependent diffusion measurements in loblolly pine cell walls by conductivity and X-ray fluorescence, and the strong correlation with the mechanical damping (tan δ) peak of hemicellulose as determined by nanoindentation-based mechanical spectroscopy. The data shows that that diffusion in wood cell walls is dependent on hemicellulose mobility and therefore highly dependent on hemicellulose glass transition. We outline the theory of diffusion around the glass transition, then discuss how molecular mobility measurements could predict performance in areas as diverse as biorefinery conversion, decay resistance, adhesive interactions and fastener corrosion.
Polymers with designer architectures prepared by 'living' radical polymerization (LRP) have allowed the synthesis of complex architectures, and moreover the applications for such architectures are slowly being realized in biomedical applications. The seminar will present work on the synthesis of complex polymer architectures and their use in vaccine delivery and the delivery of siRNA. The seminar will all discuss new methods for production of multifunctional polymer nanostructures, and their application towards stem cell expansion and drug delivery. We have developed a new technique to produce nanoworms, nanorods, tadpoles, nanorattles and torroids at high weight fractions of polymer (>10wt%) using the temperature-directed morphology transformation (TDMT) method. The nanostructures can be synthesized using multiple types of
thermoreponsive MacroCTAs, allowing multiple and orthogonal chemical functionality on the nanostructure surface. Biomolecules and water-soluble molecules or polymers can be coupled to the nanostructures, and provide a strategy to produce designer structures for a wide range of bioapplications. The nanostructures can be dried, rehydrated and stored in water for 5 months without a change in shape. This method represents a new and an important synthetic development in the design of nanoobjects.

TDMT method to produce stacked torroidal nanorattles

**CELL 192**

Additive manufacturing, degradable aliphatic polyesters and soft tissue engineering: Is that a possible combination?

Anna Finne-Wistrand¹, annaf@kth.se, T.Christian Gasser¹, Kamal Mustafa², Tiziana Fuoco¹, Hailong Liu¹, Astrid Ahlinder¹, Shubham Jain¹. (1) KTH Royal Institute of Technology, Stockholm, Sweden (2) University of Bergen, Bergen, Norway

Since we started to design degradable and porous scaffolds the interest and development in additive manufacturing has increased tremendously. In tissue regeneration, the technique has been considered useful for obtaining precise structures
and being able to personalize porous scaffolds. The problem with printing degradable scaffolds that have mechanical stability is that the degradable polymers decompose during the process. Both polymer and process must thereby be adapted to meet the requirements, where our main requirement is that the material properties should not change during the process. We have an additional requirement and that is that the degradable scaffold should be adapted to soft tissue and thus be pliable and soft. However, not as soft as a gel, we want the scaffold to be able to take load and thus both create a 3D environment for the cells to proliferate, differentiate on to and protect them against compression.

We have focused on polymers and processes that make it possible to test a prototype in clinical studies within a reasonable period of time. Poly(ε-caprolactone) (PCL) is a good polymer to use in melt-extrusion additive manufacturing because it has low melting point and the gap between the melting temperature and the temperature at which PCL is thermally decomposed is large. Unfortunately, the polymer breaks down very slowly in the body. Our solution was to incorporate p-dioxanone into the polymer chain, thus increasing the rate of degradation, while maintaining printability. By simulating different scaffold designs we also managed to find a 3D design that generated soft scaffolds. The combination of the polymer and the 3D design proved to be a good environment for adipose tissue regeneration. We managed to get all the parameters together and obtained a successful process for printing soft polyester based degradable scaffolds through close cooperation between polymer technology, mechanics and biology.

**CELL 193**

**Porous scaffolds of biodegradable polymers via templated techniques**

*Rajiv Srivastava, rajiv@textile.iitd.ac.in.* Indian Institute of Technology Delhi, New Delhi, India

Research and commercialization activities on porous scaffolds based on biodegradable polymers have seen remarkable growth since the advent of tissue engineering. The utility of porous scaffolds is also not limited to tissue engineering but has been expanded to other fields including selective sorption and separation, catalysis and energy storage. Numerous techniques to develop porous scaffolds have been developed over the years encompassing from conventional methods of particulate leaching and phase separation to advanced methods of rapid prototyping including stereolithography and 3D printing. Polymers are added and bonded in layers to form porous structures in rapid prototyping which is also known as additive fabrication or layered manufacturing. All these methods are multi step processes, typically require a pre formed polymer and fabrication is carried out at high temperatures or in presence of organic solvents. The methods are also not appropriate for scaffold formation of heat or solvent sensitive biodegradable polymers, including aliphatic polyesters, which are the polymers of choice for tissue engineering. Any trace amount of residual solvent present in the scaffold reduces the ability of cells to form new tissues and tedious efforts for complete extraction of solvent impose restrictions when the scaffold is to be used immediately in a clinical setting and requires added cost. A need for single step,
A continuous and tunable process for developing porous scaffold is therefore realized which can substitute the existing multi step processes. Templates from a high internal phase emulsion (HIPE) have been used to create porous scaffolds of biodegradable polymers in a single step process. HIPE templating also provided flexibility in conducting polymerization and scaffolding together, thereby allowing fabrication of intricate porous scaffolds with ease. Cross-linking and functionalization to impart additional benefits to scaffolds are also possible during HIPE templating and its potential extension and synchronization with other fabrication modes such as microfluidics and electrospinning.

**CELL 194**

**Functionalized silk biomaterial systems**

_**David L. Kaplan, david.kaplan@tufts.edu.**_ Tufts Univ, Medford, Massachusetts, United States

Combining the intrinsic merits of structural proteins like silk fibroin (e.g., mechanics, biocompatibility, slow degradability) with additional features from polysaccharides like hyaluronic acid (cell recognition, biocompatibility, rapid degradability) can result in new biomaterial systems with structural and functional features useful for a range of biomedical needs. These systems, generated via chemical crosslinking or various processing options provide avenues for a range of new functionalized silk-based material systems; retaining important features of sustainability, degradability and biocompatibility while adding new utility. These material systems also offer utility towards 3D printing, injectable formats, and a range of medical devices. The approaches utilized to generate such systems, along with characterization and examples of biomedical utility, will be presented.

**CELL 195**

**Designing hyaluronic acid hydrogels for commercial and clinical translation**

_**Jons Hilborn**, hilborn@kemi.uu.se, Oommen Varghese1, Oommen Podiyan2._ (1) Polymer Chemistry, Uppsala University, Uppsala, Sweden (2) Biomedical Sciences and Engineering, Tampere University of Technology and BioMediTech Institute, Tampere, Finland

Until recently, the extracellular matrix (ECM) has often referred to by ambiguous terms such as "ground substance". However, the ECM has recently received considerable attention due to its importance in cell-cell signaling, wound repair, cell adhesion and tissue function. New mechanisms of cell adhesion with the ECM are found with considerable frequency. Still, all seem to involve cell-surface receptors for molecules that are found in the space surrounding the cell (pericellular matrix) which, in turn, interact with molecules in the territorial matrix. Thus, the matrix not only exposes stores and sequesters specific molecules but can also exert a physical force on the cell and
supply feedback which is undoubted of critical in controlling the shape of the tissue. The importance of the information built into the extracellular matrix (ECM) cannot be overstated. Disruptions of ECM can lead to uncontrolled cell growth, and the developmental destruction of ECM during amphibian molting leads to tissue death. Integration of components of the ECM with cell surface receptors and the consequent transduction of signals across the cell membrane serve to alter cell behavior and developmental fate. Even the intracellular signaling pathways associated with ECM components and their cognate receptors are conserved. Therefore, it is not surprising that acellular human and animal tissues are frequently and successfully employed as scaffold materials in research. Shortcomings include source variability and lack of possibility to adjust the desired biologic response. Engineered ECM matrices may, however, provide for scaffolds that signal to regenerate tissues. We set out to engineer the ECM based hydrogels to provide biorthogonal crosslinking reactions, tune swelling, control inflammation, promote cell adhesion, enable degradation by relevant cells and to incorporate growth factors in safe ways which has allowed commercial and clinical translation.
Using phase separation of cellulose derivatives to control the drug release rate

Anette Larsson, Anette.larsson@chalmers.se. Department of Chemistry and Chemical Engineering, and the Competence Center SuMo Biomaterials, Chalmers University of Technology, Gothenburg, Sweden
Controlled drug release is a demand for many pharmaceutics to become useful. This can be achieved in different ways, for example by having a coating that surrounds a unit containing the drug. The transport of the drug can be controlled by creating pores in the coating via addition of pore forming agents. This presentation summarizes and demonstrates the ability of using the phase separation of bio-based polymers to achieve pores. We used a mixture of the cellulose derivatives hydroxypropyl cellulose (a water-soluble polymer) and ethylcellulose (water-insoluble polymer), and dissolved these polymers in an organic solvent (ethanol). During the coating process, the dry content increases, which leads to that the two polymers undergo spinodal decomposition. Upon exposure to aqueous medium the water-soluble polymer dissolves and is transport out from the coating, where the remaining coating contains a porous structure. The pore structure depends on the phase separation, which is sensitive to the ratio between water-soluble and water-insoluble polymers, the molecular weights of the polymers, the process conditions during the coating etc. It was concluded that the drug release rate correlated to the pore structure, and where we were able to simulate the permeability and drug release rate.

CELL 197

Multifunctional hydrogels for rapid hemostasis and tissue repair

Baolin Guo, baoling@mail.xjtu.edu.cn. Xi’an Jiaotong University, Xi’an, China

Uncontrolled bleeding results in more than 30% of traumatic deaths. Although currently used hemostatic agents exhibit excellent performance in hemostasis of limb surface wounds, they generally have a poor hemostatic effect on deep wound bleeding. We prepared chitosan derivatives and carbon nanotube materials to form injectable shape memory nanocomposite porous gelatin hemostatic materials. Chitosan derivatives can provide good hemostatic properties, promote wound healing and blood-triggered shape memory recovery. Due to the rapid blood absorption, blood concentration and rapid blood-triggered shape recovery of the composite gel, as a physical filling barrier with sufficient mechanical properties, it exhibits excellent performance in rabbit liver volume loss and incompressible hemorrhage death model. After the bleeding stops, the severe skin defect of the skin is a serious threat to people’s health and life. At present, most of the injectable gel dressings have only a single biological activity, which limits their multiple promoting effects on wound healing. We have reported an injectable hydrogel dressing that has both self-healing and high adhesion. The in-situ gelation and tissue adhesion properties of the hydrogel can quickly seal any shape of the wound to provide a physical barrier, while the hemostatic and antibacterial properties of the gel can allow the wound to stop bleeding quickly and prevent wound infection. Thus, the hydrogel has great potential as a bioactive dressing in wound healing applications.

CELL 198

Forensic engineering of advanced polymeric biomaterials
Marek M. Kowalczuk, cchpmk@poczta.ck.gliwice.pl. Polish Academy of Sciences, Zabrze, Poland

The biosafety of advanced polymeric biomaterials needs prediction, evaluation and indication on potential complications arising from their use and the formation of their degradation products. Thus, the methodology of forensic engineering of advanced polymeric materials (FEAPM) is currently being developed in the area of biocompatible polymers. This novel approach deals with the evaluation and understanding of the relationships between their structure, properties and behavior before, during and after practical applications. FEAPM provides a central driving force for the otherwise disconnected works and should help to design precisely structured polymer materials and to avoid potential failures of the commercial products manufactured from them. The selected prediction and case studies related with design of precisely structured polymer biomaterials for diverse applications in medicine and cosmetic industry will be presented. The molecular level characterization of polymers, including natural polyhydroxyalkanoates (PHA) and their synthetic analogues will be discussed.

CELL 199

New energy storage materials constructed from the intransigent polysaccharides

Lina Zhang, zhangln@whu.edu.cn, Lingfeng Gao, Kai Zhang, Jie Cai, Jinping Zhou. Wuhan University, Wuhan Hubei, China

We have pioneered the development of low temperature dissolution technologies to dissolve efficiently the intransigent polysaccharides such as cellulose and chitin in alkali/urea aqueous solvents with cooling. A series of the pure and composite microspheres as well as their carbonized N/S-carbon and/or N-carbon microspheres materials were constructed by using polyaniline (PANI) /cellulose solution and chitin solution. The resulted N/S doped microspheres and N-enriched microspheres showed the potential applications as electrode materials with high rate capability and cycling stability. The ultrafine metal oxide quantum dots were tightly embedded in N-enriched 3D carbon nanofiber networks in the carbonized chitin microsphere, leading to the hierarchically porous structure, which exhibited a high storage capacity and a good cycling lifespan in lithium/sodium-ion batteries. Furthermore, 2D porous chitin nanosheets and ultra-thin 2D carbon nanosheets were fabricated via a phytic acid assisted top-down exfoliation of bulk chitin and further carbonization. The as prepared 2D porous carbon nanosheets displayed remarkable electrochemical performance as electrode material for both sodium-ions battery and supercapacitors.

CELL 200

Protein plastics

Mikael Hedenqvist, mikaelhe@kth.se. Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden
In this presentation the possibilities and challenges associated with the use of protein-based materials in applications where petroleum-based plastics are used today will be discussed. The processability of protein-based materials using techniques currently used for petroleum-based plastics (e.g. injection moulding and extrusion) will be highlighted as well as the properties of the final products. Examples will be given for protein mono-materials, blends and composites that we work on or have worked on. These include materials based on wheat gluten, rape-seed, whey, potato protein and oil-crops. Special emphasis will be put on the relationship between protein structure and final properties. The protein structure has been determined using e.g. IR-spectroscopy and the physical properties have been determined by e.g. mechanical tests. The properties of fibrils, films, sheets, 3D-moulded items and foams will be given and how these can be made rubbery or glassy, showing everything from soft/resilient to stiff behaviour. Special features, obtained with the use of additives (e.g. glass, biochar, graphene and carbon nanotubes) are highlighted, such as fire-resistance, biodegradation/stability and electric properties. Moisture and microbial resistance, obtained by e.g. coatings and antimicrobial agents, are discussed and in what environments protein materials are most suited.

CELL 201

Composition of lignins isolated from low-input crops using chemometric data analysis: Comparative study

Jessica Rumpf¹, Xuan-Tung Do¹, Rene Burger¹, Michel Bergs¹,², Yulia Monakhova²,⁵, Ralf Pude³, Matthias Rehahn⁴,⁶, Margit Schulze¹, margit.schulze@h-brs.de. (1) Department of Natural Sciences, Bonn-Rhein-Sieg University of Applied Sciences, Rheinbach, Germany (2) Spectral Service AG, Köln, Germany (3) Institute of Crop Science and Resource Conservation, Rheinische Friedrich Wilhelms University, Bonn, Germany (4) Ernst-Berl-Institute, Technical University Darmstadt, Darmstadt, Germany (5) Institute of Chemistry, Saratov State University, Saratov, Russian Federation (6) Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

Besides hard and soft wood, so-called low-input plants are of special interest as lignocellulose feedstock (LCF) for second generation biorefineries. This contribution presents data obtained for lignins isolated from different low-input crops: Perennial grasses of different genotype (including M. x giganteus, M. sinensis, M. robustus, M. nagara), a fast-growing tree (Paulownia) and another perennial plant (Silphium perfoliatum L.). All biomasses are harvested at specific time/season and separated (stem versus leaf). Lignin isolation is performed via non-catalyzed organosolv pulping (170°C/15 bar, varying ethanol concentration and reaction time). Lignin application is still limited due to problems regarding fast and reliable structure analysis and quality control. In our ongoing project, chemometric methods (e.g. principal component analysis, PCA) are used to process experimental data (e.g. NMR, FTIR) of lignins extracted from different biomasses. Moreover, the ratio of the three monolignol units (H, G, S) and the linkages formed between the units have been analyzed using hetero-nuclear single quantum correlation nuclear magnetic resonance (HSQC 2D-
NMR). So M. x giganteus leaf-derived lignins showed about two-thirds of the G unit, whereas in stems and mixtures the G content was significantly lower. Based on HSQC, the ratio of most abundant monolignol linkages were estimated (β-arylether 55-65 %; about 10 % phenyl coumarane and resinol linkages, resp.). Unsaturated esters are most abundant in stem-lignins (up to 30 %). Compared to beech wood, Miscanthus lignins possess lower molecular weight and polydispersities (< 1.5) corresponding to improved homogeneity. PCA of FTIR data revealed distinct differences for aromatic in-plane deformations of stem versus leaf-derived lignins.

Structural differences are correlated with the lignin antioxidant activity (DPPH, Folin-Ciocalteu). Low-input crop lignins are compared to kraft lignins (isolated at room temperature from aqueous solution; some purified via sequential extraction). So far, kraft lignins showed highest activities (above commercial butylhydroxytoluene (BHT).

**CELL 202**

**Engineering biobased & compostable plastics: PLA story**

*Ramani Narayan, narayan@msu.edu.* Chemical Engineering, Michigan State University, Okemos, Michigan, United States

In this lecture we review the story of PLA -- from an expensive biomedical specialty polymer to the world’s foremost 100% biobased commodity polymer with environmentally responsible end-of-life options namely composting and chemical recycling. We will discuss the manufacturing process, the unique stereochemistry and associated properties that govern its application and use. Advanced polylactide - biopolyester hybrid compostable polymers address thermal and impact property weakness of PLA and expands the application base. Recyclable PLA composites offer sustainable greener alternatives. Composting and recycling end-of-life approaches will be discussed based on experimental data.

This lecture ends with a word of caution -- there is much misuse and abuse of the word “biodegradable”. Products abound in the marketplace making unqualified claims of “biodegradable” as a solution to plastics pollution. The U.S. Federal Trade Commission, the State of California, the European Union Commission provide clear guidance in this area. ASTM, ISO, and EN standards provide test methods and specifications to measure and report on biodegradability-compostability.
Review of the tailoring of cellulose surfaces with the layer-by-layer technique to create new cellulose-based materials and devices

Lars Wagberg, wagberg@kth.se. KTH Fibre Polymer Techn, Stockholm, Sweden

Close to 30 years ago the polyelectrolyte Layer-by-Layer technique was introduced by Decher et al.1 With this approach it was shown possible to tailor interfaces with self-organized films with nanometer precision using stratified layers of polyelectrolytes/nanocolloids of opposite charge. The technique has received an almost unmatched scientific attention both regarding the fundamentals of LbL formation and use for improving material properties and create new nano-tailored devices. Despite some large-scale applications, the technique is still awaiting a major breakthrough in materials production or device manufacture.

One area where the technique has gained some commercial success is in the treatment of cellulose-rich fibres for the preparation of fire-retardant paper, dry and wet strong papers and antibacterial fibrous networks just to mention a few applications. The LbL technique has also been adopted to nanocellulose based materials to create energy storage materials and antibacterial nanocellulose films. Despite the rather simple preparation of these nanostructured thin films and their excellent performance the theory behind the LbL formation on cellulose substrates and virtually any substrate is not fully known and poses a large future research challenge.

The present contribution will give a review of the fundamentals of LbL preparation on cellulose-rich materials and also to summarize the most promising LbL-treatments developed so far for these materials.

Colloidal features of softwood extracts
The transition from the current fossil-based economy to a sustainable bio-based economy requires utilization of renewable materials from natural sources, which are often complex and heterogeneous. Their macromolecular features i.e. molar mass, size, and conformation provide an insight on their structure-function relationships. Often, functionality is a result of complex macromolecular features, whose understanding requires detailed characterization. However, the macromolecular characterization is often limited to conventionally employed size-exclusion chromatography (SEC). The limitations within SEC are largely overcome by asymmetric flow-field-flow fractionation (AF4).

We studied the macromolecular features of softwood galactoglucomannan (GGM) -rich pressurized-hot water extract, without purification and after a subsequent ethanol-precipitation to remove monomers, oligomers, and the majority of non-carbohydrate residues. First, the AF4 method was optimized for efficient fractionation of multiple size classes of the extract. Secondly, the molar mass, size, and conformational properties of the fractionated classes were analyzed by coupling the AF4 with a multi-angle light scattering detector (MALS). The conformational insight obtained from AF4-MALS was further validated by small-angle X-ray scattering (SAXS) and cryo-transmission electron microscopy (Cryo-TEM).

Our results showed that both types of GGM extract were heterogeneous. In addition to low-molar mass polysaccharide fractions, colloidal entities in the form of assemblies, and/or particles were present. The results were supported by MALS and SAXS, and the entities were visualized by Cryo-TEM. From our optimized AF4 method, it was possible to fractionate multiple size-classes of GGM extract in one experimental run, which, otherwise is very challenging. The AF4 method will be helpful for the characterization of complex wood extracts, or in general, heterogeneous samples with multiple size classes. The study provides a valuable understanding of the unique macromolecular features of GGM-rich extracts, which is highly beneficial for utilizing them as a novel, bio-based materials in different applications, for example, as Pickering stabilizer particles.

CELL 205

Selective detection and recovery of polysaccharides from biorefining

Ulrica Edlund1,2, edlund@kth.se, Niklas Wahlström1, Ferdinand X. Choong2, Peter R. Nilsson3,2, Agneta Richter-Dahlfors1,2. (1) Fiber and Polymer Technology, KTH Royal Inst of Technology, Stockholm, Sweden (2) AIMES, Center for the Advancement of Integrated Medical and Engineering Sciences, Stockholm, Sweden (3) Department of Chemistry, IFM, Linköping University, Linköping, Sweden
Polysaccharides composed of glucose building blocks – glucans – have interesting properties that merit their use as renewable material components in everything from single-use to advanced, high-end applications. The concept relies on the efficient liberation of polysaccharides from plant biomass. A major challenge is to find process conditions that offer selective isolation of targeted components while minimizing deterioration of the polysaccharide structure, chemical, and energy consumption. Another challenge is the selective detection and compositional determination of polysaccharides in plant tissue and isolated fractions. Conventional carbohydrate compositional analyses are typically disruptive and the analyses report the total monosaccharide composition rather than the polysaccharide origin of the sugar units.

We devise strategies for selective polysaccharide extraction and characterization, and have developed optotracing as a novel non-destructive method for carbohydrate analysis [1-3]. Optotracing is based on luminescent conjugated oligothiophenes with conformation dependent optical properties. When bound to a polysaccharide substrate, the optotracer adopts a molecular conformation that generates an optical signature unique for the substrate. As the signal is readily detected by fluorescence microscopy, anatomical maps can be generated that show the spatial location of one or more polysaccharides in native tissue sections as sub-cellular resolution. Alternatively, optical recordings of the samples can be achieved by conventional spectroscopy. Serving as a non-destructive tool to selectively determine the components in the biomass, optotracing may facilitate efficient recovery of glucan polysaccharides in biorefining. Examples from selective detection of glucans in straw, algae and wood will be presented.

CELL 206

Bioproducts engineered from lignocelluloses: From plants and residues to next generation materials

Orlando J. Rojas1,2, ojrojas@ncsu.edu. (1) Bioproducts and Biosystems, Aalto University, Espoo, Helsinki, Finland (2) Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada

We report on the next generation supra-colloidal systems, capable of performing emergent functions by utilizing trans-disciplinary approaches for deconstruction and reassembly. Such efforts have a direct impact in water use, waste reduction, energy efficiency and carbon fixation. Yet, important gains can be achieved in terms of clean energy, industrial bioengineering, among others. Any success in related efforts, however, hinges on the application of concepts associated to formulation engineering, as will be presented. Some specific cases will be illustrated, including emulsions, foams and other multiphase systems used as intermediaries for material development. Similarly, going from molecular to colloidal scales there is a quest towards in-depth colloidal engineering of mechanical, thermal, electrical, iontronic, optical, magnetic, and biological functions. Solutions in these directions will have a major impact in the future of advanced materials and energy.
Membranes, composites, and coatings of nanocellulose biotechnologically designed by using a layer-by-layer procedure

Dieter O. Klemm, dieter.klemm@uni-jena.de, Kathrin Petzold-Welcke, Friederike Kramer, Wolfgang Fried. KKF company, Jena, Germany

Bacterial Nanocellulose (BNC) is the only cellulose type, which is produced biotechnologically from low molecular sugars such as glucose. Consequently, BNC has a great potential of a real design of nanocellulose materials. The surface and interface properties of multilayered nanocellulosics can be controlled by the process parameters of our shaping template – based layer-by-layer-formation biotechnology. That allows the production of multilayered membranes and especially the inclusion of different types of additives – dispersed in the culture medium - in all constructed layers during the biosynthesis in the bioreactor. That is of immanent interest for application in the field of electrical, optical, magnetic, barrier & topochemical Properties. It is important to note, that the described BNC – Layers do not delaminate under application. Using cellulose nanofibres from wood (CNF) as an additive allows the creation of nanocellulose hybrids. The composite membranes can also be produced on different materials (wood, ceramics, metals, and different types of polymers) as coatings. A special feature of BNC is the formation of hydrogel bodies. Our production technology enables the design shaped hollow bodies with a multilayered wall. These hydrogels are exciting candidates for novel types of medical implants in regenerative medicine. Exemplified by the healing of destroyed bile ducts with nanocellulose tubes (pig studies) the importance of surface design is demonstrated.

The layer-by-layer-formation of BNC takes place on templates, which are moving between the aqueous culture medium and the air space of the bioreactor. After wetting the template in the culture medium the BNC-formation takes place only on the template surface - not at the surface of the culture medium. Repeated dipping of the templates leads to the described multilayered structures. The shape of the template controls the shape of the resulting BNC-bodies. The properties of the surfaces results from the contact to the matrix and to the air, respectively. A longer stay in the air space results in higher density of the surface.

Nanocellulose-based polyelectrolyte membranes: Land of opportunities for application in fuel cells

Carla Vilela1, cvilela@ua.pt, Filipe Figueiredo2, Armando Silvestre1, Carmen Freire1. (1) CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal (2) CICECO - Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, Aveiro, Portugal
Bacterial nanocellulose (BNC) is a highly pure and crystalline form of cellulose with a three-dimensional nanofibrillar structure that is produced by non-pathogenic bacteria in the form of a hydrocolloid gel. This nanoscale form of cellulose exhibits intrinsic and unique properties, namely biodegradability, good dimensional stability and mechanical properties, high water retention capacity, tailorable surface chemistry and in situ moldability, that enable its application in multiple domains of materials science. In fact, BNC has become a very attractive solution for the development of bio-based ion exchange membranes for application in fuel cells that are electrochemical devices that convert chemical energy into electrical energy via redox reactions [1].

The present study describes a simple and easy method to produce partially- and fully-biobased ion conducting BNC nanocomposite membranes by combining this hydrocolloid polysaccharide gel with different synthetic (e.g., poly(4-styrene sulfonic acid), poly(methacryloyloxyethyl phosphate), poly(methacryloyloxyethyl chloride) and poly(bis[2-(methacryloyloxy)ethyl] phosphate)) and natural (e.g., fucoidan and lignosulfonates) polyelectrolytes [1]. All these membranes showed good thermal-oxidative stability, mechanical performance, and high ionic conductivity, and therefore potential as bio-based alternatives to other ion-exchange membranes for application in conventional polymer electrolyte fuels cells (PEFCs) but also in microbial fuel cells (MFCs) that use microorganisms as electrocatalysts to convert organic and inorganic matter via oxidation into electrical energy.

**CELL 209**

**Fabrication characterization and properties of magneto responsive hybrid materials based on bacterial cellulose**

*Nipaporn Sriplai*¹, s_nipaporn@kkumail.com, *Wiyada* -. Mongkolthanaruk², *Stephen J. Eichhorn*³, *Sampo Tuukkanen*⁴, *Supree -. Pinitsoontorn*¹.⁵. (¹) Physics, Faculty of Science, Khon Kaen University, Khon Kaen, Khon Kaen, Thailand (²) Department of Microbiology, Faculty of Science, Khon Kaen University, Khon Kaen, Khon Kaen, Thailand (³) CAME School of Engineering, University Walk, University of Bristol, Bristol Composites Institute, Bristol, Bristol, United Kingdom (⁴) Faculty of Medicine and Health Technology (MET), Tampere University (TAU), Tampere, Tampere, Finland (⁵) Physics, Institute of Nanomaterials Research and Innovation for Energy (IN-RIE), NANOTEC-KKU RNN on Nanomaterials Research and Innovation for Energy, Khon Kaen, Khon Kaen, Thailand

In this work, we present the study on the fabrication and properties of bacterial cellulose (BC) based nanocomposite materials. The BC scaffolding templates were biosynthesized from *Gluconacetobacter xylinum* bacteria. Magnetic nanoparticles (CoFe₂O₄, or MnFe₂O₄, Fe₃O₄) were impregnated into the structure of BC by either co-precipitation or simple immersion methods. The samples were characterized by combined techniques such as TG, FTIR, XRD, SEM, AFM, TEM, and were studied for their mechanical and magnetic properties. Magnetic paper with white color appearance was fabricated by sandwiching the BC/CoFe₂O₄ sheet between two white layers,
composing of BC/ZnO composites. The white magnetic paper showed excellent whiteness, with flexibility and foldability, just like regular paper sheets but was distinguishable by external magnetic fields, which gives potential uses as security paper or for anti-counterfeit applications. Furthermore, the BC/MnFe$_2$O$_4$ composite films were investigated for use as inexpensive and highly sensitive flexible piezoelectric sensors. The homogeneous distribution of MnFe$_2$O$_4$ nanoparticles in the BC structure improved the piezoelectric sensitivity in both normal and bending modes compared to conventional piezoelectric film. On the other hand, the magnetic membranes based on BC/Fe$_3$O$_4$ nanocomposites were fabricated by freeze-drying magnetic BC hydrogels. The BC membranes were demonstrated to show high flexibility and durability, and were highly responsive to both static and alternating external magnetic fields. Lastly, BC/Fe$_3$O$_4$ aerogels were converted to carbon nanofiber (CNF/Fe$_3$O$_4$) aerogels by pyrolysis process. The magnetic CNF aerogels showed the capability to absorb a common dye pollutant from water. The dye was absorbed efficiently, and the aerogels were easily removed from the solution by magnetic forces and were reusable.

**CELL 210**

**Tuning the physio-electro-chemical properties of bacterial cellulose derived carbon nanofibers: Effect of drying conditions on electrochemical properties**

*Mani Pujitha illa*¹, *ms15resch11002@iith.ac.in*, *Chandra S. Sharma*², *Mudrika Khandelwal*¹. (¹) Materials Science and Metallurgical engineering, Indian Institute of Technology, Hyderabad, India (²) chemical engineering, Indian Institute of Technology, Kandi, Telangana, India

Bacterial cellulose (BC) is a preferred nanocellulosic precursor due to its several advantages over plant-derived cellulose such as high crystallinity, 100% purity, high porosity, great mechanical properties with in situ manipulability. In its natural form, BC is a hydrogel, which implies high porosity and water holding capacity however to enable its use for engineering applications, water needs to be removed. The physical properties of BC such as morphology, porosity, and mechanical strength are vastly affected by the drying method employed which would ultimately affect the carbon obtained on pyrolysis of BC. This work presents a case study in which we produced BC through bacterial fermentation process using two different strains, followed by systematically studying the effect of drying (oven and freeze drying) on physio-chemical, morphological, and structural properties of as-produced bacterial cellulose using FTIR, XRD, FESEM, BET surface area, and tensile testing. Oven-dried BC showed higher crystallinity, reduced fiber diameter, narrow size distribution and higher mechanical properties as compared to freeze-dried bacterial cellulose. Finally, we successfully demonstrate the utilization of pyrolysed BC for production of functional anode materials for lithium ion batteries. The variation in the drying of BC has ultimately led to an 30% variation in the reversible capacities of lithium ion batteries. This presentation will focus on our understanding as developed about the selection of a particular drying method of BC for particular application by, weighing the gain in property vs. an increase in the amount of time and energy expenditure.
Actuation modulation by modification of substrate morphology: Bacterial cellulose/PEDOT:PSS actuator

Pintu Maity, Siju C R, sijucr@iith.ac.in, Mudrika Khandelwal, mudrika26@gmail.com. Department of Materials science and Metallurgical Engineering, IIT Hyderabad, Hyderabad, TELANGANA, India

Electroactive polymers are preferred in actuators because of their flexibility, lightweight, significant displacement, and low operation voltage. Poly (3,4-ethylene dioxythiophene)–poly(styrene sulfonate) (PEDOT: PSS) is especially promising due to its high conductivity, stable redox behavior, fast response, and relatively high stability. However, substrate plays an important role in the overall performance. Here we demonstrate bacterial cellulose as the preferred substrate due to highly flexible, porous network structure. We report actuator based on bacterial cellulose (BC) and PEDOT:PSS, which shows a displacement of 2 mm at 1.5 V. The actuator performance can be enhanced by modifying the morphology of the substrate to improve the uptake of ions and thus the electrochemical doping processes. The morphology of bacterial cellulose can be tuned by in situ as well as ex-situ methods. We demonstrate the effect of change in morphology on the actuation. This BC/PEDOT-PSS based actuator can be used as a biocompatible metal-free actuator for biomedical applications.

Sprayed flexible nanocellulose-based supercapacitors studied using surface sensitive X-ray scattering
Sustainable devices experience a massive increase of attention over the last years. Our whole economy is starting to minimize the use of fossil resources. Nevertheless, it is yet not fully understood how sustainable devices perform and degrade under environmental influences and how we could improve possible drawbacks. Wood-based cellulose as one of the most earth abundant nature materials consists of so-called cellulose nanofibrils (CNF). These nanoscale building blocks have high potential in applications due to their low density, high material strength and sustainability [1]. Nowadays it is not only in focus to study fundamental particle morphologies rather than finding techniques to be able to manufacture materials with desired physical properties. Spray deposition as industrial deposition technique with roll-to-roll compatibility is therefore our choice to fabricate large-scale films with unprecedented low surface roughness down to 2 nm [2-3]. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is nowadays widely used as high performance conductive polymer in the field of bioelectronics, solar cells, supercapacitors. It is a water-soluble polymer and fulfils the sustainable approach of using less solvents. The sprayed flexible and conductive bionanocomposite with thicknesses up to 30 µm provides high energy densities of up to 1.2 µWh/cm² with a power density of 20 mW/cm² at 0.1 mA/cm².

Elucidating the effect of additives on the three-dimensional nanoscale structure obtained while manufacturing flexible, printed organic supercapacitors will allow better understanding and improvements of future organic electronics. To achieve this we have studied self-assembly kinetics during drying of spray coated CNF thin films using grazing incidence wide/small-angle X-ray scattering (GIWAXS/GISAXS) [3, 4], and correlated this to morphological changes for two cases, when PEDOT:PSS ink is applied as multilayer, or when it is pre-mixed into the CNF dispersion prior spraying. In addition, we have studied effect of chemical additives on crystallinity.

CELL 213

Two-phase, biomass emulgels for direct ink writing of hierarchical architectures

Siqi Huan¹, huansiqi888@hotmail.com, Bruno Mattos¹, Rubina Ajdary¹, Wenchao Xiang¹, Long Bai¹, Orlando Rojas¹,². (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Department of Chemical & Biological Engineering, Chemistry, and Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

3D printing offers a customizable platform to engineer constructs with a high level of topological complexity while ensuring robust structures. Among various 3D printing techniques, extrusion-based direct ink writing (DIW) provides programmable, precise hierarchical assemblies in 3D. However, one-step, facile synthesis of such architectures via DIW has been challenging, particularly for low-solid-content biomass-based inks.
This study proposes a novel ink design strategy to create two-phase, biomass-based emulgels for direct printing and in situ formation of protecting layers enveloping multicomponent cores, mimicking hierarchically skin-bearing biological systems. The emulgel consists of a Pickering emulsion with an organic, internal phase containing poly(lactic acid) stabilized by chitin/cellulose nanofibers and a continuous, cross-linkable hydrogel containing cellulose nanofibers and any of the given solid particles. The shear during ink extrusion through nozzles of low surface energy facilitates the generation of the enveloped structures via fast and spontaneous phase separation of the emulgel. The skin-bearing architectures enable control of mass transport as a novel configuration for cargo release. As a demonstration, a hydrophilic molecule is loaded in the hydrogel, which is released through the core and skin, enabling regulation of diffusion and permeation phenomena. This 3D-printed functional material allows independent control of strength owing to the hierarchical construction. The new method of fabrication is proposed as a simple way to achieve protection, regulation, and sensation, taking the example of the functions of skins and cuticles, which are ubiquitous in nature.

CELL 214

Preparation and properties of 3D printer filament with poly(lactic acid)/lignin-containing microfibrillated cellulose(L-MFC) derived from organosolv

Ji-Ae Ryu, Jung Myoung Lee, jmylee@knu.ac.kr, Kang-Jae Kim, Tae-Jin Eom. Dept of wood and paper science, Kyungpook National University, Daegu, Korea (the Republic of)

Residual lignin-containing MFC(L-MFC) as a raw feedstock to value-added new materials has been drawn attentions due to enhanced hydrophobicity and low production costs along with increased environmental awareness. In this study, pine organosolv pulp by a high boiling point solvent assisted with catalysts was prepared and then subjected to a fibrillation and drying processing to produce L-MFCs. The L-MFCs and PLA were extruded to 3D filaments for fused deposition modeling (FDM) printer. In this presentation, we will be discussed with the effect of L-MFCs as a reinforcing material on its dispersibility to PLA, thermal and mechanical properties of L-MFC/PLA filament, and its 3D printing quality.

CELL 215

Stimuli-responsive PNIPAm-co-PAA/nanocellulose hydrogels as a flexible and 3D printable biomaterials platform

Xiaohang Sun1, xsun3@ncsu.edu, Sachin Agate1, Preeti Tyagi1, Lucian A. Lucia1, Marian McCord2, Lokendra Pal1. (1) Departments of Forest Biomaterials and Chemistry, North Carolina State University, Raleigh, North Carolina, United States (2) College of Natural Resources, North Carolina State University, Raleigh, North Carolina, United States
A hybrid double-network poly(N-isopropylacrylamide) (PNIPAm-co-PAA)/nanocellulose hydrogel was fabricated by inverted stereolithography (inverted-SLA) 3D printing to establish a new materials platform that exhibits attractive tunable properties including stretchability, thermo-responsivity, optical switching, and bio-adhesivity. It was found that PNIPAm-co-PAA/CNF hydrogels are stretchable and exhibit switchable bio-adhesivity in response to external modulation of the lower critical solution temperature (LCST). Further, changes in the transparency of the PNIPAm-co-PAA/nanocellulose as a function of elongation and LCST modulation were observed. These latter exciting phenomena in the as-printed PNIPAm-co-PAA/nanocellulose hydrogels can be attributed to an interpenetrating polymer network (IPN) of crosslinked PNIPAm and nanocellulose. The prepared PNIPAm-co-PAA/nanocellulose hydrogels can be used as durable temperature-sensitive sensors and functional biomedical devices.

CELL 216

3D printing hydrogel scaffolds of wood nanocellulose with tunable mechanical strength towards biomedical applications

Chunlin Xu, chunlin.Xu@abo.fi, Wenyang Xu, Xiaoju Wang, Stefan Willför. Laboratory of Natural Materials Technology, Abo Akademi University, Turku, Finland

3D-printing enables the creation of tailor-made scaffolds to provide desired architectures, and furthermore, integration with biological cues. Nanocelluloses stand out in the field of bioink formulation serving as platform biomaterial owing to their high mechanical strength as well as the structural similarity mimicking natural extracellular matrix (ECM). We have developed several approaches to tune the mechanical strength of printed scaffolds in order to satisfy the requirements on the ECM microenvironment of different cell lines. In the first approach, cellulose nanofibrils (CNFs) were crosslinked during printing by addition of aqueous Ca solution, followed by a post-printing chemical crosslinking with 1, 4-butanediol diglycidyl ether. With further tuning the crosslinking parameters, the mechanical strength (compressive Young’s modulus) of the printed CNF scaffolds was achieved in the range of 3 to 8 kPa. In the second approach, a novel low-concentration ink formulation based on 1 w/v% CNF and up to 1 w/v% of gelatin methacrylate (GelMA) was developed. By direct ink writing technique assisted by UV post-curing, high-resolution scaffolds of CNF/GelMA were successfully printed and demonstrated high fidelity and stability. By tuning the compositional ratio between CNF and GelMA, the compressive Young’s modulus and local surface stiffness could be well tuned. In the third approach, methacrylate (GGMMA) of galactoglucomannan (GGM), was synthesized by a facile approach and used as an auxiliary component with CNFs in the ink formulations. By tuning the DS of GGMMA and compositional ratio between CNF and GGMMA, the compressive Young’s moduli of the final scaffolds presented a tunable wide spectrum from 2.5 to 22.5 kPa. These approaches will enable formulating inks for printing 3D ECM-mimicking scaffolds to meet the requirements for a variety of in vitro cell-matrix and cell-cell interaction studies in the context of tissue engineering, cancer cell research, and high-throughput drug screening, etc.
Lignin-containing UV curable photopolymers for 3D printing by stereol lithography

Stephen Chmely\textsuperscript{1}, sc411@psu.edu, David P. Harper\textsuperscript{2}, Jordan Sutton\textsuperscript{2}, Kalavathy Rajan\textsuperscript{2}. (1) Agricultural and Biological Engineering, Penn State University, University Park, Pennsylvania, United States (2) The University of Tennessee, Knoxville, Tennessee, United States

The structural heterogeneity of isolated lignin is typically regarded as a detriment to its application in soft materials. However, its molecular weight distribution, ability to absorb UV photons, and multitude of reactive hydroxyl moieties actually make lignin a perfect candidate for incorporation into photoactive resins. These materials traditionally contain precisely engineered mixtures of oligomers, diluents, photoinitiators, and UV attenuators, the identity of which could be closely matched by judicious chemical modifications of lignin. Our groups have demonstrated the utility of lignin in such an application, and we used lignin in new resins for desktop 3D printing by stereolithography. In this presentation, I will highlight our latest achievements, including modifications to lignin that work to tune thermal, mechanical, and photoproperties of resins and cured parts from them. I will also outline our future work towards 100% renewable resins and how these could enable very-large format industrial-scale 3D printing by stereolithography.

Lignin engineering for high-value applications

Mikhail Balakshin\textsuperscript{1}, mikhail.balakshin@renmatix.com, Ewellyn Capanema\textsuperscript{2}, Orlando Rojas\textsuperscript{1}. (1) Aalto University, Espoo, Finland (2) RISE, Stockholm, Sweden

The use of lignin in high-value products requires lignin engineering via understanding structure-properties-performance correlations. This is not possible unless appropriate analytical methodologies are available. An efficient analytical approach should be not only reliable and informative but also high through-put due to very large amount of potential lignin samples to be evaluated. This is because the expected large varieties of feedstocks and biorefinery process types as well as flexibility in the process conditions. Responding to these needs, we developed a comprehensive NMR approach (quantitative \textsuperscript{13}C,\textsuperscript{31}P, 2D NMR) as a core structural analysis that is supplemented by wet chemistry methods. In addition, such important lignin physical (molecular weight distribution, Tg) and colloidal (surface energy, wettability, morphology, electrostatic charges) properties are also included.

It has been recognized that small-scale, high through-put approaches to predict lignin performance in various applications is often the bottleneck in lignin engineering. However, such methods as Automatic Bond Strength Evaluation (ABES) system for adhesive performance and surface/interfacial tension suit express screening of large
number of lignin samples and correlate well with the application performance in the pilot scale.

CELL 219

Dynamics of lignin glass transition

Loukas Petridis, petridisl@ornl.gov. Center for Molecular Biophysics, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

The full utilization of plant biomass for the production of energy and novel materials often involves high temperature treatment. Examples include melt spinning of lignin for manufacturing low-cost carbon fiber and the relocalization of lignin to increase the accessibility of cellulose for production of biofuels. These temperature-induced effects arise from poorly understood changes in lignin flexibility achieved by heating lignin to temperatures above its glass transition. We combine molecular dynamics simulations and experiments to characterize the atomic motions that lead to change in lignin flexibility with increasing temperature.
Getting to the bottom of what makes a “good” lignin for thermoplastic blends

Kim Bessler, kimmarie.bessler@gmail.com, Li-Yang Liu, Muzaffer A. Karaaslan, Qi Hua, Mi-Jung Cho, Scott Renneckar. Wood Science/Advanced Renewable Materials, University of British Columbia, Vancouver, British Columbia, Canada

With new lignin recovery technologies there is an emerging opportunity to utilize lignin in large scale targeted applications. A high-value, large-market application for lignin is the plastics industry. However, there are not clear attributes of lignin that make one lignin “good” for blending with thermoplastics. In this work, fractionated softwood kraft lignin is modified in a stepwise process and blended with a commercially available biodegradable polyester, Ecoflex™. Solvent fractionated lignin and their corresponding hydroxyethyl and ethylpropionate derivatives were melt blended and injection molded into test samples. With up to 40% lignin these materials were tested for their mechanical properties. In addition, processing temperature was evaluated on the corresponding properties. Both the fractionation and the lignin modification greatly impacted the processability of the samples, as the lignin derivative had a significantly reduced glass transition temperature. The work provides insight into structure-property relationships, where a combination of analyses including molecular weight, NMR functional group analysis, thermal analysis, and vibrational spectroscopy is connected to the mechanical performance of the corresponding lignin blends.

Profitable eco-friendly plastics with kraft lignin contents above 90 wt%

Yi-ru Chen, Simo Sarkanen, sarka001@umn.edu. Univ of Minnesota, Saint Paul, Minnesota, United States

Functionality in plastics with lignin contents above 90 wt% depends on how the constituent macromolecular species interact to create material continuity. Unfortunately, since 1960, clarity has been obscured by the working hypothesis that lignin macromolecules are crosslinked “microgels.” The experimental data at that time was not sufficient for choosing between random-coil and “microgel” descriptions of lignin chains, but crosslinking has largely prevailed until now. Nevertheless, ultracentrifuge sedimentation equilibrium studies of paucidisperse kraft lignin fractions in aqueous alkaline eluents from SEC columns clearly reveal random-coil character in the hydrodynamic behavior of individual kraft lignin components. No evidence for crosslinking or long-chain branching has emerged. The more obvious implications may be extended to the native biopolymer. However, the macromolecular species in plastics with high lignin contents differ from random-coil chains; they consist of associated complexes composed of individual components arranged in two distinct domains. The inner domains embody more stable cofacially offset aromatic-rings, while the peripheral domains encompass a higher proportion of edge-on arrangements. It is through the
Peripheral domains that adjoining complexes intermesh to establish material continuity in plastics with high lignin levels. If the chemical conditions used to produce a particular lignin preparation have eliminated many of the more flexible inter-unit linkages, a suitable plasticizer may be capable of enhancing aromatic-ring mobility in the peripheral domains of the complexes. Alternatively, blending with another lignin preparation could introduce some of the components that may revive non-functional peripheral domains. Thus, while softwood kraft lignin alone forms a weak material with 9.5 MPa tensile strength, blending with 5 wt% 1,8-dinitroanthraquinone generates formulations with 34 MPa tensile strengths that surpass polyethylene (30 MPa). Washing commercial kraft lignin with water, air-drying and blending with 5 wt% miscible 1,8-dinitroanthraquinone would produce a mixture for compounding to a plastic material with $0.86 per kg estimated production cost. The starting kraft lignin would incur the only additional cost. Otherwise, blending washed kraft lignin with 10 wt% maple γ-valerolactone lignin creates an all-lignin material with 35 MPa tensile strength, but a minimum selling price for maple GVL lignin has not yet appeared.

**CELL 222**

Lignin-polysaccharide hybrid molecules improve technical properties of polymer films

Gunnar Henriksson¹, ghenrik@kth.se, Petri Olnonen¹, Ioannis Dogaris¹, Anna Abbadessa¹, Lars Wagberg². (1) Fiber and Polymer Technology, Royal Institute of Technology, Stockholm, Sweden (2) KTH Fibre Polymer Techn, Stockholm, Sweden

It is today widely accepted that different polysaccharide molecules are covalently crosslinked by lignin in wood, which most likely has an important function for the mechanical properties of lignified cell walls. In chemical pulping and bleaching of wood, these covalent networks are degraded during the removal of lignin resulting in a more flexible fiber suitable for paper making and other applications. It has also been shown that during pulping processes, i.e., in for example sulfite pulping and thermomechanical pulping, water soluble oligomers are released that carry both polysaccharide and lignin functionalities in the same molecules. Using laccase-initiated radical coupling on these oligomers polymeric hybrid molecules that alternate polysaccharide and lignin structures can be created. Such heterogeneous and amphiphilic molecules might have properties that are interesting for several applications. In this study we investigated how polyelectrolyte multilayers are formed between anionic hybrid molecules and cationic polymers and how these films, deposited on polymer films, can modify and potentially improve different properties of the composite films. It was demonstrated that regular multilayers readily could be formed on polyethylene films. As consequences, water contact angles were decreased, UV absorbances were increased and barrier properties for oxygen and humidity were improved. Thermal stability properties were on the other side virtually unaffected. Generally, these properties increased with an increasing number of attached layers. Therefore, coatings with these bio-based lignin-polysaccharide hybrid molecules can improve the technical properties of films for various applications, such as food packaging.
Lignin-based polyurethanes adhesion to native aluminum surfaces

Demetrio J. Santos¹, demetrio.santos@ufabc.edu.br, Lara B. Tavares², Mohammad Zamanzade³, Wulff Possart⁴. (1) Engineering, Modeling and Applied Social Sciences Center, ABC Federal University, Santo André, São Paulo, Brazil (2) Entropic Solutions, São Caetano do Sul, SP, Brazil (3) Chair for Adhesion and Interphases in Polymers, Saarland University, Saarbruecken, Germany (4) Chair for Materials Science and Methods, Saarland University, Saarbruecken, Germany

The use of lignin-based reactive polyurethane (LPU) adhesive for native aluminum surfaces was investigated using thin film deposition of several lignin preparations via spincoating. Diluted solution of 4,4'-methylene diphenyl isocyanate (4,4'-MDI) and the soluble fraction of three lignins (powder Kraft lignin pH 3.5 or powder Kraft lignin pH 8.5 or oxypropylated Kraft lignin) in THF were used for LPU thin film deposition via spin coating on aluminum (PVD layer on silicon wafer). The resulting film thickness ranged from 8 nm to several micrometers. The chemical state of the three LPU compositions was assessed in the thin films by infrared external reflection absorption spectroscopy (IR-ERAS). Thus the relation to adhesion mechanisms of LPUs to a native aluminium surface was evaluated. Uniform and homogeneous films were formed with all lignin types used. Results revealed a higher consumption of NCO in the formulation with the alkaline Kraft lignin than with the acid one, despite its lower hydroxyl content. A gradient of unreacted NCO was observed into LPU thin films obtained with the powder Kraft lignin types. While residual NCO is found in thicker films, the 15 nm films did not contain unreacted NCO anymore. That indicates the activating effect of native aluminum surface on LPU formation. The results provide a novel perspective of the bonding of lignin-containing polyurethanes to native aluminum surfaces.

Uniform and size-controllable hollow carbon structure (HCS) utilizing a kraft lignin fraction as a carbon precursor

YUXIAO CUI¹, cuiyuxiao2018@gmail.com, Martin Lawoko², Anna Hanner³. (1) Fibre and Polymer Technology, KTH, Royal Institute of Technology, Stockholm, No State, Sweden (2) WALLENBERG WOOD SCIENCE CENTRE, KTH, Royal Institute of Technology, Stockholm, No State, Sweden

Hollow carbon spheres (HCS) have attracted considerable attention because their large specific surface area, chemical stability, thermal insulation, high mechanical strength and many potential applications. However, using the general templating method to prepare the HCS is either non-environmentally friendly or it is hard to control the morphology. Lignin as the world’s largest, by volume, renewable phenolic polymer. It is an inexpensive, nontoxic, and sustainable carbon-rich biomass material. Lignin contains an
aromatic backbone which is attractive because it should confer rigidity to macromolecular structures, more than other bio-based building blocks, such as fatty acids and glucose. Owing to the high concentration of hydroxyl functionality which includes both aliphatic and phenolic hydroxyls, the chemical modification of lignin is interesting, and can be applied to control the morphology. In addition, the aromatic nature of lignin may constitute a natural and sustainable alternative to petrol-based compounds such as terephthalic acid or bisphenol A, where there are concerns from the environmental and health point of view.

Herein, we chose a fractionated lignin, with a well-defined molecular structure, as the carbon precursor. The synthesis process of HCS was investigated and the effect of different processing parameters during the hydrothermal carbonization treatment step was investigated. A dynamic formation process of the hollow carbon structures was identified based on the results of SEM, TEM and FTIR. The formation mechanism was elucidated, which improved our understanding of how the hollow lignin spheres are formed during the soft templating step and consecutive hydrothermal carbonization step. The resultant HCSs were stable and of narrow size distribution, and their performances in electrochemical applications were evaluated.

**CELL 225**

Supramolecular assembly of natural polyphenols/Fe(III) coordination complexes for versatile microcapsule engineering

*Heiko Lange*, Matteo Gigli1, matteo.gigli@unive.it, Claudia Crestini1. (1) Department of Molecular Sciences and Nanosystems, University of Venice Ca' Foscari, Venice, Italy (2) Department of Pharmacy, University of Naples, Naples, Italy

Nanoencapsulation of active substances with controlled release in harmless matrices has been the subject of numerous scientific efforts mainly due to the significant biomedical potential of such endeavors. The main target of the here presented study is the contemporary exploitation of the specific high self-aggregating and iron(III) complexing ability of natural polyphenols (NPs), with other desirable features such as: (a) biocompatibility, (b) antioxidant activity to protect the active, (c) possible intrinsic relevant biological activity in synergy with the active, (d) amphiphilic characteristics, (e) targeted stimuli responsive release upon iron depletion.

In particular, we demonstrated that the combination chelation chemistry with oil in water emulsion principles and low energy sonication provides a simple, yet very effective one-pot strategy for the fabrication of NPs-based microcapsules of controlled architecture. Under these conditions capsules rapidly assemble thanks to the π-stacking propensity of NPs and their metal chelating capability at alkaline pH, without any significant chemical modifications of the NPs structure. The developed process was systematically optimized so as to create the foundations for the morphology and the yield of the capsules being modulated as a function of sonication time, power and surface contact area.

The addition of ferric ions in the initial emulsion has proven to be of pivotal importance
for increased shell stability, as an additional effect of the complexation of the phenolic groups with the metal ions. Furthermore, reduced shell thickness (allowing for greater loading efficiencies) and lower release kinetics have been observed with respect to neat NPs-based capsules.

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Lignin microcapsules: Current scope and future perspectives

Heiko Lange¹, heiko.lange@uniroma2.it, Luc Zongo³, Elisavet D. Bartzoka³, Claudia Crestini². (1) Department of Pharmacy, University of Naples 'Federico II', Naples, Italy (2) Department of Molecular Science and Nanosystems, Università Ca’ Foscari, Venezia, Italy (3) Department of Chemical Sciences and Technologies, University of Rome 'Tor Vergata', Rome, Italy

Micro- and nanostructures of natural polymers have received steadily growing interest as a result of their peculiar properties and applications superior to their bulk counterparts. Along these lines, we achieved the encapsulation of active small molecules into micro- and nano-scaled capsules made out of various technical lignins using ultrasound. The ultrasound technique proved to be an essential tool in this production of nano- and micro-scaled features, since it offers simplified ways to achieve reactions and size-determining conditions. Starting from oil in water emulsions containing lignins and eventually actives to be incorporated, we present thus a rapid, simple, and robust method of one step assembly of lignins and their suitable coordination complexes into metal-free as well as iron-re-enforced nano- and microcapsules for biomedical and agricultural applications.

In light of potential applications, stimuli responsive behaviour of lignin microcapsules (LMCs) has been investigated along with the detailed characterisation of their stability profiles. The disassembly of LMCs was found to reflect kosmotropic and chaotropic
characteristics of buffer systems and physiological solutions. A connection between the Hofmeister series and the stability profile of lignin micro-scaled materials can be delineated. LMCs showed excellent stability in water and under high temperature and pressure (autoclaving conditions). Active release is efficiently triggered by pH-changes and balancing chaotropic and kosmotropic effects via salinity tuning.

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Cellulose/lignin-based films: Tuning functional properties through phenolics organization and interactions with the matrix

veronique aguie\textsuperscript{1}, veronique.aguie@inra.fr, Guillaume Riviere\textsuperscript{2}, Elise Gerbin\textsuperscript{1,4}, Betty Cottyn\textsuperscript{4}, Florian Pion\textsuperscript{4}, Monika K. Osterberg\textsuperscript{3}, Stéphanie Baumberger\textsuperscript{4}, bernard kurek\textsuperscript{1}. (1) INRA - FARE Lab, Reims, FRANCE, France (2) Aalto University, Espoo, Finland (3) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (4) INRA-AgroParisTech, Versailles, France

Lignin is the second most abundant renewable resource from lignocellulosic biomass next to cellulose. It has multifunctional properties such as UV absorption, antioxidant, adhesive, antimicrobial, and water-proofing properties. These properties, associated to their diversity of functional groups, make lignins potential cheap fillers for well-designed nanomaterials, without any extensive chemical modification request \cite{1-3}. Nevertheless, the variability of lignin composition and the influence of lignin processing and formulation on its structure might influence the properties of the materials. The objective of this paper is to elucidate the relationships between lignin structure and their antioxidant properties within a cellulose-based solid matrix used as model biodegradable polymer carrier. Different phenolic structures and forms were prepared from a grass soda technical lignin sample (PB1000, GreenValue Enterprises LLC) and compared to the initial lignin sample: monomers, oligomers, nanoparticles (CLPs), demethylated and depolymerized fractions. Cellulose nanocrystals and nanofibrils were used to prepare the films and evaluate their lignin carrier power in water or ethanolic media. Antioxidant capacity was assessed through radical scavenging tests combined to spectroscopic and physico-chemical characterizations. The results demonstrate that lignin is a promising radical scavenger and that the control of its structuration in complex matrix is required to preserve its antioxidant property both inside the film or during release of active compounds.

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Lignin-based smart polymers: Self-healing and shape memory polymers

Hoyong Chung\textsuperscript{1,2}, hchung@fsu.edu, Sundol Kim\textsuperscript{1,2}. (1) Chemical and Biomedical Engineering, Florida State University, Tallahassee, Florida, United States (2) Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida, United States
This presentation discusses lignin-based self-healing polymers and shape-memory polymers. The lignin-based self-healing polymer is lignin-graft-poly(5-acetylaminopentyl acrylate) (lignin-graft-PAA), which has been prepared by the covalent linkage of chemically modified lignin with PAA, which is an end-group functionalized polymer. The key synthetic step is a copper-catalyzed azide–alkyne cycloaddition or “click” reaction to join together the lignin and PAA. The PAA was prepared via reversible addition–fragmentation chain transfer (RAFT) polymerization of monomers containing multiple hydrogen-bonding sites on their pendants in the form of acetylamino functional groups. The lignin-graft-PAA shows autonomic self-healing properties (93% of original maximum stress recovery) due to the high concentration of hydrogen-bonding sites from acetylamino group. The second lignin-based smart polymer is a crosslinked lignin-polycaprolactone (lignin-PCL) which has a shape memory function. The new lignin-based polymer is prepared by two steps: lignin modification/PCL preparation and crosslinking via thiol-ene reaction. Lignin’s hydroxyl groups was modified to have alkenes via carbodimide-mediated esterification with 4-pentenoic acid. Separately, PCL was prepared by stannous octoate catalyzed ring-opening polymerization. The synthesized alcohol-terminal four-arm PCL was further modified to have thiol terminals via esterification with 3-mercaptopropionic acid. The prepared lignin–alkene and PCL–SH were crosslinked by a photoredox thiol-ene reaction in the presence of Ru(bpy)₃Cl₂ catalysts and p-toluidiene. The crosslinked lignin–PCL demonstrates a thermal responsive shape memory function at 80 °C (flexible above transition temperature for deformation) and 10 °C (solidified below cool temperature for temporary shape).

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Lignin-fatty acid hybrid nanocapsules: Phase-change materials for thermal energy storage

Mika Sipponen²,¹, mika.sipponen@mmk.su.se, Alexander Henn², Paavo Penttilä², Monika K. Osterberg². (1) Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden (2) Department of Bioproducts and Biosystems, Aalto University, Aalto, Finland

To curb greenhouse gas emissions, the energy efficiency of the industry and built environment needs to be significantly increased. In particular, scalable processes are needed to produce sustainable materials for thermal energy storage (TES). We present a simple method to co-precipitate fatty acids and softwood kraft lignin to form hybrid nanocapsules (hyb-NCs) as a new type of phase-change material (PCM). Due to their particle porosity accessible to water, aqueous dispersion of hyb-NCs solves the heat conductivity issue and can be used as an active heat transfer fluid in dynamic TES systems. In dry form, hyb-NCs were stable over 290 melting-solidifying cycles. We used a combination of tp-DSC, TEM, AFM, DLS, and SAXS experiments to understand the particle morphology of hyb-NCs. Our results show that lignin was responsible for the stabilization of the internal fatty acid phase as well as the outer capsule surface, making
hyb-NCs colloidally stable. This work opens new avenues for the utilization of lignin-based hybrid materials in energy and environmental applications.
Tadahisa Iwata, atiwata@mail.ecc.u-tokyo.ac.jp. Dept. of Biomaterial Sciences, The University of Tokyo, Bunkyo-Ku, Japan

The increasing environmental and economic concerns on the utilization of petrochemicals have led researchers to rely on plant biomass as a feedstock for the synthesis of polymeric materials. Recently, our group succeeded to synthesize new thermoplastics from polysaccharides such as xylan, glucomannan, curdlan, paramylon, pullulan, etc by esterification and found interesting thermal, mechanical, optical properties. In this paper, xylan, glucomannan, curdlan, paramylon and pullulan ester derivatives are synthesized and thermal and mechanical properties are investigated. Furthermore, in the case of curdlan and paramylon ester derivatives, branched ester derivatives were also synthesized and their melt-spun fibers and injection molding could be processed and their properties were investigated (Figure 1).

More recently, we succeeded the one-pot synthesis and development of unnatural-type bio-based polysaccharide, α-1,3-glucan. The synthesis can be achieved by in vitro enzymatic polymerization with GtfJ enzyme, one type of glucosyltransferase, cloned from Streptococcus salivarius ATCC 25975 utilizing sucrose, a renewable feedstock, as a glucose monomer source, via environmentally friendly one-pot water-based reaction (Figure 2). Furthermore, acetate and propionate esters of α-1,3-glucan were synthesized and characterized. More recently, we succeeded to in vitro synthesize graft copolymers with two different kinds of α-1,3 and α-1,6 glycosidic linkages of glucose.
β-1,3-glucan (Curdlan or Paramylon)

Figure 1. Synthesis of α-1,3-glucan ester derivatives
Enzymatic Polymerization (*in vitro*) of Linear α-1,3-glucan

![Biofilm on teeth’s surface (polysaccharides)](image)

- Produced in the formation of dental plaque
- α-1,3 and α-1,6 branched polysaccharides

**Figure 2.** *In vitro* synthesis of α-1,3-glucan

**CELL 231**

**Complexation-induced shrinking of 3D-printed hydrogel constructs**

*Carl Schuurmans*¹, *Jiaxing Gong*², *Anne-Metje van Genderen*¹, *Rosalinde Masereeuw*¹, *Yu Shrike Zhang*², *Tina Vermolen*¹, T.Vermolen@uu.nl. *(1) Pharmaceutics, Utrecht University, Utrecht, Netherlands (2) Division of Engineering in Medicine, Harvard Medical School, Cambridge, Massachusetts, United States*

Hydrogels based on derivatized biopolymers have potential for use in tissue engineering and advanced *in vitro* models. When processed through 3D printing, hydrogels can be shaped to recapitulate some of the complex structures present in the human body. Most manufacturing techniques for hydrogels however fail to accurately mimic small features of the human anatomy such as vasculature.
We have established a method to shrink 3D printed hydrogels based on incubating a hydrogel in an aqueous solution containing an oppositely charged polymer. This subsequently leads to charge neutralization and water expulsion (fig. A). This technique allows for shrinking of both polycationic and polyanionic hydrogels. Fig. B shows the difference in volume between a swollen chitosan-based hydrogel and a similar chitosan hydrogel shrunk by incubation in an alginate solution. Hydrogels based on several biopolymers (i.e. GelMA, HAMA, alginate and chitosan) were shrunk with polyelectrolyte solutes of different charge densities (fig. C). The main physico-chemical parameters found to determine hydrogel shrinking capacity were the electrostatic interaction strength and the macromer weight percentage of the initial hydrogel. Shrinking was found to be compatible with hydrogels processed through various 3D printing strategies. For example, coaxial printing could be used to form hollow hydrogel tubules with an inner diameter of ~300µm (Fig. D, E). These tubes could be shrunk to an inner diameter of ~20 µm. Viability of encapsulated cells (e.g. MCF-7 and C2C12) during shrinking was retained. Culturing cells adherent to the constructs was done post-shrinking, avoiding toxicity of the non-complexed polycationic polymers present during the shrinking process.

Concluding, a method to shrink 3D-printed hydrogel structures was developed and characterized. Printed structures (e.g. hollow tubes) were obtained with feature sizes down to 10-20 µm. We expect this method to advance development of more accurate models of human tissue by allowing creation of smaller structures from hydrogels.
Everything degrades! Nanocellulose composites with on-demand degradability

Florian Mayer¹, Andreas Mautner², Alexander Bismarck¹, alexander.bismarck@univie.ac.at. (1) Faculty of Chemistry, University of Vienna, Vienna, Vienna, Austria (2) Institute for Materials Chemistry & Research, University of Vienna, Wien, Austria

Composite materials are structural materials consisting of at least two distinctive materials that have properties that outperform those of any individual component. The use of nanocellulose as reinforcement for renewable polymers has resulted in nanocomposites with attractive mechanical and barrier properties with the promise of being more environmentally benign. These composites will (bio)degrade but are problematic to be recycled. We will demonstrate a model nanocellulose composite system with triggered degradability and hence recyclability of the nanocellulose. Our model system is utilising bacterial cellulose, the purest form of nanocellulose, which was modified with a set of hydrolysable vinyl esters. Modified bacterial cellulose fibrils will be used as the reinforcing agent in a polymer matrix synthesised by photopolymerisation of divinyl ester. The use of vinyl ester-based polymer matrices allows for easy recyclability of the composites by acid or base hydrolysis. From the hydrolysate we can reclaim for reuse the cellulose fibrils, poly(vinyl alcohol), which is the backbone of the polyvinyl ester and diacids.

Polymers are enabling molecular engineering of the interface in cellulose-containing bionanocomposites

Eva E. Malmstrom¹,², mavem@kth.se, Alexandros Efraim E. Alexakis¹,², Maria Rosella Telaretti Leggieri³, Joakim Engstrom¹,², Tahani Kaldéus¹,². (1) Dept of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden

By 2050, the plastic waste accumulated in nature or landfills is estimated to be around 12 billion tons, assuming that the current production and waste management trends continue. The rapidly growing environmental awareness has increased the interest for cellulose-containing materials to a completely new level. Especially the nanocelluloses have attracted significant interest due to their low specific weight and their promising mechanical properties. However, to utilize their full potential in material applications, it is often necessary to control the surface properties to prevent aggregation, enhance thermal and water resistance as well as to impart processability for example.
The surface properties of cellulose can be modified by polymers, either by covalent or non-covalent approaches. The covalent approach can either be performed by ring-opening polymerization of lactones for instance, from the hydroxyl groups available on the cellulose surface, or by controlled radical polymerization from an immobilized initiator. The non-covalent approach is based on adsorption of a polymer to the cellulose surface. Nanocelluloses are often charged from the manufacturing process to impart colloidal stability and the charges can be utilized to electrostatically adsorb charged polymers while maintaining the colloidal stability.

Hitherto, the majority of all described routes for polymer modification of nanocelluloses involves the use of organic solvents. We have recently increased our efforts to develop more water-based procedures for efficient engineering of the interface of cellulose. So far, our work has mainly made use of tailor-made latex nanoparticles synthesized through RAFT-mediated surfactant free emulsion polymerization with subsequent polymerization induced self-assembly (PISA), and more recently also by a combination of grafting-to and grafting-from. This strategy involves the design of an oligomeric macroinitiator, containing both cationically charged groups that allow for adsorption to cellulose and initiating moieties that can be used for grafting-from once the macroinitiator is physiosorbed to nanocellulose.

The aim of this contribution is to discuss some of our most recent findings when using polymer chemistry as a tool to engineer the surface of nanocelluloses, and to present some characteristics of the corresponding materials.

**CELL 234**

**Linear polyamidoamines derived from α-amino acids as phosphorus-free surface-confined intumescent flame retardants for cotton fabrics**

Jenny Alongi¹, Paolo Ferruti², amedea manfredi¹, Federico Carosio³, Minna Hakkarainen⁴, Elisabetta Ranucci⁵, elisabetta.ranucci@unimi.it. (1) Università degli Studi di Milano, Milan, Italy (2) Dipt Di Chimica Org E Ind, Milan, Italy (3) Politecnico di Torino, Alessandria, Italy (4) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (5) University of Milan Chem, Milano, Italy

Bioinspired linear polyamidoamines (PAAs) prepared by the polyaddition of bis-acrylamides, such as for instance N,N'-methylenebisacrylamide (M), with different α-amino acids, including glycine (G) and cystine (C), were studied as surface-confined flame retardants (FRs) for cotton. The polyamidoamine deriving from N,N'-methylenebisacrylamide and glycine, coded as M-G, proved to be an effective FR in horizontal flame spread tests (HFST), extinguishing the flame at 5% add-on. Its activity was attributed to its intrinsic intumescence, which produced carbonaceous crusts sheltering the underneath fibers that remained apparently intact. In vertical flame spread tests (VFST), M-G failed to extinguish the flame even at 30% add-on. The M-C polyamidoamine, containing disulphide groups in the main chain, extinguished the flame
in VFST at add-ons ≥ 16, due to its ability to produce, upon thermal degradation, sulfur-containing volatiles capable to quench the flame radicals. The FR effectiveness of M-G-C copolymers with different G/C ratio was compared with that of the M-G and M-C homopolymers and of M-G/M-C blends of the same compositions. In HFST, both copolymers and blends extinguished the flame. For instance, M-G50-C50 and (M-G/M-C)50/50 extinguished the flame even at 7% add-on. In VFST, the copolymers with ≥50% M-C units, similarly to M-C, inhibited cotton combustion at 16% add-on. At the same add-on, the M-G/M-C blends failed to extinguish the flame. It may be concluded that, different from blends, copolymers combined the merits of both homopolymers in all tests.

In the presence of 1% cellulose-derived nano-graphene oxide (nGO) carbon dots, M-C inhibited ignition at lower add-on (12%), thus demonstrating synergism between the two components. Synergism was confirmed by assessing the synergism effectiveness parameter for the residual mass fraction and by comparing the calculated and experimental thermogravimetric curves in air for the cotton/M-C-nGO systems. In oxygen combustion cone calorimetry tests, the presence of nGO did not improve the already good performances of M-C, supporting the hypothesis that the action of both components takes place in the gas phase. During the warm-up phase, also nGO, known as radical scavengers, were transferred into the gas-phase.

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Bio-inspired anticoagulant hydrogels for blood purification

Weifeng Zhao1, zhaoscukth@163.com, Shudong Sun1, Changsheng Zhao1, Xiaohua Zhang1, Qiang Wei1, Baihai Su2. (1) College of Polymer Science and Engineering, Sichuan University, Chengdu, China (2) Sichuan University, Chengdu, China

Haemophilia are hereditary haemorrhagic disorders characterized by deficiency or dysfunction of clotting factors VIII or IX. Water-soluble anticoagulants used in traditional blood purification are commonly associated with inactivation of clotting factors to avoid forming clotting. Both of these defects are associated with bleeding episodes affecting soft tissue, joints, and muscles, resulting in internal haemorrhage or massive haemorrhage. Though the deficiency or abnormality of clotting factors pose serious risks to patients, it’s essential for the proceeding of blood purification. Sufficient anticoagulation without excessive risk of bleeding remain a significant clinical need. Inspired by anticoagulant activity of heparin and haemophilia, we prepared anticoagulant hydrogels by in situ cross-linking polymerization. We herein present a totally regional anticoagulant strategy. Completely anticoagulant micro-sized spheres capable of binding clotting factors (VIII, IX and XI) are filling into an anticoagulative cartridge. The pseudo-haemophilia blood is reached after passing through the column of hydrogel anticoagulant. After the circulation in vitro, the pseudo-haemophilia blood returns the function of coagulation to the normal level.

CELL 236
Lignocellulose derived hydrogels, thermosets and thermoplastic materials

Minna Hakkarainen, minna@kth.se. Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Lignocellulosic biomass is a fascinating and versatile source of raw materials for fabrication of functional materials. In recent works we prepared interesting hydrogels, thermosets and thermoplastic materials by modifying lignin and cellulose derivatives with functional carbon materials produced by carbonization of lignin or cellulose. Carbon products were produced by modifying previously developed microwave-assisted hydrothermal carbonization process. We have earlier shown that this type of carbon products are extremely effective property enhancers for e.g. chitosan derived hydrogels and for production of bioactive biomedical scaffolds and surfaces. Here, we fabricated carboxymethyl cellulose and lignosulfonate-based hydrogels, which were shown to be effective adsorbents for organic and inorganic contaminants, thus, demonstrating good potential for wastewater purification. The curing behavior, rheological properties, adsorption capacity and recyclability of the prepared hydrogels were evaluated. In another work cellulose derived carbon products were utilized to covalently modify cellulose, which led to interesting thermoplastic cellulose films with good mechanical properties. Finally, a series of kraft lignin based thermosets were successfully synthesized by a one-pot heat curing method composed of lignin, PEG400 and citric acid. Depending on the composition the mechanical properties were widely tunable from flexible to rigid. Some of the materials also exhibited excellent thermally-stimulated shape memory properties.

CELL 237

Spatiotemporal migration of target nucleotide in partly oligodinucleotide crosslinked hydrogels identifies toehold as a critical parameter in the swelling dynamics

Eleonora P. Jonasova, Astrid Bjørkøy, Bjorn T. Stokke, bjorn.stokke@ntnu.no. Department of Physics, NTNU The Norwegian University of Science and Technology, Trondheim, Norway

Hydrogels including oligodinucleotide (ODN) supported crosslinks alongside covalent ones in acrylamide-based networks are promising responsive soft material. The versatile molecular recognition capability of the embedded DNA strands can be transformed to affect swelling properties of the hydrogel itself. Destabilizing the hybridized ODN crosslinks in the gel by introducing target DNA strands will alter the swelling state. While the overall swelling response caused by such competitive displacement reactions has been published, insight into the molecular underlying process is not yet reported. In the present study we expand on the understanding of these materials from the overall swelling to characterization of the cascade of processes, e.g. migration and binding of the target DNA to the ODN, the subsequent crosslink opening and the altered swelling state. These interrelated processes display a
spatiotemporal evolution depending on the experimental boundary conditions. Using a combination of interferometry and confocal laser scanning microscopy (CLSM), the spatiotemporal evolution of the migrating target ssDNA in half spherical hydrogels synthesized at the end of optical fibers was determined. The fluorescence intensity profiles were converted to concentration profiles accounting for adverse optical effects. The data indicate that the faster binding of an invading ssDNA target realized by a longer base pair toehold for the initial binding to the ODN slows down the migration of the target. As a result, only a moderate increase in the overall swelling rate is observed with longer toeholds despite their faster rate of binding. The parameters obtained by fitting the data using a diffusion-reaction model were discussed in view of molecular parameters of the target ssDNA and ODN functionalized hydrogels. This study clearly identifies toehold length as a critical molecular parameter affecting the overall coupling between the migration and binding of this target in ODN-co-acrylamide hydrogels.

CELL 238

High yield process to bacterial cellulose nanocrystals

Timo Pääkkönen1, timo.paakkonen@aalto.fi, Panagiotis Spiliopoulos1, Nonappa Nonappa5, Katri S. Kontturi2,3, Paavo Pentilä1, Mira Viljanen4, Kirsi Svedström4, Eero Kontturi1. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) VTT Technical Research Centre of Finland, Espoo, Finland (3) Institute of Materials Chemistry and Research, University of Vienna, Vienna, Austria (4) Department of Physics, University of Helsinki, Helsinki, Finland (5) Department of Applied Physics, Aalto University, Espoo, Finland

Conventional CNC process is based on the use of ~65% aqueous sulfuric acid leading to difficult purification procedures, high water consumption, and poor yields. To tackle these problems, our group has recently introduced a method that utilizes HCl vapor or pressured HCl gas. Here, we describe a full, improved production process of CNCs by combining HCl gas hydrolysis and TEMPO-mediated oxidation. The degree of polymerization was successfully reduced from 2160 to 220 with a CNC yield of >80% while TEMPO-oxidation provided carboxylic charges on the CNC surface, resulting in a stable dispersion. Wide Angle X-ray Scattering (WAXS) indicated that the crystallinity index increased from 45% to 61%, i.e., a ~30% increase, which may play a role in the high yield of CNCs. It appears that HCl gas hydrolysis on BC is faster and more efficient than on plant-based fibers. A highly porous structure of the freeze-dried BC is also more accessible to cavitation during sonication when dispersing the CNCs. In terms of sustainability, the benefits of the new process can be outlined in three categories: (i) >50% higher yield of CNCs than with the usual liquid/solid procedure, (ii) BC can be prepared from, e.g., sugars in food waste, minimizing the exploitation of forest resources, and (iii) dry gaseous acid can be easily recycled and the water consumption is greatly minimized because of the simple purification procedure of CNCs. Indeed, the full recovery of aqueous acid has prevented the sustainable, large scale use of acid in hydrolysis of cellulose in the past. Furthermore, the thermal stability of carboxylic
groups should be higher than those of sulfate groups which are the norm for charged groups on CNCs.

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CNC-like cellulosic whiskers (C-LCWs): Production and evaluation of morphologically and chemically diversified lignocellulosic nanomaterials

Junyong Zhu\(^1\), jzhu@fs.fed.us, Huihui Wang\(^2\), Jonathan Zhu\(^4\), Umesh P. Agarwal\(^2\), Rolland Gleisner\(^2\). (1) USDA Forest Service, Madison, Wisconsin, United States (2) Forest Products Lab, Madison, Wisconsin, United States (3) South China University of technology, Guangzhou, China (4) Biochemistry, University of Wisconsin, Madison, Wisconsin, United States

It has been generally considered by the broad scientific community that there are only two types of cellulosic nanomaterials: cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). Yet, the range of cellulose crystallinity for CNCs was never defined in the literature. The difficulties in accurate measure cellulose crystallinity using traditional x-ray diffraction and spectroscopic techniques added more ambiguity to the definition of CNCs, and created two detrimental confusions that has significant commercial implications: (1) all morphologically CNC-like cellulosic particles, i.e., CNC-Like Cellulosic Whiskers (C-LCWs) from different processing methods, are termed CNCs. (2) CNCs have been unnecessarily used for many applications such as rheology modifiers, hydrogels, 3D printing, etc., where only individually separated and easily dispersible C-LCWs are necessary without the requirement of crystalline property. In this presentation, we will introduce the concept of CNC-like cellulose whiskers (C-LCWs) and its production using concentrated solid acid (easing recycling) hydrolysis beyond lab bench scale, i.e., in kg scale, and (2) to characterize some physical properties of C-LCWs such as crystallinity, morphology, and suspension rheology. Our goal is to clarify some misconceptions in the literature to facilitate commercialization of cellulose nanomaterials.

CELL 240

CNF from pulp fibers with different hemicellulose and lignin content

Christian Aulin, christian.aulin@ri.se, Elisabet Brännvall, Andreas B. Fall. RISE, Stockholm, Sweden

Although the energy demand is quite high during the manufacturing of cellulose nanofibers (CNF), the cost for the starting material, the pulp, is substantial as often high purity cellulose dissolving pulp is used. Pulps for board and paper have higher yield, as they also contain hemicellulosases and, in the case of unbleached pulp, lignin. These pulps would be a more economical starting material and it is of interest to understand how the presence of hemicellulose and lignin affects the fibrillation process and CNF properties.
This work reveals the structure and chemical composition of CNF prepared from different pulping processes of softwood. Ordinary kraft cooks were performed as well as kraft cooks with addition of polysulfide to increase the hemicellulose content. Part of the pulps were bleached to remove residual lignin, thus making it possible to compare pulps with and without lignin. The CNFs were prepared by high-pressure homogenization of the pulps subsequent to either an enzymatic hydrolysis or a carboxymethylation pre-treatment. The CNFs were characterized with respect to degree of polymerization, rheology, charge density and turbidity, all indicating that homogeneous CNFs were obtained with a degree of fibrillation comparable to CNF prepared from dissolving pulp. The properties of the CNFs were correlated to the performance of films prepared from the corresponding CNFs. The mechanical properties of the films were found to be dependent on the degree of polymerization of the CNF and comparable, and in some cases, outperforming those derived from dissolving pulp. The films possess excellent gas barrier properties. Oxygen and water vapor permeability did not correlate with lignin content but depended most significantly on CNF charge density.

In summary, this study provides useful information and knowledge for understanding the importance of raw material and pulping processes for the quality of CNF for various types of applications.

CELL 241

High-yield production of lignocellulosic nanocrystals using green deep eutectic solvent system

Jungang Jiang, Nancy Carrillo, Feng Jiang, feng.jiang@ubc.ca. Department of Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

In this presentation, we are proposing to produce lignocellulosic nanomaterials (LCNs) from untreated or least treated woody biomass at high yield using green deep eutectic solvent (DES). Several benefits can be envisioned by using untreated woody biomss for LCNs production. Firstly, it is much cheaper compared to chemical pulp due to the lack of chemical delignification and bleaching steps; Secondly, yield of LCNs could be increased by using raw woody materials containing all three major components; Thirdly, the presence of lignin is expected to modify the LCNs to make it more hydrophobic, which is ideal for improving the interfacial interactions with synthetic polymer when being used as reinforcing fillers. DES has been considered as a green and safe solvent as it is nonvolatile and recyclable. The low melting point of DES makes it extremely easy to be used in lab and industrial scale. DES is consisting of a hydrogen bond acceptor (quaternary ammonium salt) with a hydrogen bond donor. The hydrolysis was carried out at different reaction temperatures (80 and 100 °C), reaction times (3 and 6 h), as well as different chemical ratios. A yield as high as 68.3% of LCNs could be obtained at 80 °C for a 3 h reaction. The obtained LCN showed brown color and absorbance peak at 280 nm, indicating the presence of lignin particles. The LCNs appeared as rigid rod-like nanocrystals under TEM with width around 5-6 nm and length ranging from 200 to 500 nm. Lignin nanoparticle aggregates could also be observed under TEM with dimension ranging from several tens to hundreds of nanometers. Our
research demonstrates the feasibility of producing LCNs from woody biomass at high yield, adding new products to the lignocellulosic nanomaterials that could find potential applications as concrete and/or plastic additives.

CELL 242

**Nanofibrillated cellulose for sustainable textile coloration**

**Smriti Rai, smritirai@uga.edu, Raha Saremi, Suraj Sharma, Sergiy Minko.** The University of Georgia, Athens, GA, USA, Bishop, Georgia, United States

The conventional cotton textile dyeing process uses a significant amount of water and chemicals. According to a World Bank study, the textile dyeing industry contributes 17 to 20% of water pollution, 4% are not treatable. Treating effluents is an expensive process.

We have developed a nanocellulose gel-based dyeing/coating technology for cotton textiles which utilizes the high surface ($\sim10^3$ m$^2$/g) and fibrillary mechanism of adhesion of nanofibrillated cellulose materials. Nanocellulose gel-based dyeing of cotton fabrics with reactive dyes provides comparable dyeing performance with only $1/10^{th}$ of salt, alkali, and water consumption.

A similar methodology is used for pigment dyes, for example, indigo. Nanocellulose gel acts as a carrier for indigo particles, whereas chitosan (during post-treatment) as a physical crosslinking agent, which improves fixation and adhesion of the nanocellulose fibrillary network with indigo particles and fabrics. This method provides lighter or darker shades in a one-step process in contrast to the conventional method where several dips are required in a reduced vat followed by oxidation to develop darker shades. We have developed a green dyeing technology for indigo dyeing, which eliminates the use of any reducing agent and alkali as well as reduces water consumption up to a factor of 25.
From microfibrils to fragments: Nanocellulose deconstructed

Scott Renneckar¹, scott.renneckar@yahoo.com, Kim Bessler¹, Mi-Jung Cho¹, Pooneh Ghasvareh¹,³, Qi Hua¹, Amanda M. Johnson¹, Muzaffer A. Karaaslan², Li-Ting Lin⁴,¹, Li-Yang Liu¹. (1) Wood Science/Advanced Renewable Materials, University of British Columbia, Vancouver, British Columbia, Canada (2) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (3) Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada (4) Materials Engineering, University of British Columbia, Vancouver, British Columbia, Canada

Since the early days of cellulose research, scientists have investigated the structure of microfibrils by unraveling cell walls with chemical and mechanical treatments. These studies have provided the foundation for structural models of the cellulose microfibril. Over the years, these models have been refined through computational studies and new imaging technologies, providing insight into fibril dimensions and morphology. Further chemical modification via oxidation, followed by mechanical treatment has provided evidence that microfibrils can be deconstructed beyond the ‘elementary fibril’ level. When split along their length, fragments can have single digit Angstrom-level thickness with nanometer widths. In addition, other isolation methods of nanocellulose materials have reported the fragmentation of cellulose within the microfibril structure. These microfibril fragments, broken parallel to the length, provide interesting properties with different quantities of hydrophobic surface area, depending upon the fragmentation plane. Hence, fragmentation in this fashion yields higher surface area particles and potentially Janus like surface structures that would be important in multiphase systems. The intrigue of further creating higher surface area materials through fragmentation coupled with its significant impact on material properties when used as a reinforcement phase has not been fully explored for cellulose. The questions of how these microfibrils are split and if deconstruction can be controlled will be examined in this talk.

Facile and comprehensive approach, accounting for substrate interactions, for the characterization of the dimensions of cellulose nanofibrils

Blaise L. Tardy, blaise.tardy@aalto.fi, Bruno Mattos, Orlando Rojas. Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland

Nanocelluloses have been emerging as an outstanding building block for the promotion of circular economy concepts. Alongside tempo-oxidized cellulose nanofibers and other chemically defibrillated nanofibers, mechanically fibrillated cellulose nanofibers (CNFs) are currently amongst the most investigated in materials science. CNFs can form robust networks on their own such as nanopaper, porous materials with a low density and a high surface, and can be imbued with functionalities when they serve the role of a
cohesive matrix. However, the characterization of their morphological characteristics still poses significant challenges because of their rather high aspect ratio preventing the characterization of both their length, and their diameter simultaneously. Achievement of an in-depth characterization is required to facilitate the prediction of the properties of the materials they form. In the present work we describe an important step forward towards a complete description of the morphological characteristics of CNFs. We introduce two new concepts, negative contrast imaging scanning electron microscopy (SEM), where CNFs were spotted onto a variety of metallic surfaces prior to SEM imaging (optimized for contrast). The dimensionalities obtained with the latter method were cross-correlated with a thorough morphological mapping by atomic force microscopy to obtain a precise description of the cross sectional area of CNFs. Appropriate physical considerations such as deconvolution of tip-based artefacts and substrate adhesion of the fibers were used to correct the data obtained. The methodology was aimed for cost- and time-efficiency as nanocelluloses are regularly employed for low-cost and high-volume applications. The values we obtained for cross-sectional area, surface area and aspect-ratio of the fibrils differ substantially to the generally used value These values were used to predict the behavior of particulated nanocomposites and were shown to provide accurate description of the fiber network and their interaction with particles. Combined with the justifications for accuracy in the morphological description of CNF and formed composites, the present work highlights important considerations for future works involving nanocelluloses.

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Controlled structural polydispersity of microfibrillated cellulose

Per A. Larsson1, perl5@kth.se, Goksu Cinar Ciftci1, Anastasia V. Riazanova1, Hans Henrik Øvrebø2, Lars Berglund1, Lars Wagberg1. (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Borregaard AS, Sarpsborg, Norway

Nanocelluloses have indeed been identified as green nanomaterials of tomorrow, and are today in their most refined form commonly classified as either cellulose nanocrystals or cellulose nanofibrils based on their aspect ratio, but there is also the less refined and structurally more polydisperse grade of microfibrillated cellulose (MFC). In this work we have fractionated MFC to facilitate systematic studies and control of the effect of particle morphology and colloidal properties such as surface charge on the rheological properties of suspensions and on the mechanical and physical properties of MFC films. Fractionation and after-following scanning electron microscopy revealed significant portions of particles small as cellulose nanofibril aggregates, as well as significant portions of still remaining fibre fragments. In terms of rheology, where each fraction had distinctly different rheological characteristics, this fraction with larger particles was found to have the largest effect on the linear viscoelastic properties of the unfractionated complex mixture; a removal of the coarsest particles, constituting about 7% of the MFC, resulted in a six-fold increase in storage modulus. With respect to the making of films and their properties, the particle size, rather naturally, also had an effect. However, in
terms of mechanical properties, it could be concluded that all fractions except the one with largest particles resulted in good mechanical properties, but also that films of unfractionated MFC were not too sensitive to inclusion of larger particles. Overall, this study gives insight on how the MFC particle size contribute to the properties of films and suspensions, and that selective removal, or addition, can be used to tune system properties, especially the rheological properties.

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Potter’s wheel wood-clay

Doron Kam1,2, doron.kam@mail.huji.ac.il, Michael Layani1, Omri Fisher1,3, Oded Shoseyov2, Shlomo Magdassi1. (1) Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel (2) Plant Sciences and Genetics in Agriculture, The Hebrew University of Jerusalem, Rehovot, Israel (3) Industrial Design, Bezalel Academy of Arts and Design, Jerusalem, Israel

Pottery, the process of forming objects from clay, is one of the oldest inventions in materials, and is dated before the Neolithic period (29,000–25,000 BC). The potter’s wheel was invented in Mesopotamia in the Ubaid period (6,000 - 4,000 BC) and revolutionized pottery production (wheel invented around 3,000 BC). Around the industrial revolution, pottery was automated by Wedgwood manufacture (1759) which set another huge jump in the ceramic industry.

The word 'ceramic' comes from the Greek word meaning 'pottery', and it is most often used as a synonym. Here we present a new approach for utilizing pottery, while replacing the ceramic materials with wood powders and cellulose nanocrystals as binders. We applied the conventional potter’s wheel process for obtaining objects composed 100% wood.

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Oriented β-cyclodextrin/chitosan polymer adsorption on nanocellulose surfaces and its capability of microcystin-LR adsorption

Diego Gómez Maldonado1, dzg0023@tigermail.auburn.edu, Iris B. Vega Erramuspe1, Ilari Filipponen2, Leena-Sisko Johansson3, Matthew Waters4, Maria S. Peresin1. (1) School of Forestry and Wildlife Science, Auburn University, Auburn, Alabama, United States (2) Department of Chemical Engineering, Alabama Center for Paper and Bioresource Engineering (AC-PABE), Auburn University, Auburn, Alabama, United States (3) School of Chemical Technology, Aalto University, Aalto, Finland (4) Department of Crop, Soil and Environmental Sciences, Auburn University, Auburn, Alabama, United States

Functionalization of biopolymers, and especially lignocellulosic substrates, opens up the possibility to utilize renewable materials in different high-end products as well in day-to-day commodities. In fact, modified cellulose is currently used in a wide variety of
products such as food additives, films, cosmetics, fibers and paints. Chitosan, on the other hand is considered the second most abundant biopolymer; however, currently is less utilized even though it contains amine functional groups. These groups can be modified with a wide range of green chemistry processes, which in turn makes it an appealing substrate in the development of environmentally friendly materials. Furthermore, the irreversible adsorption between cellulose and chitosan allows for the opportunity to build composite materials using the layer-by-layer approach.

In this project, chitosan was modified with TEMPO-oxidized β-cyclodextrin (Ch-TOCD), using different NH:COOH ratios. These grafted polymers were then adsorbed onto nano-fibrillated cellulose surfaces and the material was used to capture Microcystin-LR by physical adsorption. This toxin is relevant due to its relation to liver cancer. It has been recently found in the algal blooms in concentrations hundred-folds higher than what is considered safe by The World Health Organization.

Ch-TOCD was characterized using Elemental Analysis (EA), X-Ray Photoelectron Spectroscopy (XPS), and Fourier Transform Infrared Spectroscopy (FT-IR). The ability of this material to adsorb onto cellulose surfaces and the capacity to capture microcystin-LR was studied with Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) and by Surface Plasmon Resonance (SPR), which allows the following in real time of the adsorption behavior.

**CELL 248**

**Linking adhesion force to area in molecular contact measured by FRET spectroscopy**

*Mônica Gaspar Simões, gasparsimoes@tugraz.at, Georg Urstoger, Robert Schennach, Ulrich Hirn*. Institute of Paper, Pulp and Fibre Technology, Graz University of Technology, Graz, Austria

Adhesion is caused by intermolecular forces that directly depend on the area in molecular contact (AiMC). However, there are several difficulties related with AiMC measurement, mainly because areas that appear to be in full contact, when observed at higher magnification, show no AiMC (Fig. 1).

Here, we show how AiMC can be measured using Förster resonance energy transfer (FRET) spectroscopy, a technique capable of measuring the nanometric distance (0-10 nm) between surfaces in contact (Fig. 1). FRET uses the non-radiative energy transferred between fluorescence molecules (donor and acceptor) to study their exact molecular distance. If the molecules are close enough to each other (molecular contact), a FRET signal can be detected. Through a FRET signal, it is possible to calculate the energy transfer efficiency (FRET efficiency) which indicates the degree of molecular contact between the surfaces (Fig. 1).

For the experiments, poly(2-Hydroxyethyl methacrylate) (pHema) thin films labelled with the fluorescence molecules, 7-(diethylamino)coumarin-3-carbohydrazide (DCCH, donor) and fluorescein-5-thiosemicarbazide (FTSC, acceptor) (Fig.1), were produced by the doctor blading technique at the same dye(s) molar concentration and bonded using different pressure loads. Our results reveal that AiMC increases with the pressure
applied in the bonded thin films, resulting in higher FRET efficiency and adhesion force. Hence, in this work, we implement an experimental measuring method for AiMC and validate the relationship between AiMC (measured with FRET spectroscopy) and adhesion (force energy) in polymeric thin films; what represents a breakthrough in the measure of AiMC and its influence on adhesion. Future work related with topic will be focus on the molecular interaction and bonding strength between cellulose thin films and other polysaccharides of interest.

**Fig. 1** Two surfaces in physical contact observed at the nanometric scale. AiMC decreases with magnification. In AiMC zone a FRET signal can be observed between Donor and Acceptor thin films. One can also see that FRET does not occur in the areas with no molecular contact.

**CELL 249**

**Enhanced adsorption of expansin for improved enzymatic hydrolysis of cellulose**

Peiqian Zhang\(^2,1\), zpqtu@163.com, Wim Thielemans\(^1\), Rongxin Su\(^2\). (1) Chemical Engineering, KU Leuven, Kortrijk, Belgium (2) State Key Laboratory of Chemical Engineering, Tianjin University, Tianjin, China
Effective regulation of expansin adsorption is key to improve the efficiency of the major bottleneck of lignocellulose biological pretreatment. In this work, we investigated the effect of pH, temperature, and divalent zinc cations on the adsorption of *Bacillus subtilis* expansin (BsEXLX1) onto cellulose. Increased temperatures up to 45°C increased the initial adsorption rate and the irreversible amount of BsEXLX1 adsorbed onto the cellulose. Notably, the adsorption was favored by acidic conditions (pH 4.8), whereas alkaline conditions (pH 10) facilitated BsEXLX1 desorption. Since BsEXLX1 is similar to cellulase, this can useful to guide the process to recover BsEXLX1 and cellulase together. We further researched the cellulose enzymolysis with endoglucanase Cel7B in the presence of BsEXLX1 and divalent zinc cations. Adding both BsEXLX1 and Cel7B in the presence of zinc cations improved the initial adsorption rate, adsorption capacity, and pseudo-steady-state rate when compared to the case where divalent zinc cations were absent, resulting in increased destruction of intermolecular hydrogen bonds, a decrease in cellulose crystallinity, an increase in the specific area and the accessibility by BsEXLX1 with the divalent zinc cations providing more complexation sites for the enzyme. These findings pave the way to effective regulation of BsEXLX1 adsorption and thus improve lignocellulose conversion.

**CELL 250**

**Hyperspectral near-infrared imaging assessment of confine surface anhydride modification of solid wood**

*Muhammad Awais¹, Muhammad.Awais@aalto.fi, Michael Altgen¹, Mikko Mäkelä¹,², Lauri Rautkari³.* ¹ Deparment of Bioproducts and Biosystems, Aalto University, Espoo, Uusimaa, Finland ² Department of Forest Biomaterials and Technology, Swedish University of Agricultural Sciences, Umeå, Västerbotten län, Sweden

Hyperspectral imaging is a powerful analytical technique that provides spatial and structural information of analytes into the substrate by transforming each pixel into a sampling cell. The large images set of information can be evaluated with large population statistics and multivariate data analysis. We report the spatial distribution of the confine solid wood surface modification in the tangential face of Scots pine samples using near-infrared hyperspectral imaging. Multivariate data analysis methods provide a robust distribution of acetic anhydride in wood samples. A principal component analysis (PCA) model was used to decompose the high-dimensional data into orthogonal components. Moreover, a partial least square discriminant analysis (PLS-DA) model has been developed for the classification of modified and unmodified wood. The model was optimized and validated with an external test dataset. The receiver operation characteristics (ROC) were compared at different latent variables. Confocal Raman spectroscopy was used to complement the acquired results. It was concluded that the acetic anhydride had higher accessibility in earlywood compared to the latewood. The PLS-DA model investigates spectral information and visualizes the degree of acetylation into the wood surface. It enhances the practical applicability of hyperspectral imaging (NIR) in the field of renewable materials and wood material sciences.
Effects of nanofibrillated cellulose (CNF) at the wood-based matrix/resin interface

Maria C. Iglesias\textsuperscript{1,2}, mci0006@auburn.edu, Philip McMichael\textsuperscript{1,2}, Osei Asibe Asafu-Adjaye\textsuperscript{1,2}, Brian Via\textsuperscript{1,2}, Maria S. Peresin\textsuperscript{1,2}. (1) School of Forestry and Wildlife Science, Auburn University, Auburn, Alabama, United States (2) Forest Products Development Center, Auburn University, Auburn, Alabama, United States

Wood-based panels are commonly used as building materials both for interior and exterior purposes. Their production and utilization has been increasing over the past few decades due to the good and useful properties they present. Adhesive-bonded products make up to 80% of the wood alternatives on the global market, and of that, urea-formaldehyde (UF) makes up more than 81% of the resins used. Formaldehyde-based resins are primarily used due to the combination of their effectiveness and relatively low cost, as well as their ease of application and lack of color. Nevertheless, their main disadvantages are the lack of tack and the emission of formaldehyde over time.

In an attempt to improve UF performance, the utilization of microfibrillated cellulose as an alternative, has been demonstrated to be effective. However, more understanding on
the mechanisms of the interactions at the interfaces which allow a better performance of the adhesive is of relevant importance. 

In this work, we studied interfacial interactions between UF and melamine urea formaldehyde (MUF) with bleached (BCNF) and unbleached (LCNF) cellulose nanofibrils. To this end, we used surface sensitive techniques such as Quartz Crystal Microbalance with dissipation monitoring (QCM-D) complemented with Surface Plasmon Resonance (SPR) to study system interactions on thin films. Additionally, morphology and surface free energies were investigated using Atomic Force Microscopy and Contact Angle Measurements (CAM). Finally, particle boards with different adhesive/CNF formulations were produced and tested in terms of thickness swelling (TS), water absorption (WA), modulus of elasticity (MOE), and modulus of rupture (MOR).

**CELL 252**

**Analysis of industrial pitch in biorefinery process waters using 2D thin layer chromatography (TLC)**

*Werner Schlemmer¹, werner.schlemmer@tugraz.at, Melissa Egger¹, Madeline Daechert¹, Jussi Lahti¹, Markus Gschiel¹, Andrea Walzl², Erich Leitner², Stefan Spirk¹, Ulrich Him¹*. (1) Institute for Paper-, Pulp- and Fiber Technology, Graz University of Technology, Austria, Graz, Austria (2) Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Austria, Graz, Austria

Pitch is a common impurity in biorefinery process waters. Due to the water circulation, the pitch content in the process waters is increasing, leading to problems with pulp and additives as well as the mechanical units.

The state-of-the-art analysis protocol involves silylation of the compounds with subsequent GC-MS analysis. However, it is expensive, time consuming and the results depend on the columns used as well as the operator. Herein, we present a rapid method for the separation and quantitative analysis of the main industrial pitch components (fatty acids, fatty alcohols, sterols, resin acids) using 2D TLC. The advantages of alkaline and acidic eluents are combined to achieve a good separation efficiency. Via visualization using a matrix-sensitive dye, the quantification can be carried out using the MatLab image analysis toolbox. The results of model compounds as well as industrial pitch samples are compared to GCGC-MS analysis showing good coherence.

The described protocol allows quick and simple analysis of industrial pitch mixtures. This method has the potential of becoming a standard method for industrial applications.

**CELL 253**

**Wet-spun microfibers from nanochitin for biomedical applications**
Ling Wang1, ling.wang@aalto.fi, Nazanin Z. Ezazi2, Liang Liu3, Janika Lehtonen1, Maryam Borghei1, Rubina Ajdary1, Heli Viskari1, Rafael grandee5, Helder Santos2, Orlando Rojas1,4. (1) Aalto University, Espoo, Finland (2) Helsinki university, Helsinki, Finland (3) Nanjing Forestry University, Jiangsu, China (4) University of British Columbia, Vancouver, British Columbia, Canada (5) Universidade de São Paulo, São Paulo, Brazil

We isolated chitin nanofibers from crab shells, deacetylate the fibrils and further fibrillated it into nanofibrils. The obtained aqueous colloidal nanochitin suspensions (1%, 1.5% 2%) were wet-spun into microfibers using three different coagulation baths, namely, acetone, NaOH(aq) and ammonia solution. The microfibers obtained from alkaline conditions kept a circular cross-section while the ones obtained from acetone were irregular. The wide angle X-ray scattering demonstrated that the nanochitin oriented in the longitudinal direction, with similar fibril orientation index (0.72-0.78) for all fibers. Microfibers spun from 1 and 1.5% concentration as well as alkaline baths displayed better mechanical properties compared to the ones spun from 2% or acetone bath. In contrast to nanocellulose-based wet-spun fibers, which that were too weak to measure the wet strength in water, chitin fibers had a much better wet-strength: 68% (acetone), 52% (NaOH) and 46% (NH3H2O) residual strength compared to the dry strength. Meanwhile, due to the presence of amino groups, the fibers had a high thermal stability. Finally, when applied for cardiac and bone, chitin microfibers demonstrated high biocompatibility in vitro for both types of proliferating cells. This opens new possibilities for advanced bio-based materials as healing patches and scaffolds for heart and bone tissues.

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Sustainable dimethyl ether recycle system for regenerating super absorbent polymers

Cheng-Chi Wu1, Srivatsan Raghavan1, sriva@umich.edu, Alexandra Pine1, pinea@umich.edu, Dimitris I. Collias2, Brian J. Love3. (1) Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States (2) Proctor Gamble, West Chester, Ohio, United States (3) Univ of Michigan, Ann Arbor, Michigan, United States

We constructed a system and leveraged an existing method in which Dimethyl Ether (DME) was used to evaluate extraction rates from both water and a simulated urine solution, which were saturated in commercial grade superabsorbent polymers (SAP), similar to those found in commercial diapers. Using pressurized gas inlets for both DME and nitrogen and a closed, stainless steel fluid transport system, it was possible to introduce a saturated SAP specimen in a mesh construct and allow DME to interact with the superabsorbant polymer. By toggling the pressure to levels above and below 0.6 MPa, using gravity assistance, we could drive the condensation of the DME and convey it through the system. After volatilization of the DME post extraction, we confirmed we were successful in extracting portions of the saturated liquid from the SAP. It was
hypothesized that relying on pressure induced adiabatic condensation of DME would be energetically less intensive than thermally extracting the fluids. We also considered the recyclability of the saturated and dehydrated SAP through DME extraction. We extracted ~99% of DI water from SAP and ~89% of the simulated urine solution from SAP and will present energy and material cost assessments linked with recycling superabsorbent polymers.
Enhancing the surface area and porosity characteristics of cellulose-based monoliths using inorganic salts

Prakash Parajuli, prakash.parajuli@ttu.edu, Yang Hu, Noureddine Abidi. Fiber Biopolymer Research Institute, Texas Tech University, Lubbock, Texas, United States

Aerocellulose with high surface area and better pore characteristics have attracted considerable attention due to their properties such as biodegradability, biocompatibility, etc. In this study, aerocellulose monoliths with enhanced surface area and porosity were prepared by adding inorganic salts into the cellulose solution. The effects of the concentrations (0 – 10%) of monovalent salts with different cationic radius (LiCl, NaCl, and KCl) on the surface area, pore characteristics and microstructure were investigated by means of Nitrogen adsorption-desorption isotherm and Scanning electron microscopy. Moreover, the effects on physicochemical and thermal stability were studied using Fourier transform infrared spectroscopy (FTIR) and Thermal gravimetric analysis (TGA). The results showed that the aerocellulose prepared using inorganic salt particles achieved improved porous characteristics, lightweight, lower crystallinity, and better thermal stability, as compared to the control. Specifically, the addition of 5% NaCl...
particles led to about 80% increase in specific surface area and about 5% increase in porosity as compared to the control. Furthermore, when the concentration of salt particles was maintained at 1%, the use of KCl led to aerocelluloses with the highest porosity and the lowest density whereas LiCl gives the highest specific surface area. This shows that the salt with different cationic radiiues behaves differently in tuning the porosity characteristics of the aerocellulose. This study demonstrates the effectiveness of inorganic particles to manipulate the surface area and the pore characteristics which provides a facile route to achieve enhanced surface area and improved pore characteristics of the aerocellulose.

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Electron paramagnetic resonance analysis of moist heat-treated wood

**Jeffrey A. McVay**, mcvay018@d.umn.edu, **Steven M. Berry**, Wim Willems. (1) Chemistry and Biochemistry, University of Minnesota Duluth, Plymouth, Minnesota, United States (2) Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, Minnesota, United States (3) Firmolin Technologies BV, Deurne, Netherlands

The process of heat-treating wood can impart desirable properties, such as dimensional stability, aesthetically appealing color, and increased resistance to moisture and fungal decay, without the addition of chemicals. It also allows for the potential broader applications of indigenous softwoods, instead of relying on the often, slower growing hardwoods. A means to quantify the extent of heat treatment is therefore desired. Correlation between free radical content and the temperature of heat treatment has been explored by others. We therefore measured the radical content of samples with electron paramagnetic resonance (EPR) spectroscopy. We treated samples in a pilot-scale kiln (an industrially relevant process), as well as in the highly controlled and quantifiable environment of a thermogravimetric analysis (TGA) instrument. With these samples we measured the free radical content using EPR to determine the rate of radical formation with temperature and the effects of moisture content. Our long-term goal is to find reliable methods for quantifying the extent of heat treatment in thermally treated wood, and to be able to correctly account for the effects of moisture.

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Tetra-functional furan-based epoxy-amine thermosetting systems with superior characteristics

**Xi Chu**, xichu1007@gmail.com, Giuseppe R. Palmese, John J. LaScala. (1) Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States (2) Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States (3) Army research laboratory, Aberdeen Proving Ground, Maryland, United States
Current research in thermosetting formulations for adhesive applications has investigated the incorporation of furan based building blocks in epoxy-amine networks through chemistries designed to achieve superior thermal and mechanical properties. This study investigates the structure-property relationships of furan-based epoxy monomers and the influence of functionality. Epoxy-amine thermosets were prepared using novel tetra-functional and di-functional furan-based monomers cured with a furan-based amine hardener. In comparison to the di-functional epoxy monomer, the tetra-functional epoxy showed a significantly higher glass transition temperature. Mechanical testing in compression reveals that both systems possess high room temperature Young’s modulus (above 5 GPa) and high yield strength compared to traditional epoxy systems while maintaining high strain to failure values. This behavior is attributed to the presence and the interactions of the furan rings within the network structure. Ongoing work seeks to elucidate this behavior. Thermogravimetric analysis shows the furan-based systems possess nearly 50% of char yield, which promotes potential use in fire protection applications. The unique properties of the furan-based systems could be useful for adhesive, coating and composite applications that require high stiffness, creep resistance, and toughness.

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Single-molecule protein-carbohydrate dissociation characterization using acoustic force spectroscopy

Markus Hackl, markus.hackl@rutgers.edu, Bhargava Nemmaru, Shishir P. Chundawat. Chemical and Biochemical Engineering, Rutgers University, Piscataway, New Jersey, United States

Carbohydrate-based biopolymers are found abundantly across all forms of life and play a major role in biomolecular recognition processes. For example, cellulosyltic microbial enzymes adsorption to carbohydrate polymers like cellulose plays a critical role in the deconstruction of lignocellulosic biomass to fermentable sugars. Hence, characterization of protein adsorption to carbohydrates is often the focus of various fields of research ranging from targeted drug delivery to cellulosic biofuels production. Several bulk-ensemble based analytical methods have been developed to characterize the adsorption/desorption kinetics of proteins to carbohydrate polymers. However, many such methods rely on over-simplified models to characterize binding interactions that often do not reflect the underlying molecular mechanism of protein binding to highly multivalent carbohydrate-based ligands. But we have so far lacked access to suitable analytical methods to carefully probe protein-carbohydrate binding interactions from a first-principles point of view.

In this study, we use a highly multiplexed Acoustic Force Spectroscopy technique to measure the single-molecule binding lifetimes and unbinding rupture forces of carbohydrate-binding module (CBM) proteins to model cellulosic films. We characterize the dependence of the piconewton force loading rates on the non-equilibrium unbinding forces of various CBM proteins and use established theory to extract relevant equilibrium binding constants. Furthermore, we elucidate the role of conserved aromatic
residues in the CBM carbohydrate recognition sites on the unbinding process to develop binding models that provide insight into the molecular mechanisms of protein adsorption and orientation on multivalent cellulosic polymers. In summary, our single-molecule force spectroscopy method allows us to systematically probe the structure-function relationships driving multivalent protein adsorption to carbohydrate-based polymers.

**CELL 259**

**Effects of dehydration on plant primary cell wall cellulose from grazing-incidence wide angle X-ray scattering**

Joshua T. Del Mundo¹, jtd37@psu.edu, Sintu Rongpipi¹, Daniel Cosgrove⁵, Esther Gomez¹,², Enrique Gomez¹,²,³. (1) Chemical Engineering, Pennsylvania State University, State College, Pennsylvania, United States (2) Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania, United States (3) Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania, United States (4) Biomedical Engineering, Pennsylvania State University, University Park, Illinois, United States (5) Biology, Pennsylvania State University, University Park, Pennsylvania, United States

Cellulose is a major component of plant primary cell wall, which is a highly hydrated system of polysaccharides responsible for the mechanical properties of plant tissues during growth. Much of the characterization of plant cellulose has been conducted in the dried state, mainly due to the instrumental limitations of various techniques. For example, in the case of X-ray scattering, the amorphous scattering of water often dominates data. Nevertheless, drying of the sample may lead to artifacts that are not representative of the highly hydrated plant primary cell wall. Thus, we have examined the crystalline parameters of hydrated plant primary cell wall using Grazing-Incidence Wide-Angle X-Ray Scattering (GIWAXS). GIWAXS enables high signal-to-noise from thin, wet tissues due to enhanced scattering near the critical angle of cellulose. Scattering experiments on onion epidermis under humid conditions reveal Angstrom-level changes in the structure of semi-crystalline cellulose microfibrils. The removal of water around the microfibril was found to interfere with (110/1-10) lattice packing, as indicated by changes in peak intensities and lattice spacings.

**CELL 260**

**Use of high frequency ultrasound for the depolymerization of cellulose into glucose**

SOMIA haouache¹, somia.haouache@univ-poitiers.fr, Isabelle Capron², francois jerome⁴. (1) 86000 Poitiers, Institute of Chemistry of Environments and Materials of Poitiers, Poitiers, France (2) INRA, Nantes, France

The depolymerisation of cellulose to glucose has become an important reaction paving the way to various relevant biobased chemicals. However this reaction requires
overcoming a high energy barrier, essentially because cellulose exhibits a strong hydrogen bond network and highly cohesive van der Waals interactions. Nowadays the selective depolymerization of cellulose can be carried out with enzymes or supercritical water. However, these technologies are still limited in few applications due to either a low space time yield or severe reaction conditions of temperature or pressure. We show in this communication that high frequency ultrasound (HFUS) can selectively depolymerize cellulose into glucose in water without any catalyst, at low temperature (60°C) and pressure (P_{atm}). The concept is based on the formation of cavitation bubbles inside which water is dissociated to H and OH radicals. Once these cavitation bubbles implode, radicals are propelled onto the surface of cellulose where they induce the cleavage of the glycosidic bond. We will show that the nature of the gas atmosphere (O_2, Ar, H_2 and mixtures of Ar/H_2 and Ar/O_2) plays a very important role by increasing or lowering the amount of radicals formed. Under optimized conditions, glucose was quickly obtained with 60% yield within only 2 min of ultrasonic irradiation at 520 kHz. Very importantly, we will show that during the depolymerization of cellulose, in situ generated radicals are selectively transferred on the cellulose particle surface, avoiding any side oxidation of released glucose in the bulk solution. The depolymerization of cellulose was visualized by electronic microscopies (STEM and MED), monitored by means of X-ray diffraction and chromatographic technics (SEC-MALLS, A4F-MALLS and HPLC), and glucose production estimated by mass spectrometry. Finally, we will discuss the applicability of this process to different grades of cellulose with different purities and particle sizes.

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Robust cathodes for structural batteries from cellulose nanofibrils and chiral cobalt oxide nanoparticles

Hugo Françon¹, francon@kth.se, Per A. Larsson¹, Nicholas Kotov², Lars Wagberg¹. (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) University of Michigan, Ann Arbor, Michigan, United States

The adoption of electric vehicles (EVs) needed to mitigate the climate change is forestalled by their short operating range compared to gasoline vehicles. EVs need to store a larger amount of energy, without significantly increasing their weight. An elegant way of achieving this is to replace inert structural components in EVs with structural batteries that can serve in dual capacity – charge storage and load-bearing. For that purpose, structural batteries must present a combination of mechanical strength, low weight and high capacity, while being made of safe and environmentally friendly materials.

Cellulose nanofibrils (CNFs) have a remarkably high stiffness (E = 138 GPa) and display high compatibility with electrically active materials, such as carbon nanotubes (CNTs) and conducting polymers. These and other properties including safety and environmental friendliness make them particularly promising nano materials for the preparation of robust composite materials for energy storage.

Another active component of interest is cobalt oxide (Co_3O_4), a well-studied, high
performance cathode material used in commercial Li-ion batteries. A recent study also
demonstrates the preparation of chiral Co₃O₄ nanoparticle by using a simple aqueous
oxidative reaction. Compared to their non-chiral form, these nanoparticles present a
more open structure that could enable the preparation of cathodes with improved
charge transport and capacity. Moreover, assemblies of chiral Co₃O₄ nanoparticle on
CNFs are expected to show enhanced cyclability due to spring-like mechanics of helical
structures.
In this study, we present the preparation of novel composites based on CNFs and chiral
Co₃O₄ nanoparticles as well as their subsequent use as state-of-the-art cathodes for
structural batteries. These high-specific-energy materials were also tailored to have a
high-electrical conductivity by using a controlled incorporation of either CNTs or
conducting polymers. Cathodes in the form of both highly porous aerogels and dense
nanopapers were prepared, providing a wide window of structural, mechanical and
energy storage properties.

CELL 262

Lignin first using benign catalysts

*Joseph S. Samec*, joseph.samec@su.se. Organic Chemistry, Stockholm university,
Stockholm, --- Select One ---, Sweden

The "Lignin-First" has received considerable attention as a promising technology to
fractionate and valorize the three major components of lignocellulosic biomass. The
process comprise a solvolysis step that is responsible for the liberation of lignin and
hemicellulose from the cellulose and also a transition metal catalyzed reduction of the
lignin fraction to generate high yields of monophenolic compounds. An obstacle to
overcome in order to commercialize this process is the use of either precious metals in
catalytic amounts or less precious ones in large amounts.
We have developed a few methodologies that overcome the shortcomings described
above: In one approach, a cobalt catalyst on N-doped carbon support has showed
equivalent yields to the ones reported; in another approach, a zeolite-based catalyst
that uses control with both reactive sites and confinement control has been employed to
reach reasonable yields of monomers from both lignin and carbohydrates. Also, an
organocatalytic approach to convert bark to yield suberin derived fatty acids and lignin is
described. Examples to convert these monomers to useful chemicals will be given.

CELL 263

Formic acid fractionation of lignocellulosic biomass and valorization of lignin

*Yongchao Zhang¹, Xiaoju Wang¹, Pedram Fatehi², Qingxi Hou³, Menghua Qin⁴, Stefan
Willför¹, Chunlin Xu¹*, chunlin.Xu@abo.fi. (1) Laboratory of Natural Materials
Technology, Abo Akademi University, Turku, Finland (2) Lakehead University, Thunder
Bay, Ontario, Canada (3) Tianjin University of Science Technology, Tianjin, China (4)
Taishan University, Taian, China
Lignocellulosic biomass, which mainly consists of cellulose, hemicellulose, and lignin, is the most promising substitute to fossil-based resources. To profitably valorize the lignocellulosic biomass, efficient and green approaches need to be developed for fractionation and sequential conversion of each fractionated streams to high-value products. In this work, formic acid fractionation under pressure was firstly explored for the selective separation of lignocellulosic biomass. The process under optimized conditions using 85% formic acid, a liquor-to-solid ratio of 7:1, and a temperature of 145 °C for 45 min presented a high-performance in fractionating bamboo into 42.2% cellulose fiber, 31.5% lignin, and 8.5% hemicellulose fractions. To reveal the structural features of the fractionated lignin and to facilitate the subsequent valorization, different analysis techniques, including FTIR, GPC and NMR, were performed. The results proved that the formic acid fractionation under pressure could accelerate the isolation of lignin by enhancing the cleavage of interunitary bonds in lignin (β-O-4, β-β, and β-5′). Moreover, the high purity and abundant functional groups in the isolated lignin, such as phenolic hydroxyl and carboxylic groups, greatly increase its possibility of the subsequent conversion. It was found that the formic acid lignin could be processed into nanoparticles, which exhibited spherical morphology and a uniform particle size distribution. Thereafter, multi-functional nanocomposites based on lignin nanoparticles and nanocellulose prepared from the fractionated cellulose fiber were developed and characterized. Moreover, modified lignin-based hybrid magnetic nanoparticles were also prepared and presented excellent performance for the adsorption of heavy metal ions. This work has demonstrated the feasibility for building an integrated biorefinery platform based on formic acid fractionation of lignocellulosic biomass.

CELL 264

Continuous purification and fractionation of corn stover lignin with renewable aqueous solvents for high-value applications

Graham W. Tindall, Evan A. Miyasato, Joshua Chong, Mark C. Thies, mcths@clemson.edu. Clemson Univ, Clemson, South Carolina, United States

Two renewable solvents in aqueous solutions, namely acetic acid and ethanol, were each investigated for the purification and fractionation of crude corn stover lignins via our Aqueous Lignin Purification with Hot Agents (ALPHA) process. Initial results and phase-behavior measurements were performed on the lab scale in small (~10 g) batches, but the work was subsequently scaled up to continuous-flow operation (~50 g/hr), so as to produce the quantities of lignin needed for processing and conversion into carbon fibers, and for polyl substitution in the production of polyurethane (PU) foams. Results indicate that when the continuous-flow unit incorporates a static mixer for the mixing and equilibration device, residence times at temperature (e.g., 90 °C) are reduced to 20-30 s, significantly minimizing if not eliminating any possible undesirable condensation reactions within the lignin. The reduction in metals and silica content obtained with each solvent, and the ability to obtain the desired ultrapure lignin having a metals content of < 100 ppm will be discussed. In addition, the performance of each aqueous solvent in partitioning the lignin by molecular weight into each of the two liquid
phases created via ALPHA (i.e., a solvent-rich and a polymer-rich phase), will be presented. Finally, the ability of continuous ALPHA to isolate a metals-free corn-stover lignin of well-defined and controllable molecular weight will be assessed, with the results being compared to our previous, successful work with Kraft lignins.

CELL 265

Can biogenic formaldehyde provide a novel lignin analysis?

Niloo far Shivyari, shivyari@vt.edu, Charles E. Frazier. Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States

Thermochemical reactions of lignocellulose feature formaldehyde generation, and lignin is probably the main source because in alky-aryl ether bonds the gamma methylol-carbon is activated by benzyl cation formation. For instance, short periods of heating (~80-150°C) generate formaldehyde and reduce beta-O-4 levels, but with little or no change in sugar composition. While lignin appears to be the principal source of biogenic formaldehyde, unequivocal proof is elusive due to the complex role played by nonstructural phytochemicals, the extractives. The stable carbon isotope ratio \(^{13}C/^{12}C\) could perhaps prove the molecular source of biogenic formaldehyde; that is because lignin, polysaccharides, and extractives respectively exhibit distinct isotope ratios. On behalf of the wood-based composites industry, our long-term goal is to distinguish biogenic and synthetic formaldehyde; but our short-term goal is to determine if isotope ratios can prove that most biogenic formaldehyde is from lignin. Using *Pinus taeda* wood flour, a thermochemical reactor was devised to collect biogenic formaldehyde in silica gel cartridges loaded with sodium bisulfite (NaHSO\(_3\)). The resulting formaldehyde adduct, sodium hydroxymethanesulfonate, may be recovered and subjected to isotope ratio mass spectroscopy, IRMS. This presentation will feature IRMS measurements of formaldehyde adducts formed during continuous heating profiles. If we could prove that biogenic formaldehyde is principally from lignin, then simple formaldehyde analysis would be an effective complement to lignin monomer analysis for the elucidation of lignin acidolysis pathways.

CELL 266

Electrochemical degradation of lignin

Siegfried R. Waldvogel\(^1\), waldvogel@uni-mainz.de, Michael Zirbes\(^2\), Jana Strugatchi\(^2\), Jesco Panther\(^2\), Manuel Breiner\(^2\), (1) Johannes Gutenberg University Mainz, Mainz, Germany (2) Organic Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

After cellulose and hemicellulose, lignin represent the most abundant part of the plant biomass. Due to the large waste stream originating from pulping processes, only Kraft lignin and lignosulfonates are of technical interest. Using electric current as sustainable reagent for degradation avoids transition metal catalysts and makes this approach very
attractive. However, the natural complexity and stability of lignin make the depolymerization to useful organic building blocks a highly challenging task. The state of the art in the selective anodic degradation of Kraft lignin and lignosulfonates will be reported. This contribution exclusively deals with the direct electrolysis and no ex-cell approaches. The major focus will be given on the generation and cost efficient isolation of vanillin.

CELL 267

Selective depolymerization of kraft lignin using electrolyzed carbonate

Michael Zirbes, mizirbes@uni-mainz.de, Siegfried R. Waldvogel. Johannes Gutenberg University Mainz, Mainz, Germany

Lignin is besides cellulose and hemicellulose major part of the plant biomass. Particularity of the biopolymer lignin is its polyphenolic structure, which qualifies itself as a potential renewable feedstock for the production of bio-based aromatic fine chemicals. However, the natural complexity and degradation stability of lignin make the depolymerization a highly challenging task. We developed an electrochemically supported method for the highly selective
degradation of Kraft lignin to the fine chemicals vanillin and acetovanillone. Thereby, ex-situ electro-generated peroxodicarbonate (PODIC) was used as sustainable oxidizer for the depolymerization of lignin. This oxidizing agent could be simply produced through the continuous electrolysis of an aqueous sodium carbonate solution at a boron-doped diamond anode. After the ex-situ electrolysis, the PODIC solution was added to an alkaline Kraft lignin solution. Afterwards the oxidized lignin was thermally induced depolymerized. Vanillin and acetovanillone were obtained with excellent selectivity and in relatively high yields. In summary, the developed method was able to realize the selective degradation of Kraft lignin to vanillin, where only electrolyzed carbonate served as oxidizer.

CELL 268

Development of electrochemical strategies for lignin valorization

Cheng Yang, yacheng@umich.edu, Stephen Maldonado, Corey Stephenson. Chemistry, University of Michigan, Ann Arbor, Michigan, United States

Lignin is the second most abundant biopolymer on Earth and is the only naturally occurring source possessing a high content of aromatic units. This unique structural feature of lignin marks it as an ideal renewable resource for the production of aromatic commodity chemicals. The depolymerization of native lignin is challenging due to the complex structure of lignin as well as its known lack of solubility. Our group’s long-term goal is to develop practical methods to afford useful commodity chemicals under mild and cost-effective conditions. We have previously reported electrochemically enabled oxidations as well as photochemical methods on lignin depolymerization. We are currently investigating the expansion of electrochemical methods for the selective oxidation and reductive fragmentation of lignin. Mechanistic studies using electroanalytical methods are under investigation and are reported herein.

CELL 269
Selective conversion of lignin to aromatic acids in high yield via two-step oxidation method

ZhaoHui Tong, ztong@ufl.edu, Hanxi Bao, wenbo peng. Agricultural and Biological Engineering, University of Florida, Gainesville, Florida, United States

Aromatic acids have wide applications in pharmaceutical industry, antioxidant in the food industry, and monomeric precursor for high performance plastics. Therefore, the conversion of lignin, the most abundant aromatic polymers in nature, to value-added aromatic acids, serves as a critical sustainable approach. However, instead of aromatic acids, current research shows aromatic aldehydes represent a significant portion of the lignin depolymerized products. Lignin derived aromatic aldehydes usually have hydroxyl group at para position and methoxy groups at para position. These substitute groups introduce possibilities of generating unwanted byproducts during an oxidation reaction, resulting in low yield of aromatic acid products. Previous research also show that expensive and complicated catalysts or harsh reacting conditions are required to oxidize phenomonomeric aldehydes to corresponding aromatic acids. The conversion from lignin is even more challenge due to the complicated and heterogeneous structure of lignin polymer. In this study, we investigated that the introduction of acetyl group in vanillin or lignin derived aromatic aldehydes prevents unwanted side reactions. The yield of aromatic acids could be significantly increased up to 90% conversion yield using eco-friendly and economical catalyst system from the lignin model compound study. After that, the method was tested for three pristine lignins under the optimized reaction condition. The total yield of aromatic acids could be up to 17.9% (based on lignin) via a two-step oxidative process from the pristine lignin.

CELL 270

Fusion of fiber networks with ionic liquids to produce new type of cellulose materials for biodegradable packaging applications

Hannes Orelma1, hannes.orelma@vtt.fi, Atsushi Tanaka1, Alexey Khakalo2, Antti Korpela2. (1) VTT-Technical Research Centre of Finland, Espoo, Finland, Finland (2) Biomass Processing and Products, VTT Technical Research Centre of Finland LTD, Espoo, Finland

Package industry is demanding new type of cellulose-based materials for producing food and goods packages that are biobased, biodegradable, and recyclable. In this study, we investigated the utilization of the partial dissolution with an ionic liquid to fusion (“chemoweld”) fiber networks (paper) to produce fusioned papers with high dry and wet strength. The IL-fusion was carried out by using [EMIM]OAc that was impregnated into the pre-made fiber network with an assistance of a co-solvent (water). The use of the co-solvent made it possible to transport the ionic liquid evenly throughout the fiber network. The IL-fusion was performed by first evaporating the co-solvent in an oven, followed by a partial dissolution of the fibre surfaces. The IL-fusion between fibers was performed subsequently with a regeneration in water and drying under
compression. It was observed that the IL-fusion intensity was possible to be tuned with the treatment conditions. The IL-fusion triplicated the dry strength of the original paper. Moreover, the IL-fusion improved the wet strength of paper. The harshest IL-fusion condition transformed the paper into a transparent cellulose film, with properties that were similar to the commercial cellophane film, and also had excellent oxygen and grease barrier features. The biodegradability studies show that the produced material is biodegradable in both nature and industrial composting conditions. The studied method makes it possible to produce new type of paper products to paper and regenerated cellulose based packaging applications.

CELL 271

Understanding cellulose dissolution in ionic liquids and their solutions in molecular solvents: Physical organic chemistry approach

Omar El Seoud\textsuperscript{1}, elseoud.usp@gmail.com, Marc Kostag\textsuperscript{1}, Paulo Augusto R. Pires\textsuperscript{1}, Daniela C. Ferreira\textsuperscript{2}. (1) University of Sao Paulo, Sao Paulo - SP, Brazil (2) Nanotechnology, IPT, Sao Paulo, Brazil

Ionic liquids (ILs) are efficient cellulose solvents because of their structural versatility. The high viscosity of cellulose solutions in some ILs is attenuated using molecular solvents (MSs) as diluents. The usual approach is to synthesize a series of ILs and then assess their efficiency (pure or as mixtures with MSs) as cellulose solvents. This screening requires a robust cellulose dissolution protocol, and techniques/tools to explain the observed order of dissolution ability, hence establish guidelines for solvent efficiency. We constructed a mechanical stirring system that allows reproducible agitation speed and temperature control with minimum solution/air contact during the experiment. We recommend using the mole fraction scale for reporting dissolution data. We assessed the efficiency of dialkylimidazolium- and quaternary ammonium ILs (as acetates; AcO\textsuperscript{-}) and their mixtures with DMSO by solvatochromic parameters and enthalpy of interactions (using ITC) of cellobiose and b-cyclodextrin (cellulose models) with the IL-DMSO mixtures. Efficient solvents are associated with relatively large effective basicity (Lewis basicity- Lewis acidity; ca. 0.8), and large values of solute-solvent interaction enthalpy, ca. 16 kcal/mol. We corroborated these conclusions with results of molecular dynamic simulations: efficient ILs form a larger number of Cel-OH---OAc bonds.

CELL 272

Conducting cellulose nanopapers as platform for sensing applications

Eduart Gutiérrez Pineda\textsuperscript{1}, eduaragp@inifta.unlp.edu.ar, Cristian Blanco-Tirado\textsuperscript{2}, Marianny Y. Combariza\textsuperscript{3}. (1) Universidad Industrial de Santander (UIS), Bucaramanga, Colombia (2) Chemistry, Universidad Industrial de Santander, Bucaramanga, Colombia (3) Escuela de Química, Universidad Industrial de Santander, Bucaramanga, Santander, Colombia
Nanocellulose is a promising material for producing biocomposites due to its mechanical properties. By decorating nanocellulose surface with conducting polymers a new generation of materials with a wide range of applications can be obtained. Among those polymers, Polypyrrole (PPy) is especially promising for commercial applications due to its facile synthesis, high conductivity, and biodegradability. In this work, we show how conductive cellulose-based nanopapers can be obtained. Three different kinds of highly oxidized cellulose nanofibers (CNF) are involved in the chemical polymerization induced adsorption process of PPy on the surfaces of oxidized CNFs in aqueous media. Resulting CFN/PPy nanocomposite was evaluated by X-ray photoelectron spectroscopy (XPS), Fourier transformed infrared (FTIR) spectroscopy, scanning and transmission electron microscopy (SEM and TEM respectively), thermogravimetric analysis (TGA), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy. Morphological characterization clearly shows the formation of core-shell structures in which PPy nanoparticles are covering the CNF’s surface. The resulting CNF/PPy nanocomposites presented diameter sizes in the range of 70 – 90 nm, which are relatively higher in comparison to the initial CNF’s diameters. XPS analysis shows a centered N1s peak at 399.1 eV indicating a successful integration of PPy in the CNF structure. FTIR spectra show signals around 3350 cm⁻¹ and 1600 cm⁻¹ which indicate that CNF has changed into CNF/PPy nanocomposite. Moreover, electrochemical characterization indicates that the composite fabricated exhibits excellent electrical conductivity in comparison to uncoated CNF or pure PPy. The resulted CNF/PPy nanocomposite synergistically combines the electronic characteristics of conducting polymers with the structural advantages of bio-based cellulose polymers. This nanocomposite is being explored as a matrix for the chemical and electrochemical deposition of metal nanoparticles. Finally, in this work, we show that these nanocomposites are useful for developing biosensing devices.

CELL 273

**Synthesis and cross-linking reaction of biobased polyesters composed of bi(furfuryl alcohol)**

**Yuya Tachibana**, tachibana@gunma-u.ac.jp, Senri Hayashi, Azumi Narita, Ken-ichi Kasuya. Gunma University, Kiryu Gunma, Japan

Furfuryl alcohol is a promising biobased chemical made from inedible biomass. In this study, we coupled furfuryl alcohol to bi(furfuryl alcohol) (BFA) as a bifunctional monomer. The single crystal X-ray crystallography of BFA revealed that bifuran moiety was a rigid structure because the geometries of two furan rings are an anti-parallel and a coplanar, and π-conjugation of a furan ring expands to another furan ring. BFA was polymerized with succinic anhydride to poly(bifurfurylene succinate) (PBFS). The glass transition temperature (Tg) and melting temperature of PBFS composed of bifuran were higher than those of polyester composed of mono furan ring. The cross-linking reaction of PBFS with bismaleimide formed the cross-linked PBFS. The cross-links in PBFS causes increases in the Tg and the mechanical strengths as a result of the restriction of mobility by the formation of the cross-linking point.
Award Address (ACS Award for Affordable Green Chemistry sponsored by Dow and endowed by Rohm and Haas Company). Renewable Acrylic Acid enables Bio Economy of Superabsorbent Polymers, Coatings, Adhesives, etc.)

Dimitris I. Collias, collias.di@pg.com, Jane Godlewski, Juan Velasquez. Procter & Gamble, West Chester, Ohio, United States

Incumbent fossil-derived acrylic acid (petro-AA) is produced today from propylene oxidation via a 2-step process and is used primarily in superabsorbent polymers (SAPs), coatings, and adhesives. Procter & Gamble (P&G) recently developed a proprietary gas-phase chemical process technology to produce renewable acrylic acid (bio-AA) via lactic acid (LA) dehydration in one step and with the highest ever reported yield and selectivity, and long catalyst longevity. The process is a heterogeneous gas-phase dehydration of LA that occurs over an amorphous and partially-dehydrated polyphosphate catalyst $\text{MH}_2(1-x)\text{PO}_{(4-x)}$. The process requires an elevated partial pressure of water since the water transforms the catalyst from its precursor form to its active form. However, the presence of water is deemed counterintuitive since the reaction being catalyzed removes water from the lactic acid feed.

The residence time of the reactants in the reactor is less than 3 s, and the bio-AA yield and selectivity achieved are 85 - 90 mol%. Bio-SAP produced from this bio-AA had the same performance as incumbent petro-SAP. Compared to the petro-AA process, the P&G gas-phase process emits less greenhouse gases (GHG), uses less non-renewable energy (NREU), and is expected to have lower production costs long term. Finally, the P&G technology is based on 22 granted US patents, 74 granted patents in other geographies, and a number of patent applications.
Selective oxidation of hydroxypropyl ethers of cellulose and dextran: Efficient approach to Schiff base polymeric prodrugs and hydrogels

Brittany L. Nichols¹, brittan@vt.edu, Junyi Chen¹, Petra Mischnick², Kevin J. Edgar³,⁴. (1) Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States (2) Institute of Food Chemistry, Technical University of Braunschweig, Braunschweig, Germany (3) Department of Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States (4) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States

Oxidation of polysaccharides has been a useful approach to new materials, for example in C-6 oxidation to uronic acids, and in periodate oxidation of 2, 3-diols to prepare ring-opened dialdehydes. Selectivity in oxidation of polysaccharide macromolecular polyols
remains, however, a significant challenge. Selective oxidation of polysaccharide derivatives to ketones could have special utility, since there are few methods for imparting ketone groups to polysaccharides, and the existing methods have restricted scope and significant complications. We report here a simple, selective, practical, and efficient process, beginning with hydroxypropyl ethers of polysaccharides which are simple and economical to prepare, and in some cases are commercial products. We demonstrate this approach herein using commercial hydroxypropyl cellulose (HPC), as well as hydroxypropyl dextran (HPD) prepared by our lab. We oxidize the terminal, secondary alcohols of the oligo(hydroxypropyl) substituents with sodium hypochlorite, affording ketones, so that the product has oligo(hydroxypropyl) side chains terminated by an acetone moiety. We demonstrate the high chemo- and regioselectivity of this oxidation by a variety of analytical methods including hydrolysis to monosaccharides and HPLC/MS of the resulting monosaccharide mixture. We provide an initial demonstration of the potential utility of these keto-polysaccharides (oxidized hydroxypropyl cellulose, or Ox-HPC, and oxidized hydroxypropyl dextran, or Ox-HPD) by reacting them with primary amines to form Schiff base imines, providing pro-active polymers that are models for delivery of drugs and other bioactive species. The resulting Schiff bases are stable when dry, but hydrolyze slowly in neutral aqueous solutions, and quickly in aqueous acid. This acid sensitivity can be advantageous for lysosomotropic delivery of antibiotics, as well as for targeted delivery to tumors. Here we report synthesis, characterization, and physical properties of amphiphilic cellulose and dextran Schiff base polymers and delivery systems, with successful drug conjugation confirmed with FTIR, ¹H and ¹³C NMR spectroscopy. We also evaluate the effects of oxidation on the molecular weight and glass transition temperature of the starting material.

CELL 276

Modification of plant-derived nanoglycogen for applications in sustainable agriculture

Alyssa R. Deline¹, adeline1@jhu.edu, Elizabeth Hazen², Howard Fairbrother¹. (1) Department of Chemistry, Johns Hopkins University, Baltimore, Maryland, United States (2) Department of Chemistry, Mount Holyoke College, South Hadley, Massachusetts, United States

Controlled delivery of nutrients to plants can increase agricultural yields while decreasing the negative economic and environmental impacts of the broad application of conventional fertilizers. Phytoglycogen nanoparticles (PhG NPs), a renewable polysaccharine material naturally produced in corn, offer distinct advantages as a nutrient delivery platform. The dendritic structure of PhG NPs facilitates the embedding of nutrient materials within, while the surface chemistry can be modified to optimize PhG NP binding to plant surfaces (e.g. hydrophobic leaves or roots). In this work, x-ray photoelectron spectroscopy (XPS) and quartz crystal microbalance (QCM) were used to probe the adhesion of PhG NPs with different surface functionalizations to a model hydrophobic surface. The hydrophobic character of the PhG surface was found to be
the driving force in attachment; therefore, a series of hydrophobic hexyl ester-functionalized PhG NPs was prepared with systematic variation in the degree of substitution. The balance between enhanced hydrophobic character and decreased aqueous stability was explored to optimize attachment. In addition, zinc phosphate and zinc oxide NPs were nucleated within PhG NPs as model systems for the delivery of metal micronutrients and phosphorus macronutrients. The nanohybrids were characterized using a variety of techniques (e.g. AAS, XRD, TGA, EDX) to identify the zinc structure, content, and release kinetics. Ultimately, the renewable PhG platform represents a sustainable approach to agrichemical delivery that can be extended to a variety of nutrients (e.g. nitrogen or copper) while taking advantage of the optimized surface chemistry presented in this work.

CELL 277

Morphological change in the microphase separation of cellulose diacetate/diblock copolymer blends

Shota Morimoto, Kazuki Sugimura, kazusugi@kais.kyoto-u.ac.jp, Tatsuya Awano, Hiroshi Kamitakahara, Yoshiyuki Nishio. Graduate School of Agriculture, Kyoto University, Kyoto, Japan

Microphase separation behavior was found and investigated for blends of cellulose diacetate (CA) with a diblock copolymer, PVP-b-PVAc, made up of poly(N-vinyl pyrrolidone) (PVP) and poly(vinyl acetate) (PVAc) chains. Three PVP-b-PVAc samples with different copolymer compositions were successfully synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization and characterized by 1H NMR and GPC measurements. CA/PVP-b-PVAc blends cast in film form were all highly transparent, but showed two Tgs in their DSC thermograms. This indicates that the PVP sequence in PVP-b-PVAc was miscible with CA on a scale of a few tens of nm, whereas the other sequence PVAc formed a single domain by itself due to its repellent character to both PVP and CA components. The microphase-separated structures into the CA/PVP and PVAc domains were visualized by TEM observations using ultra-thin slices of each CA/PVP-b-PVAc film. It was shown that the domain size and morphological pattern of the two-phase structure were controllable by changing the blend composition (CA: copolymer in wt.) as well as the copolymer composition (VP:VAc in mol).

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Potential uses of MVG (methyl vinyl glycolate) derived from glucose cracking

Stefan Lundmark1, stefan.lundmark@perstorp.com, Samuel G. Elliot2, Bo M. Jessen2, Robert Madsen3, Esben Taarning4, Irene Tosi2, Pia Wennerberg1. (1) Innovation, Perstorp AB, Perstorp, Sweden (2) Department of Chemistry, Technical University of Denmark, Kgs. Lyngby, Denmark (4) RD Division, Haldor Topsoe A/S, Kgs. Lyngby, Denmark
The sugar conversion into C1-C3 oxygenates with Sn-Beta catalysts opens up for the production of chemicals such as for instance glycolaldehyde, ethylene glycol, glycolic acid and methyl vinyl glycolate (MVG). Although MVG fulfills the requirements for a sustainable platform molecule, its applications are relatively unexplored. Examples of general strategies suggested for transformation of MVG into other valuable compounds are homo methathesis, cross methathesis, Calisen-type rearrangements, and oxygen-centered rearrangement. In this talk we will present and discuss results describing the potential use of MVG in UV-curing formulations. Properties such as reactivity, film formation, hardness, chemical resistance, adhesion and scratch resistance have been evaluated.

CELL 279

Opening Rings: From biopolymers, in water and beyond

Peter Olsén, peter.olsen82@gmail.com. Wallenberg Wood Science Center, WWSC, Fibre and Polymer Technology, KTH, Stockholm, Sweden

The ability to create functional molecules for a diverse set of applications continues to be one of the cornerstones of modern-day chemistry. However, as we embark towards the future the “greenness” of the synthesis becomes more and more important. Current work focuses on functionalization chemistry, with the interest to create both new functional green building blocks and new modification strategies. The developed strategies include selective ring-opening reaction with unprotected amino acids in an aqueous environment. Through this we could create an inexpensive, green protocol towards highly functionalized building blocks. One of these building-blocks can also be used as amine protecting-group. From biomass we have explored both green modification strategies of lignin and fundamental aspects of surface initiated ring-opening polymerization from wood cellulose fibers. In the first part we combined lignin fractionation with ring-opening polymerization (ROP). This enabled us to create functional and structural defined lignin star-copolymers. In the latter part, we tried to understand how the polarity of the surrounding system affect the grafting outcome. To address this, we performed the same polymerization, at the same temperature, with the same equivalents of reactants, and the same cleaning procedure, but in different solvents. It was evident that the solvent, in particular the hydrogen-bond donor strength of the solvent, dictates the grafting outcome. The results presented, and the strategies developed, focus on the fundamental aspects of chemical modification via ring-opening reactions. Trying to address questions like, how do we design our systems to achieve the envisioned transformation, and how does this translate to chemical modification of biopolymers.

CELL 280

Polypeptides as functional nanomaterials toward achieving plant organellar engineering through cell walls
Peptides and polypeptides are versatile tools in biotechnology, especially in gene/protein delivery area. The individual character of each amino acid can be combined, resulting in huge advantage for targeted delivery systems. Cationic components make efficient gene delivery agents due to membrane-destabilizing, DNA-condensing and proton sponge effects. A group of molecular transporters such as cell penetrating peptides (CPPs) are short peptide sequences that vary significantly in sequence, hydrophobicity, polarity, and have the remarkable capacity for membrane translocation. To deliver gene/protein efficiently into plant cells, the plant cell wall is the major barrier to prevent it. By visualizing the cell walls of alive plant cells, we characterized the alive plant cells by high-speed atomic force microscopy as well as investigated an efficient pathway to introduce bioactive molecules into plant cells. Meanwhile, targeted delivery to essential organelles such as the mitochondria can be achieved with mitochondrial-targeting peptides, which are typically N-terminal motifs predicted to form amphipathic helixes and enriched in positively charged basic residues. The combination of cationic, cell-penetrating and mitochondria-targeting components reported here is an exciting new design parameter that enabled cellular uptake, localization and expression of exogenous DNA in the mitochondria of living plants. We rationally developed dual-domain peptides containing DNA-condensing/cell-penetrating/endosome-disruptive and mitochondria-targeting sequences. Secondary structures of the dual-domain peptides were analyzed, and variations in the physicochemical properties (stability, size and ζ-potential) of peptide/DNA complexes were studied as a function of peptide-to-DNA ratio. An optimized formulation, identified through qualitative and quantitative studies, fulfills the fundamental prerequisites for mitochondria-specific DNA delivery, successfully transfecting a high proportion of mitochondria in plant cells and human cell lines. Furthermore, peptide-based gene carriers carrying chloroplast transit peptide were prepared for the delivery of exogenous DNA into plastids. This advance in plant biotechnology not only provides a stable transformation method but will also facilitate organelle genome editing to maximize biomass production via plant breeding.

**CELL 281**

**From ring-opening reactions to renewable functional materials**

*Karin Odelius, hoem@kth.se.* KTH Royal Institute of Technology, Stockholm, Sweden

Achieving more sustainable synthetic pathways, usage and waste management of polymeric materials are all important elements of a circular bioeconomy. Aspects such as benign synthetic methodologies, utilizing renewable resources, structure-property relationships that match the targeted application and intended end-of-life handling methodologies are in focus. With the proper synthetic design, ring-opening polymerizations of lactones and carbonates from renewable resources inherently contribute with important characteristics that enable the creation of renewable functional and recyclable materials. In this presentation examples of our work within the field will
be highlighted. This includes the one-pot, solvent-free synthesis of a family of cyclic carbonates and the organocatalytic regioselective ring-opening polymerization to polycarbonates, utilization of naturally derived small- and medium-sized lactones and their controlled polymerization into aliphatic polyesters and polyamides as well as chemical recycling methodologies.

CELL 282

Renewable fats and oils based long chain polyamides

Jukka Seppala, jukka.seppala@aalto.fi, Huy P. Nguyen. Chemical Engineering, Aalto University, Espoo, Finland

Bio-based fats and oils were used as feedstocks for difunctional monomers utilized in melt polyamidation. In addition thiolene based click chemistry was applied in chain extension to prepare difunctional monomers with up to 32 carbons [1]. The synthesized bio-based polyamides displayed number average molecular weights up to 55,000 g/mol. This class of polymers exhibited an impressive property profile, polyolefin-like impact strength, tear strength, high elasticity, very low water absorption and yet high oxygen- and water vapor permeability. The technical advantages of these polymers encourage further development of composite materials with various fibers. Heat deflection temperatures were above room temperature (45–55 °C), while melting temperatures ranged from 121 to 200 °C [2]. Relatively low melting temperatures of these bio-polyamides enable favorable compounding with some sensitive bio-based fillers and fibers. Thus, bio-based composites were prepared by unifying the bio-based polyamides with pulp fibers, nano-crystalline cellulose and lignin. The key role of interfacial compatibilization will be discussed. Favorable rheological properties of the synthetized bio-based polyamides enable the use of advanced processing technologies like additive manufacturing.

CELL 283

Synthetic cells and other assemblies from bio-renewable starting materials

Virgil Percec, percec@sas.upenn.edu. Univ of Penn, Philadelphia, Pennsylvania, United States

Reconstruction of life's functions with natural and unnatural components represents one of the great challenges of natural sciences. Compartmentalization, encapsulation, surface decoration and interaction with living matter of globular assemblies, known as vesicles, represent the earliest and the most primitive steps towards synthetic cells. This lecture will discuss the used of bio-renewable starting materials components to construct synthetic cells and other assemblies of interest to understand the origins and role of biological homochirality.
New paradigm in the design of degradable and renewable polymeric materials

**Ann-Christine Albertsson, aila@kth.se.** Dept of Fiber and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Polymeric materials are based on common elements such as carbon and hydrogen with or without nitrogen, oxygen, halogen, phosphorus or sulphur. Their properties are given by the molecular structure and independent of the origin of the atoms, they are renewable or not. A key property in technological applications is durability of materials, while recycling in nature is an increasing demand from the environmental point of view. In the design of degradable and renewable polymeric materials, the macroscopic performance has to be translated to all levels of order. Regardless of a simple macromolecular structure, materials could be macroscopically homogenous but microscopically heterogeneous.

Hemicellulose-rich and lignin containing wood hydrolysates can be recovered from the liq. process streams in wood processing operations such as pulping. Using this, instead of pure hemicellulose in a film, some of the properties from nature are preserved, and have low oxygen permeability even at high humidity, in contrast to the pure hemicellulose.

Hydrolysates as well as pure polysaccharides can be also used to build up homogenous/heterogenous hemi gels for a series of applications. For medical applications, it is usually necessary to start from monomers in order to achieve high reproducibility. Systems built from monomers such as lactides are also composed of micro- and/or nanoparticles along with changeable strength in the secondary bonds.
The American Chemistry Society exists to serve all chemists. Early in its history it realized that strong groups of chemists wished to organize technical sessions at national meetings on special topics. In 1903, Arthur Noyes proposed that Technical Divisions be organized within the overall ACS umbrella. In 1908, the Division of Industrial Chemists and Chemical Engineers was formed. After World War I, there was a large growth in the forest products industry. In 1920, a provisional technical Section on Cellulose Chemistry was organized. It held its first meeting in 1921 in Rochester, New York. The Division of Cellulose Chemistry was approved in 1922 and held its first official meeting in Pittsburgh, PA. The Division has continued to grow and thrive ever since, and now includes the designation Renewable Materials in its title. This talk will present the history of the CELL Division from its genesis in 1920 to the present, in 2020: 100 years of progress.

CELL 286

Anselme Payen: Forgotten histories of our pioneering founder

Stephen J. Eichhorn, s.j.eichhorn@bristol.ac.uk. University of Bristol, Bristol, United Kingdom

This talk will cover what we know, and what we don't know about the life and times of Anselme Payen, the French chemist who discovered cellulose. We know little about his early life, nor his heritage. This talk will try to uncover some of this information and give insight into his science and the contributions he made, both to cellulose and other technologies but also to social justice. Payen was certainly a very unique person in Parisian life, and we do well to try and better understand his motivations and ethos in supporting others as a division. This talk aims to address both these aspects of his life.

CELL 287

Chemical history of cellulose

Gary D. Patterson, gp9a@andrew.cmu.edu. (1) Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (2) Science History Institute, Philadelphia, Pennsylvania, United States

Humans have been using cellulose for many millennia, but, until the late 19th century, it was just an item of technology. The first step in the chemical history of cellulose was the realization that it was a polysaccharide. Like starch, it is a polymer of C₆H₁₀O₅. While this was proven in 1883, substantial controversy persisted well beyond the founding of the Division of Cellulose Chemistry in 1920.

Major progress was achieved by Sir Walter Norman Haworth in 1925 when he proved that the repeating unit in cellulose is a six membered ring structure. His extensive structural studies of sugars earned him the Nobel Prize in 1937. More detailed studies of the structure of cellulose required X-ray crystallography, and Sponsler and Dore exhibited the results of such an analysis in 1926. The structure proposed by Haworth
was confirmed by Herman Mark and Kurt Meyer in 1928, with help from Michael Polanyi.
A detailed history will be presented surrounding this discovery and applied to many developments in the chemistry of cellulose.

CELL 288

Cellulose solutions: Early discoveries and applications

Nicolay V. Tsarevsky, nvt@smu.edu. Department of Chemistry, Southern Methodist University, Dallas, Texas, United States

In the 19th Century, numerous efforts were made to dissolve cellulose and examine (and find applications of) the formed solutions. Some of the early attempts involved chemical transformations (e.g., nitration and later acetylation) of the natural polymer, which afforded soluble cellulose derivatives. Regeneration of cellulose was not possible in these cases. The preparation of solutions of cellulose, from which it could be isolated
unchanged, proved more challenging until 1857 when the Swiss chemist Eduard Schweizer (1818–1860) reported that the dark blue solutions formed by the reaction of copper(II) compounds with excess of strong ammonia dissolved efficiently plant fibers. It was ascertained that when the solutions of cellulose thus prepared were added to acids, cellulose precipitated again – a process, which served as the basis of the viscose process for production of cellulose (rayon) fibers, patented in 1890 by the French chemist Louis-Henri Despeissis. In 1892, another important finding was patented by Charles Frederick Cross (1855-1935), Edward John Bevan (1856-1921), and Clayton Beadle (1868-1917), namely the dissolution of cellulose in carbon disulfide in basic media with the formation of soluble cellulose xanthate, which could then be easily converted (by acidic hydrolysis) again to cellulose. The early research on cellulose solutions and their uses in the production of fibers (“artificial silk”) and films will be described.

CELL 289

Study, stabilization and utilization of gun-cotton by Frederick Abel

Seymour H. Mauskopf, shmaus@duke.edu. Duke Univ, Durham, North Carolina, United States

Frederick Augustus Abel (1827-1902) was the first official government military chemist in Great Britain: Chemist of the War Department (1854-1888). His activities in this position resulted in his focus on gun-cotton. The material that Abel used was fabricated in 1845-1846 by Christian Friedrich Schönbein although it had its precursors in a French tradition of reacting cellulose materials (wood or cotton) in nitric acid. Schönbein produce a highly nitrated cellulose by steeping cotton in concentrated nitric and sulfuric acid. After washing and drying, the resultant material looked much like the original cotton but readily combusted and even exploded without, however, producing smoke. Schönbein immediately recognized the potential of the material as a military propellant (he gave the name “guncotton” to his product), patented his fabrication, and set to work arranging for both its manufacture and military use. But the material proved to be lethally and destructively unstable.

Abel himself had fabricated a sample of guncotton “according to Schoenbein’s receipt” in 1846.[i] But it was in 1863, as Chemist of the War Department, that he received a request from the Secretary of State for War to investigate all aspects of the chemistry and fabrication of guncotton in order to stabilize it and make it useful. Abel's involvement was intense through the rest of this decade; then it went more-or-less dormant until rekindled in 1888 in connection with an “Explosives Committee,” whose President Abel was named and under whose direction Britain’s first smokeless military propellant, Cordite, was developed. Guncotton was a component of Cordite.

In my talk, I shall discuss Abel’s multifarious activities regarding guncotton, including: (1) his investigations of its general chemistry; (2) his devising means of stabilizing it; (3) his patenting his stabilizing procedure and arranging for the manufacture of “patent safety guncotton” primarily as a blasting agent; (4) his attempts to develop it use as a military propellant, for many years unsuccessful but finally achieved in Cordite. A
number of these enterprises, notably the promotion of guncotton as a commercial
blasting agent and the development (and patenting) of Cordite, brought Abel into direct
competition – and collision – with Alfred Nobel.

CELL 290

Direct ink writing of lignin/hydroxypropyl cellulose solutions

Lisa Ebers¹,², Marie-Pierre G. Laborie¹,², marie-pierre.laborie@biomat.uni-freiburg.de.
(1) Chair of Forest Biomaterials, Albert Ludwig University of Freiburg, Freiburg,
Germany (2) Freiburg Materials Research Center, Albert Ludwig University of Freiburg,
Freiburg im Br, Germany

Organosolv Lignin / hydroxypropyl cellulose (HPC) aqueous solutions have been shown
in prior work to exhibit shear thinning properties and thereby be potentially amenable to
3D printing by direct ink writing. In this work, solutions of organosolv lignin and
hydroxypropyl cellulose were screened for their amenability to direct ink writing. Fiber
formation tests, recovery tests and rheological characterization were performed on a
series of lignin/HPC solutions. The optimum formulations for direct ink writing was
thereby determined. In addition, the process parameters and the crosslinking route were
optimized for the direct ink writing of selected solutions. Altogether, it was found that
selected lignin/HPC solutions were well amenable to direct ink writing for the production
of 3D objects.

CELL 291

Use of lignocellulosic-derived components to develop novel biobased 3D
printable polymeric materials

Nejib Kasmi, Nejib.Kasmi@list.lu, Grégory Mertz, Vincent Berthé, Riener Dieden,
Youssef Habibi, Youssef.Habibi@list.lu. Materials Research and Technology
Department, Luxembourg Institute of Science and Technology (LIST), Esch-sur-Alzette,
Luxembourg

The omnipresence and overconsumption of plastics and commodity materials is causing
several environmental and climatic global challenges mainly because of the use of
depleting fossil resources and also subtractive manufacturing processes. To face these
challenges, the development of circular economy by exploring sustainable alternatives
both in term of resources and also in term of processing technologies. Tremendous
development has been achieved to identify renewable raw materials with intent to
gradually replace fossil-based plastics by transforming lignocellulosic feedstock. Indeed,
lignocellulosic biomass is an attractive, non-edible, low-cost, and inexhaustible starting
material that could be generated in huge quantities from agricultural and forestry activity
worldwide. In term of manufacturing, additive manufacturing, commonly known as 3D printing, is surfacing a potential solution for a sustainable use of the raw materials during processing. Several technologies are being developed requiring feeding materials with distinct intrinsic properties.
Under this trend lignocellulose-derived substrates were modified and blended to prepare novel biobased 3D printable composites to lead functional materials. Such materials are highly sought for myriad practical applications.

CELL 292

TPO nanoparticle as water-soluble photoinitiator and CNC as a rheological modifier for extrusion-based 3D printing technique

Doron Kam1,2, doron.kam@mail.huji.ac.il, Ariel Braner1,3, Liraz Larush1, Annalisa Chiappone4, Oded Shoseyov5, Shlomo Magdassi1. (1) Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel (2) Plant Sciences and Genetics in Agriculture, The Hebrew University of Jerusalem, Rehovot, Israel (3) Alpha program, Future scientist center, Jerusalem, Israel (4) Applied Science and Technology, Politecnico di Torino, Torino, Italy

3D printing UV curable inks by extrusion-based technologies requires tailoring of the rheological properties of the inks, since the ink must flow through the extruder but maintain structural stability on the printing platform, until UV light initiates its polymerization. In an aqueous ink, another problem arises due to lack of efficient water-soluble photoinitiators. We present inks for making 3D objects composed of hydrogels, by combining photopolymerization and rapid fixation by cellulose nanocrystals. The ink is composed of acrylic acid monomer with PEGDA cross-linker, while the polymerization process is induced using a novel nanoparticles of a water-soluble photoinitiator, 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (TPO), prepared in our lab. The cellulose nanocrystal (CNC) are used as a rheological modifier to 3D print objects, while enabling the printability of the ink and improving Young’s modulus while not effecting strain to break of the printed objects.

CELL 293

Photoablation of cellulosic films for 3D patterning and microroughening

Sachin Agate, sragate@ncsu.edu, Lucian A. Lucia, Lokendra Pal. Departments of Forest Biomaterials and Chemistry, North Carolina State University, Raleigh, North Carolina, United States

Selective 3D patterning and attainment of microroughness on the cellulosic surfaces can lead to improved surface energy and tunable adhesion for various applications such as flexible electronics, coatings and printing. Cellulosic films were treated using laser and UV light to photopattern selective areas. Further, various patterns and degree of photoablation were controlled using special masks and levels of UV energy. Finally, 3D
patterned films were flood coated using a conductive ink that allowed on demand, personalized production of electronics. Such a process as described can be employed for numerous applications.

CELL 294

Effect of colloidal lignin nanoparticles on the cell viability and robustness of nanocellulose-based bioinks for 3D printing

Xue Zhang¹, xue.2.zhang@aalto.fi, Maria Morits¹, Christopher Jonkergouw¹, Ari Ora¹, Juan Jose Valle-Delgado¹, Muhammad Farooq¹, Siqi Huan¹, Rubina Ajdary¹, Orlando Rojas¹, Markus Linder¹, Mika Sipponen¹,², Monika K. Osterberg¹. (1) Aalto University, Espoo, Finland (2) Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

Three-dimensional (3D) bioprinting has been an emerging technique to fabricate precise scaffolds for biomedical applications. As a biocompatible, non-cytotoxic and renewable material, cellulose nanofibril (CNF) hydrogels are investigated as bioink for 3D printing. Pure CNF hydrogels lack in form stability after 3D printing and often require post-treatment, like cross-linking. Supplementation of polymers is an option to enhance the strength of the hydrogel. CNF hydrogels in combination with alginate are an effective method to enable cross-linking of the printed scaffolds in the presence of Ca²⁺ ions. Addition of new components to the CNF hydrogel can provide additional material functionality. Colloidal lignin nanoparticles (CLPs) produced from lignin, a phenolic component of wood is of high interest due to their antioxidant, antimicrobial and potential drug carrier properties.

In this work, CLPs were used to prepare CNF-alginate-CLP nanocomposite scaffolds. According to atomic force microscope (AFM) topographical images, CLPs were homogeneously mixed with the CNF hydrogel. As expected from their polyphenolic structure, CLPs brought antioxidant properties to CNF-alginate-CLP scaffolds in a concentration-dependent manner. Besides antioxidant activity, supplementation of CLPs increased viscosity of hydrogels at a low shear rate, which can provide better shape fidelity and printing resolution to printed scaffolds. The CNF-alginate-CLP scaffolds demonstrated shape stability after 3D bioprinting, cross-linking and storage in Dulbecco’s phosphate buffer solution containing Ca²⁺ and Mg²⁺ ions for 7 days. The 3D printed scaffolds showed relative rehydration ratio values of around 80% after freeze-drying, demonstrating high water retaining capability. Cell viability tests using hepatocellular carcinoma cell line HepG2 showed no negative effect of CLPs on cell proliferation. The number of living HepG2 cells increased at least two times for all the formulated scaffolds within 5 days of cell culturing. Overall, our results demonstrate that nanocomposite CNF-alginate-CLP scaffolds have high potential in soft tissue engineering and regenerative medicine applications.

CELL 295
Conversion of steam-explosion poplar lignin by LMS/formic acid degradation with comparison to TEMPO-FeCl₃ and Raney-Nickel induced degradations

Paula Nousiainen, Riku Maltari, Jussi Kontro, Joona Mikkilä, Kristiina Hildén, Jussi Sipila, jussi.sipila@helsinki.fi. University of Helsinki, Helsinki, Finland

New sustainable technologies and raw-materials are key elements in transition to new bio-based economy. Modern 2G biofuel plants utilize lignocellulosic side streams as their raw material but subsequently create new lignin enriched material pool that is left after saccharification of carbohydrates. This lignin enriched residue provides an important alternative for fossil based chemical resources. Here we describe research performed in EU Horizon 2020-project FALCON, Fuel and Chemicals from Lignin through Enzymatic and Chemical Conversion. FALCON aims to valorize this lignin waste stream by enzymatic and mild chemical conversion to produce fuels, such as low sulfur marine fuel, fuel additives and chemical building blocks. In our case the lignin raw material was obtained from steam-exploded poplar wood and contained lignin (80%), carbohydrates and ash. Lignin was fractionated by hot ethanol to give highly soluble native like lignin fraction in about 20% overall yield. This material was then subjected to laccase-mediator oxidation followed by formic acid-treatment using laccase from *Obba rivulosa* and syringyl nitrile among others as a mediator. The analysis by GPC, NMR, Pyrolysis-GC/MS and elemental analysis showed that LMS/FA and TEMPO-FeCl₃/FA gave comparable results with substantial reduction in molecular weight. The direct Raney-Nickel reduction of lignin formed notable amounts of aliphatics and yielded markedly degraded material.

CELL 296

Exploring lignin transformation mechanisms under pyrolysis conditions to create value-added products using atomistic modeling

*TANZINA AZAD¹, tza0035@auburn.edu, Jonathan Schuler¹, Hazl Torres¹, Maria L. Auad¹,², Thomas Elder², Andrew J. Adamczyk¹, aja0056@auburn.edu. (1) Chemical Engineering, Auburn University, Auburn, Alabama, United States (2) USDA, Auburn, Alabama, United States (3) Center of Polymer and Advanced Composite, Auburn, Alabama, United States*

Computational modeling of lignin at the atomistic scale has the potential to provide new insights for its tailored valorization. In this work, we have analyzed the homolytic cleavage of β-O-4 bonds in a model lignin oligomer under pyrolysis reactor conditions. Although lignindepolymerization has been studied for over a century, model systems with a large number of monolignol units has yet to be studied extensively. Herein, we have investigated the reactivity of a model lignin oligomer with a structure size comprised of 10 monolignols, Guaiacyl (G) and Syringyl (S) units. Our study quantified the bond dissociation energy variance of the b-O-4 bond cleavage at different positions along the full oligomer chain. Our computational methods included both classical molecular mechanics and quantum chemical methods for advanced conformational
sampling and Density Functional Theory (DFT) calculations, respectively. We have developed a novel and robust method for conformational sampling, which maps the conformational energy landscape efficiently and provides multiple low energy structures for the corresponding DFT reaction energetics calculations. In addition, we have predicted thermodynamic properties (enthalpy, entropy, and heat capacity) at various temperatures which are critical for model validation against experimental data on both lignin pyrolysis and advanced structural characterization.

CELL 297

Polyacids from lignin

*Michael Kent*¹,³, mskent@sandia.gov, *Jijiao Zeng*¹,³, *Daniella Martinez*¹, *Miranda Juarros*¹, *Nadeya Rader*¹, *Isaac Avina*¹, *Casey Simoes*¹, *Christopher Brenden*¹, *Michael Busse*¹, *John Watt*¹, *Nicholas Giron*¹, *Todd M. Alam*¹, *Mark Allendorf*¹, *Blake Simmons*²,³, *Nelson S. Bell*¹, *Kenneth Sale*¹,³. (1) Sandia National Labs, Albuquerque, New Mexico, United States (2) Lawrence Berkeley National Lab, Berkeley, California, United States (3) Joint Bioenergy Institute, Emeryville, California, United States

Valorizing lignin is critical for economically-viable conversion of biomass to fuels and chemicals. However, generating value from lignin is difficult and success to date has been very limited. We describe a method to treat lignin using a room-temperature, one-step oxidative process to selectively open the aromatic rings and generate carboxylic acid groups. The approach largely avoids depolymerization and results in a water-soluble polyacid that constitutes a valuable product, for example as a dispersant, without need for further upgrading. Polymeric dispersants are used extensively in dyes, paints, concrete, pharmaceuticals, cosmetics, paper and paperboard, ceramics processing, and to inhibit fouling in cooling water systems. Our approach uses chelator-mediated Fenton chemistry (e.g., FeCl₃ + chelator + H₂O₂).¹ The Fenton reaction, reaction of hydrogen peroxide and ferrous salt, is used to treat industrial waste and organic contaminants in groundwater and has been employed in biomass pretreatment strategies. Use of an Fe chelator in the Fenton system leads to substantially higher yields of solubilized polyacid product per oxidant (H₂O₂) consumed. We also show that the amount of aromatic ring opening can be controlled by the reaction conditions. By controlling the extent of ring opening, the relative amounts of hydrophobic and charged groups can be tailored to produce polyacids with properties optimized for specific applications. The economic feasibility of this process depends on maximizing the yield of solubilized lignin material per amount of H₂O₂ consumed and also minimizing or eliminating separation steps. We will describe progress on those aspects and report the best results achieved to date. We will also show that the material solubilized by this reaction behaves as an effective dispersant.

CELL 298

Controlled development of carbon structure from lignin feedstocks
We investigated the development of lignin-based carbon materials from softwood, hardwood, and herbaceous sources isolated by kraft and organosolv methods. Feedstock and pulping methods were selected to provide a range in principal monomeric units—guaiacyl, \( p \)-hydroxyphenyl, and syringyl—and physicochemical characteristics of the lignin. Carefully controlled processing methods were used to obtain either fiber, porous, or graphitic structure. Small angle and total scattering data were collected at neutron and synchrotron sources for lignin-based carbons to determine the influence of feedstock and processing conditions. Statistical analysis for over fifty carbon materials was performed to determine the influence of lignin chemistry and processing conditions, which include feedstock, extraction method, gas composition, and reducing temperature. Results indicate that the correlations between reduction temperature and intensity of various x-ray peaks are qualitatively different and sometimes of opposite sign as a function of feedstock. All the analyses support that graphitic structures form and grow in size as reduction temperature increases. These results suggest that kraft softwood and organosolv switchgrass produce large graphitic structures of size comparable to commercial graphite.

**CELL 299**

**Enhancing the broad-spectrum ultraviolet adsorption of lignin through grafting modification and reverse self-assembly**

**Yong Qian, ceyqian@scut.edu.cn, Ying Wu, Xueqing Qiu.** South China University of technology, Guangzhou, China

Lignin is a natural macromolecular sun blocker with excellent absorbance on medium wave ultraviolet (UVB) rays, but it has poor adsorption on long wave ultraviolet (UVA) radiations, which have strong penetration and cause cumulative damage to materials and human skin. Lignin nanospheres with broad-spectrum UV adsorption and excellent antioxidant property were obtained by demethoxylation of alkali lignin (AL), grafting benzophenone moiety (UV0), followed by a reverse self-assembly. The critical wavelength (\( \lambda_c \)) of the optimal AL-UV0\(_3\) sample was \( \sim 375 \) nm while the UVA/UVB ratio reached 0.84. When it was applied as unique active in sun cream, the sun protection factor (SPF) value of the cream containing 10 wt% AL-UV0\(_3\) was 22.81, which could further increase to 56.14 when it formed reverse colloidal spheres (LRCS) with size of \( \sim 130 \) nm. The self-assembly process as well as the UV-absorbing enhancement mechanism of LRCS were monitored and revealed by fluorescence, UV and light scattering analysis. In addition, AL-UV0\(_3\) exhibited superior photo stability due to three dimensional network structure of lignin. The antioxidant activities of AL-UV0\(_3\) and LRCS were better than AL and could increase continuously with the dosage. Both AL-UV0\(_3\)
and LRCS exhibited good biocompatibility. HaCaT cells activity maintained 72-78\% when their concentration was as high as 1.0 mg/mL. The novel lignin broad-spectrum UV-blocker and antioxidant show good potential in skincare products and polymeric materials.

**CELL 300**

**Sustainable added-value lignin materials for specific molecules separation**

Tetyana Budnyak\(^1\), tetyanabudnyak@yahoo.com, Jedrzej Piatek\(^3\), Ievgen Pylypchuk\(^2\), Mikael Lindström\(^2\), Olena Sevastyanova\(^3\), Adam Slabon\(^1\). (1) Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden (2) Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (3) Fibre Wood Tech/Wood Chem Pulp Tech, Stockholm, Sweden

Lignin – cross-linked natural phenolic polymer – based on its chemical structure could have a wide range of applications. It has a high reactivity due to its aromatic nature and presence of various functional groups, and thus, can be used as high performance adsorbent. However, its sorption capacity and sorption rate need to be further enhanced for industrial applications. In general, chemical modification, including crosslinking and functionalization, are necessary to impart sufficient adsorption properties. Another approach is the combination of biomacromolecules and inorganic carriers to form organic-inorganic hybrid materials. In that case, properties of inorganic sorbents can be upgraded by the valuable characteristics of the organic polymer.

Hybrid materials based on lignin and silica in different mass ratios were prepared by several synthetic approaches: electrostatic attraction of modified lignin to aminosilica surface, sol-gel method, crosslinking of functional groups of lignin and inorganic carrier with different agents.

The peculiarities of different approaches to synthesis of lignin/silica hybrid materials were studied and the influence of synthetic conditions on physicochemical properties of obtained composites were investigated by infrared spectroscopy, thermogravimetric analysis, nitrogen adsorption/desorption, and scanning electron microscopy.

It was found that changing the pH of system, variations with inorganic filler (carrier) mass content, type of crosslinking agent applied, time of preparation are greatly affected by physicochemical characteristics of obtained materials, such as specific surface area, porosity, morphology, and thermal stability.

Synthesized hybrid composites were found to be effective as sorbents for the removal of heavy metal ions and synthetic dyes from aqueous solutions. Thus, obtained lignin-based composites are prospective materials for water remediation processes as well as metals recovering from aqueous solutions.

**CELL 301**

**Processing and upscaling potential of functionalized nanocellulose as films and coatings for various purification applications**
Nanocellulose is a renewable and biodegradable material offering a high surface area along with a versatile surface chemistry. The combination of these properties makes nanocellulose a very promising material for application in high-performance membranes and filters that can selectively remove contaminants from polluted gas, air and water. The application of nanocellulose materials in such applications requires their conversion into at least one of the following structures: a stand-alone film; a stand-alone foam/gel; or a coating on another surface (as film or foam). Nanocelluloses are generally produced as water based suspensions at quite low solids content, ca. < 10 %. The high surface area of the constituent units and their hydrophilic nature confers these suspensions with a high viscosity even at low solids concentrations. The resultant complex rheological behavior of the nanocellulose suspensions poses a challenge to their processing into the desired structures/shapes, especially at large scale. Furthermore, there are challenges related to the post-processing performance of these nanocellulose materials in filtration applications, e.g. adhesion of nanocellulose to the substrate after coating, mechanical performance of the stand-alone foam/film structure, etc. It is critical to understand these challenges and recognize their impact on the upscaling potential of these novel solutions. At VTT, along with functionalizing and tuning various nanocellulose grades for these applications, we have also been working on the processability of these functionalized nanocelluloses into the above-mentioned structures, especially films and coatings at pilot scale. This work discusses these processing challenges through examples from pilot scale trials and presents some potential ways to overcome them. Some methods for improving the post-processing performance are also presented.

CELL 302

Surface modification of commercial membranes using antifouling nanocellulose coatings

Andrea Aguilar Sanchez¹, andrea.aguilar@mmk.su.se, Blanca Jalvo¹, Andreas Mautner², Samer Nameer³, Aji Mathew⁴. (1) MMK, Stockholm University, Stockholm, Stockholm, Sweden (2) Institute for Materials Chemistry & Research, University of Vienna, Wien, Austria (3) Kungliga Tekniska Högskolan, Stockholm, Stockholm, Sweden

Polymeric membranes are widely used for industrial water filtration processes due to their energy efficiency and safeness. Nevertheless, this type of membranes are adversely affected by fouling. In this case, fouling refers to the accumulation of undesirable materials on the membrane surface, or within the pore structure, on detriment of its function. The aim of this work was to develop a simple and highly efficient coating method to mitigate fouling and improve the sustainability of commercially available membranes using nanocellulose coatings. A nanoscale surface
modification was made to the membrane, which slightly diminished the permeance of the original substrate, but improved the hydrophilicity. Furthermore, in dry conditions, the surface modification of the membranes positively influenced the Young’s-modulus. The coated membranes also showed significant reduction in organic fouling after exposing them to dynamic adsorption of proteins. The coating exhibited effective antifouling activity against biofoultants, avoiding the biofilm formation of bacteria. Successfully preliminary upscale of the coating process was done, demonstrating that the method could be easily implemented at an industrial level. The impact of this work relies on the simplicity of the method, the effectiveness of the coating and the demonstrated fast implementation at industrial scale.

CELL 303

Nanoscopically engineered microfibrillated cellulose composite membranes for removal of charged impurities

Zoheb Karim¹, zoheb.karim@gmail.com, Dimitrious Georgouvelas², Anna Svedberg¹, Aji Mathew², (1) MoRe Research Örnsköldsvik AB, BOX 70, SE-891 22, Örnsköldsvik, Västernorrland, Sweden (2) Department of Material and Environmental Chemistry, Stockholm University, SE-10691, Stockholm, Sweden

In this study, flat sheet composite membranes based on microfibrillated cellulose (MFC) and softwood pulp fibers were produced using Dynamic Sheet Former (Formette) and further subjected for the adsorption of metal ions and dyes from water. The manner of MFC assembly (hybrid and layered structures) in the composite membranes has direct influence on morphology, density, porosity, water flux, pore size distribution and mechanical properties of composite membranes. Layered MFC architecture has low density and tensile strength compared to its hybrid counterpart. High removal efficiency of metal ions and dyes using composite was recorded in dynamic mode. The effective separation is due to and combined effect of electrostatic interactions/hydrogen bonding and steric hindrance of charged impurities through the flat sheet composite membranes. The assembled MFC composites could be used as affinity membranes for the production of a new generation of water cleaning membranes because of their high adsorption capacity, flexibility, hydrolytic stability and mechanical robustness. The fabrication of full-scale online membranes in continuous mode could be the aim in future for industrial use of these composite membranes.

CELL 304

Tempo-CNF coated viscose: Water treatments applications

Alejandro Pérez Marz, alejandro.perez@acondaqua.com. ACONDAQUA Ingeniería del Agua S.L., Manises, Spain

Water treatment technologies tend to represent important costs for Industry in order to obey legal limits for discharge of used water or to achieve a certain quality of water for
drinking or production purposes. Besides that, the impact of these technologies must be improved to avoid problems in wastewater treatment plants or directly in the environment. Technologies nowadays used for anions and cations removal, ionic exchange for instance, generate a salty concentrate or a flow of diluted chemicals that ends up in the environment. Using reverse osmose membranes a continuous flow of at least 30% of inlet water is created, in addition to high salt concentrations. Furthermore, in water treatment, suspended solids have to be removed as much as possible, which could be achieved with a combination of an adsorbent material and a filter substrate. Integrating this real requirement with research performed, and still ongoing, regarding nanocellulose in water treatment, it appears to be an opportunity to seek for new products developed in a clever way. Presenting a nowadays problem in pump stations and waste water servers, this study aims to present the advances achieved in water treatments using TEMPO-CNF retaining metals and the applications arisen from these results, describing how to place them on the market at reasonable cost. Using existing manufacturing processes and available, cheap raw materials, this paper shows how to apply a hierarchical cellulose material, TEMPO-CNF coated viscose, in water treatment applications in a sustainable way and to show potential applications.

CELL 305

Lignin-based graphene encapsulated iron nanoparticles for water purification

Xuefeng Zhang, njfuxf@gmail.com, Jilei Zhang. Department of Sustainable Bioproducts, Mississippi State University, Starkville, Mississippi, United States

Water pollution is a global environmental issue that threatens food safety and human health. Activated carbon materials have been utilized as absorbents for water purification, but they suffer low selectivity, low regeneration yield, and high cost. Yet, magnetic zerovalent iron nanoparticles stabilized by a graphene shell result in effective and facile absorbents featuring high selectivity, high recovery yield, and high absorption capacity. Herein, we synthesized graphene encapsulated iron nanoparticles (GEINs) from wood pulping byproduct lignin. The lignin-based GEINs were then used for the removal of heavy metals and organic pollutants from aqueous solutions. The effects of initial pH, concentration, and contact time on the adsorption were investigated. The adsorption result demonstrated an effective absorbent of lignin-based GEINs, which offers a simple way for heavy metals and organic pollutants removal from aqueous solutions.

CELL 306

Elucidation of chemical reactivity of cellulose nanofibrils with varying degree of fibrillation for barrier properties application

Khandoker Salem¹, ksalem@ncsu.edu, Lokendra Pal², Lucian A. Lucia³, Hasan Jameel³. (1) Forest Biomaterials, North Carolina State University, Raleigh, North Carolina, United States (2) Forest Biomaterials- 3205 Biltmore Hall, North Carolina
Bio-based materials have garnered significant attention as packaging materials for food preservation and food security around the worlds due to their green, renewable and sustainable properties. Therefore, cellulose nanofibrils (CNF) has become a key bio-economic priority due to its abundance, high surface area, excellent mechanical properties and most importantly presence of abundance of hydroxyl group in the structure that can be chemically modified. However, their high hydrophilicity and gel-like behavior, limits their use in some applications. Thus, to overcome this limitation, the available hydroxyl groups can be chemically modified to increase their compatibility and to impart desirable novel properties. Thus, CNF samples with different levels of fibrillation and fines were produced by controlling mechanical energy and a mild acetylation reaction was carried out to chemically modify CNF while preserving the integrity of the original morphology and native crystalline structure. Degree of substitution (DS) was measured to quantify surface modification of NFC, which increased with mechanical energy to reach a maximum value and dropped after continuing to increase the energy levels despite reaching the highest level of fibrillation and fines content. The CNF samples showing highest reactivity was used for barrier properties evaluation. The oxygen permeability of CNF films was studied at different relative humidity (RH). The effect of moisture on the barrier and mechanical properties of the films was further studied using water vapor sorption isotherms and by humidity scans in dynamic mechanical analysis. Air and oil resistance increased with the increase in degree of fibrillation of CNF. The influences of the degree of fibrillation on the microstructure and optical properties of the films were evaluated by scanning electron microscopy (SEM) and light transmittance measurements, respectively. This study provides a promising ecofriendly strategy to use modified CNF for optimized performance in barrier properties applications.

CELL 307

Conversion of softwood biomass into thermoreversible supramolecular hydrogel, nanoparticles, and surfactant via methylation-triggered fractionation followed by click reaction

Hiroshi Kamitakahara, hcamitan@kais.kyoto-u.ac.jp, Kentaro Miki, Arata Yoshinaga, Yuki Tobimatsu, Toshiyuki Takano. Graduate School of Agriculture, Kyoto University, Kyoto, Japan

We found that methylation of sawdust of Larix Laempheri promoted the fractionation into methylated cellulose, lignin, and hemicellulose. Aqueous solution of methylated hemicellulose exhibited surface activity similar to that of commercially available methylcellulose. Methylated cellulose fraction was azido-endo-functionalized to give a fraction of methylcellululosyl azide. Methylated lignin was converted to methylated lignin azido-functionalized at Cα position. Azido-functionalized methylated cellulose and lignin
were coupled with alkyne-functionalized cellobiose acetate to afford acetylated methylcellulose-\textit{block}-cellobiose and methylated lignin-\textit{graft}-acetylated cellobiose, respectively, by click reaction. The removal of acetyl group of two copolymers afforded methylcellulose-\textit{block}-cellobiose and methylated lignin-\textit{graft}-cellobiose. Methylenecellulose-\textit{block}-cellobiose self-assembled in water to form thermoreversible supramolecular hydrogels. Methylated lignin-\textit{graft}-cellobiose self-assembled in water to form nanoparticles. This talk will address a new concept for the conversion of woody biomass into three independent functional materials.

**CELL 308**

**New high performance starch based emulsifiers using amylose inclusion complexes**

**Gordon W. Selling, gws1961@hotmail.com, William Hay.** NCAUR ARS USDA, Peoria, Illinois, United States

Amylose inclusion complexes can be formed when corn starch (having 70% amylose) is gelatinized in the presence of hydrophobic ligands. As the components cool, the amylose wraps around the ligand to form an amylose inclusion complex (AIC). The properties of the AIC will be dependent on the selection of the ligand. AIC formed from fatty sodium salts were found to be effective non-foaming emulsifiers. These AIC fatty acid salts were produced using either steam, jet cooking or microwave techniques. Various fatty acid salts (C12-22) were produced and evaluated. Colloidal suspensions were produced using the AIC at concentrations of 0.1-3% solids, and their surface and rheological properties were then characterized. The AICs successfully formed stable emulsions with corn oil. The emulsification properties of the AIC is dependent on pH, with superior emulsifying activity at neutral and alkaline pH when compared with commercial octenyl succinic anhydride (OSA) starch. Emulsions formed with the AIC were stable during long-term storage as the oil droplets were resistant to coalescence. Emulsion stability increased with fatty acid salt chain length due to viscosity differences (higher molecular weight fatty acid salt AICs have greater viscosity). The AIC are effective emulsifiers produced from readily available inexpensive food grade ingredients formed via association rather than chemical bonds using current inexpensive industrial techniques.

**CELL 309**

**Assembly of cellulose nanocrystals into 2D cellular networks during spin coating**

**Eero Kontturi, eero.kontturi@aalto.fi.** Department of Forest Products Technology, Aalto University, Aalto, Finland

The assembly of small molecular compounds, polymers, and nanoparticles in a confined 2D space – generally on flat surfaces – is often altered when compared to their behavior in bulk. From the materials perspective, the 2D assembly is interesting for
sensors, transistors, or optoelectronic templates among many others. Here, we focus on understanding how 2D structures are formed from ordinary sulfated cellulose nanocrystals (CNCs) when deposited by spin coating on flat substrates. To understand the mechanisms behind the formation of the 2D structures, different parameters were probed: pH of the nanocellulose suspension, nature of the counter-ion, concentration of nanocrystals in the spin coating suspension and the nature of the substrates. The resulting morphologies showed that the decisive factor for the assembly of the nanocrystals during spin coating was the pH and concentration of the CNC dispersion. Under specific conditions, the formation of micron-sized cellular networks from the nanosized cellulose nanocrystals was detected. These cellulose networks were essentially 2D structures because their height corresponded to the height of single CNCs. (Not to be confused with molecular 2D structures such as graphene.) Such networks have been previously reported with, for example, spherical gold nanoparticles and their formation has been assigned to relatively complex hydrophobic forces during evaporation. The results in this work show that a robust spin coating method with straightforward control over electrostatic forces can be used to prepare cellular networks from biologically derived nanorods. Such structures can be interesting, for example, as templates for various micro- and nanostructures in 2D space.

CELL 310

Control of coffee ring formation during CNCs droplet drying by polymer addition: Application to enzymatic activity detection

Malika Talantikite, malikatalantikite@outlook.fr, Nadege Leray, Céline Moreau, Bernard Cathala. Institut National de la Recherche Agronomique, Nantes, France

Sulphated cellulose nanocrystals (CNCs) have the ability to self-assemble in suspension above a critical concentration into chiral nematic structures due to the helicoidal orientation of the CNCs that can lead to iridescent/birefringent films when dried. Critical concentration conditions can be reach during evaporation of dilute CNCs suspension droplets since drying induces concentration of CNCs at the edge of the sessile droplet to form a ring-like solid deposit. This process, also termed coffee ring effect, is due to faster evaporation rate at the pinned three-phase contact line than in the center of the droplet. This inhomogeneous evaporation results on fluid flow from the interior of the drop to the contact line to compensate the loss of solvent carrying the particles and accumulates them on its perimeter to form coffee ring.

One strategy to inhibit coffee ring formation is to increase the viscosity of the suspension by the addition of polymers for instance. We investigate the effect of viscosity during drying by focusing on the mixture of CNCs and wheat arabinoxylan (AX). Drying CNCs/AX droplets results in the formation of maltese cross due to gel formation. Recovery of coffee ring can be achieved thank to the hydrolysis of AX by xylanase that breaks the gel structure. The work presented reports the description and the modelling of the drying process in presence and absence of polymer and open the way to fast, easy to handle and efficient enzymatic activity detection method.
Spherically confined cholesteric liquid crystals of hydroxypropyl cellulose

Arindam Chakrabarty, arindam.polym@gmail.com, Kazuma Miyagi, Yoshikuni Teramoto. (1) Gifu University, Gifu, Japan (2) Graduate School of Agriculture, Kyoto Univ., Kyoto, Japan

Cholesteric liquid crystal (ChLC) in a confined space has significant scientific interest. Microfluidic technique is the only reported method to obtain ChLCs in the form of microspheres. However, microfluidics cannot be used for hydroxypropyl cellulose (HPC) due to the very high viscosity at lyotropic condition (≥ 50 wt% concentration). Here, we demonstrate the spontaneous formation of HPC-based lyotropic ChLC microspheres in w/o emulsion. In this case, a functional block copolymer (BCP) was synthesized via reversible addition-fragmentation chain transfer (RAFT) process and it was grafted to HPC. We found that the BCP-grafted HPC spontaneously self-assembled in w/o emulsion, forming the ChLC microspheres where the HPC segments were organized in aqueous phase under lyotropic condition. Interestingly, the microspheres had a clear topological transition from bipolar to radial and vice versa by the influence of different factors like type of solvent (oil phase), degree of substitution of HPC by BCP, molecular weight of BCP, lyotropic concentration of HPC. We studied the effect of such factors that can tune the nature of self-assembly and thereby visualized the change in helical pitch and topologies of ChLCs under spherical confinement.
Enzymatically polymerized polysaccharide stabilized emulsions: Microstructure, rheology, droplet-droplet interactions and comparison to nanocellulose stabilized emulsions

Stephanie A. Kedzior¹, stephanie.kedzior@ucalgary.ca, Sierra Cranmer-Smith¹, Brandy Kinkead¹, Steven Bryant¹, Milana Trifkovic¹, Natnael Behabtu², Kyle Kim², Douglas J. Adelman², Sarah H. Privette². (1) Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada (2) DuPont Biomaterials, Wilmington, Delaware, United States

Emulsions find use in a wide variety of applications ranging from enhanced oil recovery to cosmetics and coatings. Compared to their surfactant-stabilized counterparts, particle stabilized (Pickering) emulsions show enhanced stability and resistance to coalescence and allow for tunable emulsion properties based on the stabilizing particle choice. In this work, enzymatically polymerized polysaccharide particles with varying morphologies (spherical aggregates or fibrils) were used to stabilize dodecane-in-water emulsions. The emulsions were characterized using laser scanning confocal microscopy (LSCM), rheology, and photonic force microscopy (PFM). The emulsion microstructure, rheological properties, emulsion stabilization mechanism, and droplet-droplet interactions were tunable based on the stabilizing particle morphology. Spherical aggregates were present at the oil/water interface and were seen via LSCM to network in the water phase, providing steric stabilization which hindered droplet coalescence and led to adhesion between droplets measured via PFM. Similarly, fibrils were observed networking in the water phase which prevented droplet coalescence in the same manner as spherical aggregates, however the network strength was increased as measured via rheology and no droplet-droplet adhesion was measured using PFM. When compared to emulsions stabilized by cellulose nanocrystals and cellulose nanofibrils, these enzymatically polymerized polysaccharide stabilized emulsions showed similar or higher linear viscoelastic storage moduli, resulting in emulsions with unique and tunable properties based on the stabilizing particle morphology.

CELL 313

Controlled supramolecular assembly of reducing end-functionalized tunicate cellulose nanocrystals

Maud Chemin, Céline Moreau, Bernard Cathala, Ana Villares, ana.villares@inra.fr. INRA, Nantes, France

In this work, we present a straightforward method towards the supramolecular assembly of cellulose nanocrystals by their reducing end. Taking advantage of the parallel organization of the cellulose chains in cellulose I structure that provide the inherent chemical asymmetry to cellulose nanocrystals we have selectively modified only one end of these rigid rod-like crystals. We have introduced the functionality by a carbodiimide-mediated reaction at the reducing ends of tunicate cellulose nanocrystals (CNC). Tunicate nanocrystals were obtained from Styela clava and presented high
aspect ratio (about 100 defined as the length-to-width) and rather homogeneous length distribution (1.5 μm length).
The nature of the functionality introduced at the reducing end determines the supramolecular assembly of CNCs. Hence, the functionalization by biotin allows coupling up to four nanocrystals by the addition of the protein streptavidin (SAV) driven by non-covalent interactions. Differently, the introduction of a polyamine facilitates the assembly of several CNCs or their binding to solid substrates by their reducing ends. Also, the resulting assemblies show swelling and shrinkage in response to pH changes. This work demonstrates that reducing end-functionalized CNCs can be viewed as novel patchy nanoparticles to fabricate complex responsive architectures.
resulting illusion of depth. Angular-resolved optical spectroscopy and K-space optical microscopy analysis both converged toward a quantified illusion of depth in qualitative agreement with the profile expected from the magnetic field mapping and cross-section observations in SEM.

CELL 315

Ion-specific assembly of nanocellulose: Theory and applications

Tobias Bensfellt, bense@kth.se, Lars Wagberg. Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

The properties of nanoparticles with dimensions below roughly 20 nm are highly influenced by the properties of the counter-ion cloud that occupies a significant portion of the effective nanoparticle volume in aqueous dispersions.[1] Exchange between counter-ions of different properties thus have significant impact on the colloidal behavior of nanoparticles and their salt-controlled assembly into materials. Most nanocelluloses have diameters within this critical size range, and even down to a few nanometers where the use of continuum theories, such as the DLVO theory which is based on the Poisson-Boltzmann theory to describe double layer repulsion and the Hamaker theory to describe van der Waals attraction, becomes at least questionable. These highly charged nano-systems are better described by ion-ion correlation and specific ion effects (Hofmeister effects), which currently are the most accepted theories.[2]

In this contribution the colloidal behavior of nanoparticles will be described on the basis of ion-ion correlation and specific ion effects, and some examples are provided where this knowledge can be used to understand assemblies of nanocellulose, such as hydrogels,[3] water-resilient films,[4] filaments prepared by flow-focusing, and chiral nematic phases.[5] The aim is to provide a comprehensive overview without excessive details and to discuss how this knowledge can be used in the rational design of nanocellulose-based materials.

CELL 316

More than paper: Cellulose printing for custom-tailored photonics

chu guang1, chuanguang88@gmail.com, Eyal Zussman2, Orlando Rojas1,3. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Technion-Israel Institute of Technology, Haifa, Israel (3) University of British Columbia, Vancouver, British Columbia, Canada

Nature’s light manipulation strategies, especially those at the origin of bright iridescent colours, have fascinated humans for centuries. Many arthropods display polarization sensitive iridescent colours for communication and aid its camouflage against predators. This phenomenon is due to the hierarchical Bouligand-type structures that exhibit helical organization and periodic surface structure. Knowledge about the interplay between the
morphology, composition and optical appearance of biological photonic systems can provide inspiration for novel artificial photonic devices. Inspired by the beetle of *Chalcothea smaragdina*, here we demonstrate a scalable route for the manufacture of custom-tailored photonic cellulose paper with hierarchical architectures. We combine the nanoscale self-assembly of cellulose nanocrystal with microscale imprinted surface grating-like structure, exhibiting dual structural colour that derived from the helical matrix and circularly polarized light diffraction. We disentangle the hierarchical cellulose printing in different steps: the microscale surface structure of the patterned template, the drying dynamics of the nanoscale cellulose self-assembly and, finally, the coupled optical properties of bulk films. The resulting photonic cellulose paper is particularly important to understand how hierarchy affects the properties of chiral light-matter interactions in the living organism, not only provides inspiration for designing of biomimetic artificial counterparts, but also allows to further understand their biological significance in nature.

CELL 317

Nanofibrillar networks from cellulose biocolloids enable universal assembly of superstructured particle constructs

Bruno Mattos¹, bruno.mattos@aalto.fi, Blaise Tardy¹, Luiz Greca¹, Tero Kamarainen¹, Wenchao Xiang¹, Orlando Rojas¹². (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Departments of Chemical & Biological Engineering, Chemistry and, Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

Self-assembly of nanoparticles into macroscopic constructs, *i.e.* superstructuring, is a powerful framework to extend nano-scaled properties to the macroscopic scale. Superstructured colloidal materials exploit the synergies between components also to develop new or enhanced functions. Cohesion is a primary requirement for scaling-up such assemblies into bulk materials, but it has only been fulfilled in case specific bases. Thermal annealing and polymeric binder have been often applied to introduce interparticle bonding; however, such strategies either erase or modify the functionalities of the primary building blocks. The compositional dependence on the formation process
is a major issue for scale-up efforts, and it expressively limits developments of new nanomanufactured materials. Here, we demonstrate that the complex topology of highly interconnected fibrillar networks formed by supramolecularly cohesive cellulose nanofibrils (CNFs) can be used as a cohesion-inductor co-component in particulated networks. The variety of fibrillar networks formed from CNF (from foams to aerogel-like) enables robust superstructuring with virtually any particle – broad range of sizes and surface chemistries. An intermixed network of fibrils with particles increases the toughness of the assemblies by up to three orders of magnitude compared, for instance, to sintering. Using a variety of SPs, a numerical correlation between the relative surface area between particles and CNFs with the cohesion of the formed network was described. Supramolecular cohesion is transferred from the fibrils to the constructs following a power law, with a constant decay factor for particle sizes from 230 nm to 40 µm. The hierarchical architecture of the intermixed particle-fibril network, however, is strongly dependent on the surface potential of the particles. Hydrophobic building blocks intensify interfibril interactions, while positively charged particles favor strong interactions at the fibril-particle interface. Such behavior is also described by our scaling law for cohesion. These findings are applicable to other nanofiber dimensions via a rationalization of the morphological aspects of both particles and nanofibers. CNF-based cohesion will move developments of functional colloids from laboratory-scale towards their implementation in large-scale nanomanufacturing of bulk materials.

CELL 318

Wrinkling to align cellulose nanocrystals and bacterial cellulose for enhanced applications

Ragesh Prathapan¹, rageshp1989@gmail.com, Jinguang Hu¹, Rico F. Tabor³, Gil Garnier², Andreas Fery⁴. (1) Schulich School of Engineering, University of Calgary, Calgary, Alberta, Canada (2) Bioresources Processing Research Institute of Australia (BioPRIA), Department of Chemical Engineering, Monash University, Melbourne, Victoria, Australia (3) School of Chemistry, Monash University, Melbourne, Victoria, Australia (4) Institute for Physical Chemistry and Polymer Physics and Technical University Dresden, Leibniz Institut für Polymerforschung Dresden e.V, Dresden, Germany

High-resolution inkjet printing of a hydrophobic polymer surface (polystyrene, PS) was accomplished using a patterned coating of cellulose nanocrystals (CNCs) that prevents the ink from bleeding. A periodically crack-free, wrinkled (wavelength of around 850 nm) stamp was prepared by surface oxidation of an uniaxially stretched poly(dimethylsiloxane) (PDMS) elastomeric substrate and was used as a template to transfer aligned patterns of cellulose nanocrystals (CNCs) onto PS surfaces by wet stamping. The morphology of the aligned CNC coatings on PS was then compared with randomly deposited CNCs on PS using atomic force microscopy. The wettability of the CNCs and polymer surfaces with water and ink was measured and analyzed in the context of inkjet printing. This biomaterial coating technique enables high-resolution printing of modern water-based inks onto hydrophobic surfaces for applications in
renewable packaging and printing of biomolecules for high throughput diagnostics. With suitable modifications, the technology demonstrated potential for scalable roll-to-roll manufacturing for industrial flexo printing. When this wrinkling technique was further applied to in-situ align bacterial cellulose (BC) during cultivation, well orientated BC fibers were observed within BC pellicles with enhanced mechanical strength and reduced surface wettability, which also opens the door for a range of novel BC application.

Enhancing Printing Resolution on Hydrophobic Polymer Surfaces Using Patterned Coatings of Cellulose Nanocrystals
Dispersing graphene in water with nanocellulose and materials thereof

Andreas B. Fall¹, andreas.fall@ri.se, Wei Zhao¹, Abhilash sugunan¹, Niklas Nordgren¹, Jens Bodelsson⁴,², Anna E. Carlmark¹,³, Tiffany Abitbol¹, Thomas Gillgren². (1) Bioeconomy, RISE, Research Institutes of Sweden, Stockholm, Sweden (2) BillerudKorsnäs, Frövi, Sweden (3) Royal Inst of Technology, Stockholm, Sweden (4) Chemistry, Lund University, Lund, Sweden

Understanding the interactions between nanocellulose particles and other components will be a key step in the valorization of nanocellulose, as many future materials will be hybrids/composites. Properties such as strength, electrical/thermal conductivity, magnetism, barrier, water/moisture sensitivity and much more can be tuned for nanocellulose-hybrids by smart selections of the other material components. A
fundamental understanding of how nanocellulose interact with other components is necessary to reach the full potential of these materials. Graphene has attracted a lot of attention lately due to its fascinating properties; stiff, strong, flexible, thin, conductive and impermeable. However, it has been shown challenging to create macroscopic materials realizing these impressive properties. One hurdle is the difficulty to disperse graphene, especially in water, due to its hydrophobic character. Nanocellulose have previously been shown to disperse various components not otherwise water dispersible and recently also graphene. To further optimize the dispersibility and the properties of the final dry hybrid materials we investigated the interaction between graphene and nanocellulose. Low nanocellulose concentrations were used in order to avoid the possibility of dispersing by entrappment in a nanocellulose network. Hence, their had to be an interaction between the two components in order to disperse and stabilize the graphene. The results show clear interaction, highly dependent on the charge type of the nanocellulose. The nanocellulose adsorbs to the graphene surface, forming dispersion/materials with clear hybrid-properties.

CELL 320

Bound oligosaccharides and their interactions with water on CNCs produced using aqueous versus gaseous acid hydrolyses

Elina Niinivaara¹,², elina.niinivaara@ubc.ca, Timo Pääkkönen³, Eero Kontturi³, Emily D. Cranston²,³. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Department of Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (3) Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada

The process of isolating cellulose nanocrystals (CNCs) through a controlled sulphuric acid hydrolysis has been shown to result in the precipitation of hydrolyzed cello-oligosaccharides (COSs) onto the surface of CNCs (Bouchard et al. Cellulose 2016, 23, 3555). Although COSs make up a minute mass fraction of the cellulose hydrolysis product, the implication of their presence is wide spread; CNC surface COSs have a significant effect on CNC/water interactions, which in turn reflect on CNC processability, surface functionalizability and reproducibility, and even on their self-assembly. While the extent of precipitation can be controlled by tuning the acid hydrolysis conditions, here we study the degree of COS precipitation as a result of varying the hemicellulose content in the hydrolysis raw material. Furthermore, the conditions necessary for precipitation to occur are investigated by comparing nanocellulosic materials isolated using two distinctly different hydrolysis methods, namely, controlled sulphuric acid hydrolysis in aqueous conditions and high-pressure hydrochloric acid vapour hydrolysis in dry conditions.

CNC/water interactions were investigated using a quartz crystal microbalance with dissipation monitoring (QCM-D) through water/deuterium oxide solvent exchanges on ultrathin CNC films. The water binding capacity of CNCs hydrolysed with H₂SO₄(aq) and HCl(g) from both Whatman1 (cotton) filter paper and bleached birch Kraft pulp were
determined in order to demonstrate the effect of varying amount of surface COSs on said interactions. QCM-D data provided interesting insight into the surface water content of CNCs in relation to their COS content. Additionally, the molecular weight distribution of each CNC type was investigated using a cellulose tricarbanilation derivatization and subsequent analysis through gel permeation chromatography (GPC). Through QCM-D and GPC we were able to infer the presence of precipitated COSs on CNCs produced following various hydrolysis routes and their interactions with water.

CELL 321

Water molecule interactions with nanofibrillated cellulose and its application in humidity sensing

Katariina Solin¹, katariina.solin@aalto.fi, Maryam Borghei¹, Hannes Orelma², Ozlem Sel³, Leena-Sisko Johansson¹, Orlando Rojas¹. (1) Bioproducts and biosystems, Aalto University, Espoo, Finland (2) VTT, Espoo, Finland (3) Sorbonne Universités, Paris, France

In this work, water molecule interactions with nanocellulose and conductive nanocellulose films were studied. The conductive films consisted functionalized multi-walled carbon nanotubes (MWCNT) dispersed in a network of TEMPO-oxidized cellulose nanofibrils (TOCNF). For the first time, adsorption and desorption of water vapor into TOCNF and TOCNF-MWCNT thin films were studied in a climatic chamber equipped with a quartz crystal microbalance (QCM). Herein, the effect of film thickness on water-uptake and swelling was investigated at 30-60% relative humidity and temperature range 25-50 °C. Both films showed fast response to humidity variations by 10% (TOCNF) and 20% (TOCNF-MWCNT) of mass increase. Thus, MWCNT made the fibril network more accessible to water molecules. Besides, by increasing temperature from 25 to 50 °C, the water adsorption decreased by 13% at similar humidity conditions. Further, humidity sensing behavior was characterized by measuring resistance of the films printed on glass and paper substrates. It was observed both films behaved similarly that resistivity followed humidity variation in a cyclic manner from 20 to 60% humidity, i.e. the resistance increased by 12-14% with the increase of relative humidity (See figure). Thus, the paper substrate did not affect the humidity sensing compared to glass counterpart. Further, the effect of MWCNT concentration was analyzed and it was concluded that a humidity sensitive system was produced with films containing only 10% MWCNT. These humidity responsive conductive films provide a great potential to develop biobased humidity sensors for smart packaging applications to monitor conservation conditions of food and medicine products.
Utilization of aqueous cellulose–assisted dispersion of carbon nanotubes

Alireza Hajian¹, hajian@kth.se, Lars Wagberg². (1) Fiber and polymer, KTH Royal Institute of Technology, Stockholm, Sweden (2) KTH Fibre Polymer Techn, Stockholm, Sweden

Carbon nanotubes (CNTs) are among the nanomaterials that are being used in composite structures, due to their high values for strength and conductivity. The dispersion of the CNTs in a composite, however, is challenging. Conventional approaches of mixing the CNTs (e.g. melt mixing with polymers) cause an increase in viscosity when high CNT content is required. Thus, the properties of the composite (with high CNT content) deteriorate, due to relatively inhomogeneous dispersion of the CNTs in polymer matrices. To overcome this problem, aqueous CNT suspensions have been explored. Nevertheless, due to hydrophobic surface of the CNTs, debundling and dispersion of the CNTs in water becomes challenging. Many water-soluble polymers are able to disperse CNTs in water. Among all, cellulose as a biopolymer from renewable resources (plants) is a suitable candidate, because of their abundance in nature, and mass-production. Amongst cellulose derivatives, carboxymethyl cellulose -CMC- sodium salt has been shown to be the most efficient polymeric dispersant for CNTs in terms of colloidal stability, high concentration and film formability. Another form of cellulose derivatives is called nanocellulose that are highly crystalline nanoparticles with colloidal stability in a long range of salt and pH. Aqueous dispersion of nanocellulose are also able to disperse and stabilize unmodified CNTs in water. The major advantage of using such dispersions is less surface coverage of the CNTs when it assembles with nanocelluloses, so the CNT-CNT contacts will be less hindered for carrier hopping,
compared to the case of a polymer wrapped around CNTs. Overall, by different water-removal techniques from cellulose-CNT hybrid dispersions, a wide range of composite structures with various functionalities and properties can be fabricated. Herein, we investigate how cellulose derivatives (in particular CMC and nanocellulose) can assemble with CNTs in water. Based on that understanding, we could optimize the electrical and mechanical properties of the resultant composites and demonstrate potential engineering applications.

**CELL 323**

Swelling and visco-elastic behaviour of wood in mixed solvents: Stationary and transient states

Julie Bossu¹,², Gilles Dusfour¹,², Stéphane Com¹, Philippe Trens²,³, Quoc K. Tran⁴, Nicolas Le Moigne¹, nicolas.le-moigne@mines-ales.fr, Francesco Di Renzo²,³. (1) C2MA, IMT Mines Alès, Alès, France (2) MACS, ICGM, Montpellier, France (3) ENSCM, Montpellier 34296, France (4) ARC-Nucléart, CEA, Grenoble, France

The relevance of solvents and technical treatments used for wood-based products requires a proper identification of the specific role of each solvent on wood biopolymers to better understand their influence on wood properties. In particular, wood impregnated with aqueous solutions of organic solvents has shown to give rise to a stronger swelling than that observed in pure water. This unexplained phenomenon, described as “hyperswelling”, can hardly be elucidated because of the complexity of wood microstructure. In this study, the effect of the impregnation of mixed solvents (with a focus on water / ethanol) of variable concentrations on the physico-mechanical properties of poplar wood has been investigated. The sorption behaviour of veneer sapwood samples has been investigated by vapour sorption gravimetry, dynamic mechanical analysis and optical microscopy monitoring. Pure water and organic solvents showed two really contrasting sorption behaviours. Despite comparable amounts sorbed, organic solvents leads to lower swelling and very limited softening, suggesting different affinities of organic solvents and water for wood biopolymers. With mixed solutions, larger swelling and stronger variations in visco-elastic behaviour than in pure solvents were observed, confirming the synergistic effect of mixed solvents on wood cells physico-mechanical properties. Besides, microscopic observations revealed intercellular decohesion. Such phenomenon is likely to be at the origin of the hyperswelling observed in mixed solvents. Swelling and visco-elastic behaviour of wood in transient states were also studied and highlight peculiar behaviour with mixed solvents in terms of swelling and softening kinetics. Finally, the methodologies developed in this study opens interesting perspectives for the analysis of the swelling, visco-elastic behaviour and stability of technical wood-based products in controlled environmental conditions. In this regard, dynamic mechanical analysis in controlled RH was conducted on pine and beech wood impregnated with polymers having different Tg and hydrophilicity. The results showed contrasted visco-elastic behaviour according to relative humidity and wood – polymer systems.
CATIONIC STARCH IN JET COOKING: DISSOLUTION, RHEOLOGY AND INTERACTION WITH CELLULOSEC SURFACES

Martin Gabriel, Florian Gomernik, Ferula Thaler, Angela Chemelli, Stefan Spirk, stefan.spirk@tugraz.at. Institute of Paper, Pulp and Fiber Technology, Graz University of Technology, Graz, Austria

The optimized use of any raw material in large scale industries is a prerequisite to contribute to a more sustainable environment. However, often the raw materials themselves are tricky to analyze particularly if they involve biobased materials of high inhomogeneity. In addition, slightly different modification and processing may result in unexpected properties, in both positive and negative direction.

One of this tricky raw materials is starch, which poses several challenges in the analytics and the subsequent processing. In this talk, we focus on a rather simple task at first glance-to dissolve industrially relevant cationic starches of different origins. The main theme of the talk will be to use jet-cooking under various conditions and to correlate the rheological behavior of the starches to their affinity to interact with fibers as well as cellulose thin films. These studies will be complemented with in-situ studies using a pressurized rheological cell where insights during dissolution are obtained.

TOWARDS LIGHTER AND STRONGER FIBER BASED PACKAGING MATERIALS: INFLUENCE OF WOOD EXTRACTIVES ON PAPER STRENGTH

Jussi Lahti3,1, jussi.lahti@tugraz.at, Werner Schlemmer3,1, Roman Poschner3,1, Andrea Walzl2, Erich Leitner2, Stefan Spirk3,1, Ulrich Hirn3,1. (1) CD Laboratory for Fiber Swelling and Paper Performance, Graz University of Technology, Graz, Austria (2) Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Graz, Austria (3) Institute of Paper, Pulp and Fiber Technology, Graz University of Technology, Graz, Austria

Wood extractives entering the paper mill along with mechanical pulp are well known to cause various problems, such as deposition issues, reduced paper machine efficiency and decreased paper quality. In the case of kraft pulping many of these problems can be expected to occur to a considerably lesser extent due to efficient washing of the extractives dissolved during cooking. However, it has been previously shown that the strength of softwood kraft pulp hand sheets is very sensitive to the extractive content, i.e. almost 50% decrease in tensile index has been observed with the addition of wood extractives.

Softwood kraft pulp is added to provide strength to the fiber based packaging materials. Thus, the wood extractive induced strength decrease of this pulp potentially disturbs the desired shift towards stronger and lighter packaging papers and boards. In order to better understand the effect of extractives on packaging papers and boards strength the
The objective of our work was as following:

1. Investigate which softwood extractive compounds, \textit{i.e.} fatty acids, resin acids, sterols and other unsaponifiables, are efficiently carried over with kraft pulp to paper mill. This was done by separating the carry-over pitch through acetone extraction and analysing it by 2D GC-MS.

2. Study the harmfulness of these extractive compounds carried over to paper mill on packaging paper and board strength. This was done through papermaking simulations in the laboratory with extractive model compounds, softwood kraft pulp and functional/process chemicals.

Through these investigations we identified the softwood extractive compounds which are most problematic for packaging paper and board strength. This enables us to develop strategies to overcome the harmful effect of extractives, and thus contribute to the development of high-performance renewable packaging materials.

**CELL 326**

**Imaging of micro- and nanocellulose to elucidate their role in paper sheets**

\textit{Mathias A. Hobisch}\textsuperscript{1}, mathias.hobisch@student.tugraz.at, Simon Zabler\textsuperscript{3}, Sylvia Bardet-Coste\textsuperscript{2}, Armin Zankel\textsuperscript{4}, Rene Eckhart\textsuperscript{1}, Wolfgang Bauer\textsuperscript{1}, Stefan Spirk\textsuperscript{1}. (1) Institute of Paper, Pulp and Fiber Technology, Graz University of Technology, Graz, Austria (2) CNRS, XLIM, UMR 7252, Université Limoges, Limoges, France (3) Fraunhofer IIS, Würzburg, Germany (4) Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz, Austria

The impact of micro- and nanocellulose on paper sheet properties is well known. However, their distribution inside paper sheets is still not completely explored. Here we show that the combination of two independent labeling techniques provides valuable information improving the fundamental understanding of the distribution of cellulosic particles in paper sheets. \textit{In-situ} nanoparticle labeling of the small cellulosic particles enhances the contrast to the paper sheet matrix and enable the application of SEM/energy dispersive x-ray spectroscopy and x-ray microtomography both resulting in 3D images. Fluorescence imaging using dyes achieves higher resolutions and investigations with the multiphoton microscope suppress out-of-focus light. The combination of these techniques allows the identification of these particles inside a cellulose matrix. Advantages and limitations of the approach will be discussed.

**CELL 327**

**Wood-based cellulosic fibers and how they can help solving environmental issues**
Martina Opietnik, m.opietnik@lenzing.com, Christian Weilach, Stephan Kulka, Josef Innerlohinger. Lenzing AG, Lenzing, Austria

Environmental challenges (marine pollution, climate change, waste production…) are major concerns of our society. We have to step up in our thinking and behavior to start solving these topics. Materials made from sustainable and renewable resources nowadays experience an upsurge going along with global megatrends. One of these materials are wood-based regenerated cellulose fibers. Lenzing AG is producing such fibers for over 80 years, offering the full range – viscose, modal and lyocell fibers. These fibers are made from renewable raw materials, are produced in closed-loop, environmental friendly production processes and finally are fully biodegradable.

In this paper the question on how innovations of Lenzing AG can further contribute to the changing environmental conditions will be addressed. On the one hand a strong focus on the development of new technologies and products allows entering new markets and offering 100%-cellulose based product solutions - TENCEL™ Luxe (lyocell filament) and LENZING™ Web Technology (nonwoven fabric made of 100% lyocell filaments).

On the other hand reduction of waste and recycling is addressed by introducing REFIBRA™, a fiber from recycled pre-consumer cotton scraps and pulp, being the first cellulose fiber featuring recycled material on a commercial scale. Environmentally conscious customer want complete transparency and honesty throughout the whole value chain – from pulp to end-products. ECOVERO™ fibers set a new standard of eco-friendly viscose production and being transparent through the whole supply chain.

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Wood for energy 2.0

Kati Miettunen1, kati.miettunen@aalto.fi, Jaana Vapaavuori2, Orlando Rojas1. (1) Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Chemistry and Materials Science, Aalto University, Espoo, Finland

Wood has served as the main source of energy throughout most of the history of mankind. In the future, wood-based materials could serve again as building blocks for advanced energy devices, including solar cells. Notably, the current aim in emerging photovoltaic technologies is on cost and reduction of embedded energy (energy payback time). Thus, investigation of affordable and environmentally friendly materials for solar applications is a hot topic. Most recently, investigation of wood and other plant-based materials has taken off in the field of photovoltaics. These bio-based materials can serve in active (photoactive material, catalyst) as well as passive (substrate, electrolyte gelators, insulator layer) functions in the solar device. The important question is where most advantage can be gained and what are the most promising areas of research, considering the implementation of bio-based materials in solar cells. This contribution showcases the recent developments in the field regarding the different
components. While replacement of materials is interesting itself, wood-based materials can even exceed the performance of conventional counterparts. For instance, wood and nanocellulose substrates have shown to give superior optical performance compared to glass and plastic substrates while increasing photocurrent production by 18%. Furthermore, compared to conventional approaches, our recent results show how the utilization of cellulose structures as electrolyte membranes has allowed omitting significant efficiency losses (up to 35%) in the upscaling of the device. Besides relieving environmental impact of the components, the utilization of wood-based materials can play a major role in the recovery of rare and expensive metals from used devices.

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Functionalization of man-made cellulose fibers: Cellulose fibers with high toughness to replace polyester

MOST KANIZ MORIAM, most.moriam@aalto.fi, Kaarlo Niemen, Daisuke Sawada, Michael Hummel, Herbert Sixta, herbert.sixta@aalto.fi. Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland

Ioncell-F is a recently developed process to produce man-made cellulosic fibers from ionic liquid solutions by dry-jet wet spinning. Ioncell-F is an environmentally friendly process and considered as an alternative to the viscose and N-methylmorpholine N-oxide (NMMO)-based Lyocell processes. The ionic liquid ‘1,5-diazabicyclo[4.3.0]non-5-ene acetate’ is used as excellent cellulose solvent allowing for a rapid dissolution at moderate temperatures and subsequent shaping into continuous filaments. Highly orientated cellulose fibers with high tenacity are obtained by coagulation in cold-water bath. These staple fibers are further converted to yarn and applied in knitting and weaving process.

Nowadays, synthetic fibers such as polyesters are widely used for technical application as, for example, sportswear, work wear. However, those synthetic fibers are the major sources of microplastics that are increasingly burdening the environment. To compete with the synthetic fibers, cellulose fibers need to be functionalized and modified in order to obtain good mechanical properties. Although recently developed strategies of cellulose fiber production and their modification are gaining much interests, those approaches have some limitations. As for example, commercially available high tenacity cellulose fibers compromise the good elongation property and vice versa. In this study, using Ioncell-F technology, regenerated cellulose fibers with high tenacity and elongation were produced via different spinneret geometry and selective pulp. Cellulose fibers with such properties yield better tensile strength and toughness. The special Ioncell fibers can be used in sustainable textiles with a long life and in textiles or technical applications where high toughness is required such as in workwear. Considering the higher strength of the fiber, we hypothesize that this fiber might be used as microfiber, which might result lighter yet strong & durable fabric.
Ionic liquid facilitated partial fiber surface dissolution of wood-derived hierarchical scaffolds towards mechanically robust and functional materials

Alexey Khakalo, alexey.khakalo@vtt.fi, Atsushi Tanaka, Antti Korpela, Hannes Orelma. Biomass Processing and Products, VTT Technical Research Centre of Finland LTD, Espoo, Finland

Functional materials based on renewable building blocks are highly demanded for material applications. In this perspective, wood is increasingly considered in sustainable structural materials development due to its inherent hierarchical structure and an oriented reinforcing cellulose phase. In this study, structure-retaining controlled delignification of wood was performed to provide direct access to the hierarchical cellulose scaffold. Next, obtained bio-based scaffold of an increased porosity was infiltrated with an ionic liquid and heat activated to partially dissolve the fiber surface. Optimized fabrication process revealed possibility to avoid wood drying, thus lowering the manufacturing costs. Afterwards water-washed to remove IL samples exhibited pronounced isotropic flexibility, which upon combined compression and lateral shear allowed fabrication of desired 3D shapes with tunable fiber architecture. The obtained cellulosic materials were also structurally, chemically and mechanically characterized revealing superior tensile, optical and barrier properties compared to native wood. Furthermore, while retaining unidirectional fiber orientation, suggested approach allows almost 8-fold tensile strength improvement in the direction perpendicular to fiber orientation, which is otherwise very challenging to achieve. Main results and multifunctional applications of the developed fully biodegradable and totally additive-free materials will be discussed.
Green, rapid and direct preparation of lignin nanoparticles from alkaline pulping liquor

Melissa B. Agustin¹, melissa.agustin@helsinki.fi, Paavo Penttilä², Maarit H. Lahtinen¹, Kirsi S. Mikkonen¹,³. (1) Department of Food and Nutrition, University of Helsinki, Helsinki, Finland (2) Department of Bioproducts and Biosystems, Aalto University, Aalto, Finland (3) Helsinki Institute of Sustainability Science, University of Helsinki, Helsinki, Finland

Extensive efforts to valorize lignin have led to isolating them as nanoscale particles, which unlocked their enormous potential for advanced applications. Numerous methods for preparing lignin nanoparticles (LNPs) were proposed but a method that can easily be adapted on an industrial scale remains a challenge. In this study, we demonstrated a green, rapid and direct method for preparing LNPs from alkaline pulping liquor (APL) by
combining acid-precipitation and ultrasonication. The mild ultrasonication, which only required 5 min, was achieved by sonicating directly without prior drying the acid-precipitated and dialyzed lignin. The process enabled the production of monodispersed, spherical LNPs (Fig. 1) with an average hydrodynamic diameter ($D_H$) of 80 nm and with a zeta potential of -63 mV. The nanostructure of the LNPs in aqueous system studied by small-angle x-ray scattering showed hierarchical structure (Fig. 1) consisting of mass fractal aggregates, with radius of gyration of 23-27 nm, of compact, smaller subunits. Based on the FTIR and 2D-HSQC NMR spectra of the LNPs, the chemical structure remained the same after ultrasonication. Optimization of the method showed the potential for minimizing acid consumption, shortening the dialysis time, and processing directly the APL with as much as 20 wt% lignin. The LNPs were stable during storage for 180 days, at a pH range of 4-7 and in a dispersing medium below 0.1 M NaCl. Furthermore, the isolated LNPs without additional surfactant can emulsify oil in water and form stable emulsions for several days.

Thus, the developed method, which does not use hazardous organic solvents or intensive ultrasonication, opens a sustainable and highly scalable approach to producing LNPs directly from APL. The organic solvent-free LNPs can be further explored as bio-based interfacial stabilizers in the food and medical industries.
Figure 1. Suspension of the isolated LNPs and their characteristics.

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Fundamental understanding of surface chemistry of colloidal lignin particles using model film approach

Muhammad Farooq¹, muhammad.farooq@aalto.fi, Tao Zou¹, Mika Sipponen², Juan Jose Valle-Delgado¹, Maria Morits¹, Monika K. Osterberg¹. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Uusima, Finland (2) Division of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden
“Nanomaterials” as an innovative zone of research offers versatile platform for biomass valorization broadening their application spectrum. Lignin, one of the major constituents of lignocellulosic biomass, encounters multiple challenges in term of utilization, largely due to the complexity of its macromolecular structure and poor dispersibility. In this respect, recent studies have demonstrated that the transformation of lignin into spherical lignin nanoparticles (or colloidal lignin particles, CLPs) can overcome its structural heterogeneity and poor mixability. Furthermore, the high surface area of CLPs along with excellent anti-oxidative properties and biocompatibility, can unlock new frontiers for lignin as biocatalyst, drug delivery vehicles, or bioadsorbents. However, these applications require tailoring of the particle surface properties and understanding of their behavior in different media. Surface sensitive methods, such as atomic force microscopy (AFM), quartz crystal microbalance with dissipation monitoring (QCM-D), surface plasmon resonance (SPR), and ellipsometry are designed to answer these questions, but they require well-defined, thin model substrates.

Previously used lignin model films have been prepared directly from lignin dissolved in organic solvents. However, we suggest that the surface chemistry of CLPs is different because they are formed in water. Here, we propose a method for preparing well-defined lignin model surfaces using CLPs. Straightforward adsorption technique was employed for depositing aqueous CLPs dispersions onto silica substrates. To improve the film coverage poly-l-lysine (PLL) was used as an anchoring substance. CLPs prepared from two different solvent- systems tetrahydrofuran (THF)/water and acetone/water were compared to each other. AFM confirmed that the substrates were well covered with nanoparticles. The swelling and stability of the CLP films at different pH values were examined, and the adsorption of polyelectrolytes and proteins onto CLP surfaces was studied. The presented work is anticipated to elucidate the influence of CLP’s physicochemical properties on interactions with biological systems, advancing their utilization in biomedical applications.

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Lignin nanoparticles as vehicles for transport and release of actives

Simone Cailotto, Matteo Gigli, matteo.gigli@unive.it, Claudia Crestini. Department of Molecular Sciences and Nanosystems, University of Venice Ca' Foscari, Venice, Italy

Lignin particles offer a versatile platform for the development of advanced materials based on renewable resources. When their production can be coupled to simple protocols such as sonochemistry, innocuous solvent-antisolvent approaches or recyclable hydrotrope solutions, they become suitable tools for applications ranging from health & cosmetic, food & feed, agriculture & renewable high performance composites.

Here we describe generation of lignin nanoparticles through a flexible methodology that additionally allows for the incorporation of actives. Following these criteria, in the concept frame of a circular approach to the exploitation of forest and agricultural biomass, lignin nanoparticles (LNPs) were synthesized to be used as synergistic active carriers for plant growth adjuvant and infection control.
applications. The synthesis of lignin nanoparticles was carried out following a hydrotrope approach on different lignin sources, with the optimization of process parameters (such as concentration and mixing rate). The efficacy of the hydrotropic solution recycling was also investigated. The LNPs morphology was studied by means of fluorescence microscopy, DLS and SEM, which confirmed the particles’ spherical shape and highlighted a mean diameter in the range 100 to 200 nm. The evaluation of the Z-potential indicated, as expected, values of about -10 mV. Characteristics of the LNPs generated by the hydrotrope strategy are compared to those obtained by sonochemistry and solvent-antisolvent methodologies to prove the validity of the here presented technique as compared to better established strategies, with a particular focus on process sustainability (e.g. avoidance of toxic organic solvents, solution recycling) and scalability.

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Valorization of side-products from biorefineries by integration of colloidal lignin particles for environmental applications

Guillaume Riviere1, guillaume.riviere@aalto.fi, Muhammad Farooq1, Florian Pion2, Mika Sipponen3, Hanna Koivula4, Antti Korpi1, Tao Zou1, Mauri Kostiainen1, Stéphanie Baumberger2, Monika K. Osterberg1. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Institut Jean-Pierre Bourgin, INRA, Versailles, France (3) Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden (4) Department of Food and Nutrition, University of Helsinki, Helsinki, Finland

Lignin, an underexploited byproduct from biorefineries, pulp and paper industries, has been widely studied during the last decade for sustainable applications. However, due to its structural heterogeneity and especially its low aqueous solubility, this main polyphenolic component of lignocellulosic biomass is still not fully utilized. One technical solution to overcome this limit is the preparation of colloidal lignin particles (CLPs), leading to new potential applications for the lignin nanoparticles.

In the case of lignin-enriched residue from 2G bioethanol production, its use is challenging due to its low solubility linked to the association of lignin and cellulose. Herein we describe a “zero-waste” approach to fractionate the residues into a lignin rich fraction that can be used to prepare CLPs and a carbohydrate rich fraction that can be used to prepare cellulose nanofibrils (CNF). This work shows an example of this fractionation, a detailed characterization of the obtained components and describes a few examples of applications. CLPs are evaluated as agglomeration agents for water purification, while the composite materials made of CNFs are studied for coating and packaging.
Facile method to stabilize colloidal lignin particles by intraparticle cross-linking

Tao Zou¹, tao.zou@aalto.fi, Mika Sipponen¹,², Monika K. Osterberg¹. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

Colloidal lignin particles (CLPs) fabricated from lignin have been demonstrated as high-value products in manifolds including drug-delivery carriers, Pickering emulsions and nano-composites, due to their spherical shape, nanoscaled size, water dispersibility and well-defined surface chemistry. However, the dissolution of CLPs at alkaline condition and organic solvents hurdles their application in processes and products requiring harsh conditions.

In this study, we propose a simple and low-cost method to cross-link CLPs via epoxy reaction by employing bisphenol A diglycidyl ether (BADGE). The cross-linking follows two steps: first, BADGE is encapsulated in the CLPs via co-nanoprecipitation of
softwood kraft lignin (SKL) and BADGE solution against water; second, CLPs are cross-linked by BADGE from inside out at elevated temperature. This approach enables stabilization of the particles while avoiding inter-article crosslinking and aggregation. Overall, we found that the mass ratio of BADGE to SKL played a pivotal role in the encapsulation as well as cross-linking step. At too low mass ratio, BADGE is not sufficient to cross-link CLPs. Too high mass ratio, on the other hand, reduces the uniformity of the particles. With well-tuned mass ratio of BADGE to SKL, CLPs can efficiently be cross-linked yet maintaining their size uniformity, resulting in particles around 90 nm (PDI < 0.2). Preliminary results indicate that the cross-linked particles are stable against high pH and organic solvent. Further surface-functionization of the cross-linked particles at alkaline condition or in organic solvent will be investigated and demonstrated.

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Lignin/Fe₃O₄ nanoparticles derived from different eucalyptus lignin fractions

Ievgen Pylypchuk²,³, ievgenpylypchuk@gmail.com, Anastasia V. Riazanova¹,³, Mikael Lindström², Olena Sevastyanova². (1) fibre and polymer technology, KTH, Stockholm, Sweden (2) Fibre Wood Tech/Wood Chem Pulp Tech, Stockholm, Sweden (3) Wallenberg Wood Science Center (WWSC), KTH Royal Institute of Technology, Stockholm, Sweden

Lignin is the most dominant aromatic polymer on Earth and its valorization technologies are still under development. Typically, in order to obtain value-added products from lignin, it undergoes depolymerization and fragmentation. We believe that development of lignin NPs (LigNPs) and technologies for their functionalization can become a new and emerging trend in lignin valorization. Due to natural origin of lignin and good biocompatibility, multifunctional magnetic LigNPs can find application as targeted drug delivery vehicles for future implementation in biomedicine.

In current work, we investigated influence of lignin fractions molecular weight, concentration of -COOH, Aliph-OH and Ph-OH groups on the LigNPs formation process, and resulting LigNPs characteristics. It was found that size distribution range and polydispersity index of LigNPs can vary significantly, depending on nanoparticles synthesis parameters, e.g. solvent, Mₜ of lignin fraction, water content, etc. For instance, developed synthetic approach to obtain magnetic lignin nanoparticles from different Eucalyptus lignin fractions revealed that Eucalyptus lignin fraction with Mₜ~2000 kDa and PDI 2.20 can form magnetic Lignin/Fe₃O₄ NPs from dioxane/water solution, which are of spherical shape and 650 nm in diameter (Fig.1), with PDI 0.54.

Fig. 1. SEM image of magnetic lignin nanoparticles derived from Eucalyptus lignin with Mₜ~2000 kDa and PDI 2.20.

In contradiction, non-magnetic ethanol-soluble fraction of Eucalyptus lignin (Mₜ~1.390 kDa, PDI 1.60) was able to form LigNPs in size range about 140-200 nm with PDI 0.1. Ethyl acetate-soluble fraction of lignin with Mₜ~0.950 kDa forms LigNPs of average size
around 200 nm and PDI 0.078. Combination of magnetic properties in LigNPs, simultaneously with their further functionalization can reveal their potential in development of targeted platforms for different biomedical diagnostic modalities and drug loading.

Nitrogen-doped lignin-derived carbon supraparticles for CO$_2$ adsorption

Bin Zhao$^2$, binzhao0910@163.com, Bruno D. Mattos$^2$, Maryam Borghei$^2$, Mika Sipponen$^2$, Monika K. Osterberg$^2$, Orlando Rojas$^{2,1}$. (1) Departments of Chemical & Biological Engineering, The University of British Columbia, Vancouver, British Columbia, Canada (2) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland

Nitrogen-doped carbon nanoparticles are attracting increased attention for CO$_2$ capture due to the low energy consumption associated with CO$_2$ regeneration (less than 40 kJ/mol CO$_2$). Carbon nanoparticles with highly accessible surface area facilitate the diffusion kinetics of the CO$_2$ molecule. However, nanoparticles may not be as efficient adsorbents due to mass loss and pressure drop when installed in adsorption columns, e.g. packing column. In such case, macroscopic, bulk carbon is better suitable due to their better handability and higher packing constructions, but it sacrifices the benefits that otherwise arise from nanoscaled materials, such as the high and fast uptake and release of CO$_2$. Herein, we bridge the advantages of the nano and the macroscale by self-assembling 400-nm lignin particles – a biosource for carbon – into milimetric
supraparticles (SPs). We present a versatile self-assembly methodology that introduces cellulose nanofibrils (CNF) as binder to enhance cohesion while preserving the inherent nano-morphologies. SPs were prepared by evaporating the aqueous droplets containing lignin nanoparticles and CNF onto a superhydrophobic substrate. The SPs, comprising 1-15 wt. % CNF, display extremely high mechanical resistance owing to the entangled CNF-particle network. The carbonization of the lignin-CNFSPs produces pomegranate-like carbon SPs with improved strength. Low amounts of CNF allow a partial melting of the lignin’s primary particles during carbonization. Higher amounts of CNF hinder the interparticle connections and create high defect volume across the SP upon carbonization. The SPs were pre-oxidized by slow heating in air before carbonization to turn the lignin system from a thermoplastic to a thermoset. The carbon SPs were subsequently activated by blowing N₂ through ammonia aqueous solution into the furnace tube, allowing control on the porosity and nitrogen content. Specific surface area of 2000 m²/g and 5.5 wt. % nitrogen content were obtained. The lignin-based carbon SPs adsorbs CO₂ at concentration as high as 80 mg/g at 40 °C, which is highly competitive compared to the most recent literature. By self-assembling lignin nanoparticles into macroscopic supraparticles, we created a system with a three-level hierarchy as far as porosity: micropores within the primary particles, mesopores in nanoparticle interstices, and macropores when packing the SPs upon application.

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Biobased water-born polyelectrolyte hybrid nanostructures

Simone Cailotto, Matteo Gigli, matteo.gigli@unive.it, Claudia Crestini. Department of Molecular Sciences and Nanosystems, University of Venice Ca' Foscari, Venice, Italy

Nanostructures of natural polymers have received steadily growing interest as a result of their peculiar properties and applications superior to their bulk counterparts. These structures can be generated in aqueous medium, thus avoiding the use of environmentally non-benign organic solvents. Further, the exploitation of oppositely charged polyelectrolytes allows for the formation of stable interpolymer complexes that can find use in industrial applications as flocculants, binders, and nanocomposites, as well as in agriculture, biological systems and biomedicine.

In this study, the interaction between two biopolymers, i.e. lignosulfonate (polyanion) and chitosan nanowhiskers (CsNWs, polycation) is studied, the main target being a synergistic coupling of the antioxidant properties of lignin-based materials with the antibacterial and antifungal biological activities of chitosan. Lignosulfonates are byproducts of the sulfite pulping process, while CsNWs can be prepared by acid hydrolysis of chitin followed by deacetylation of the obtained chitin nanowhiskers (CtNWs). The as-prepared CsNWs were fully characterized in terms of amino groups content (CHNS), deacetylation degree (FT-IR), morphology (SEM), crystallinity (XRD) and thermal stability (TGA).

A rapid, simple, and robust method for self-assembly of biobased polyelectrolyte complexes starting from a water solution of lignosulfonate and a chitosan nanowhiskers suspension has thus been developed. Different sulfonate/amino group ratios have been
employed in the preparation of the particles, which have been subsequently
classified from the morphology point of view by means of SEM and DLS. Their
stability over the entire pH range and the Z-potential were as well evaluated. The
results have been compared to those obtained by mixing lignosulfonates with CtNWs.

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Sustainable water purification using biomass nanofibers

**Benjamin S. Hsiao**, benjamin.hsiao@stonybrook.edu, Priyanka R. Sharmar. Stony
Brook University, Stony Brook, New York, United States

Nanoscale cellulose fibrous materials obtained from the chemical treatment of biomass are very effective agents for the removal of toxic species from water, including heavy metal ions. Our team at Stony Brook University has developed a simple, inexpensive and environmentally friendly approach to preparing nanostructured cellulose fibers for water purification, based on a nitro-oxidation reaction carried out on untreated (raw) biomasses of diverse origins. There are three key advantages of the nitro-oxidation method. First, the method greatly reduces the consumption of chemicals, energy and water. Second, the processing effluent can be efficaciously neutralised to produce plant fertilisers. Third, the method is effective to extract nanostructured cellulose from underutilised raw biomass such as agriculture waste. The resulting nanocellulose is proven to be an efficient water purification material (membrane or adsorbent) that can treat a wide range of water pollution problems. The demonstrated technology represents an innovative means to enhance the nexus of food, energy, and water systems, and has many far-reaching impacts to improve quality of life.

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Water filters by foam coating of TEMPO-CN

**Andreas Mautner**¹, andreas.mautner@univie.ac.at, Qixiang Jiang¹, Kunnari Vesa², Aayush Jaiswal², Alexander Bismarck³. (1) Institute for Materials Chemistry & Research, University of Vienna, Wien, Austria (2) High Performance Fibre Products, VTT, Espoo, Finland

Clean potable water has become one of the most valuable commodities on this planet. Thus, also technologies for water remediation, e.g. membrane and filter processes, have become an increasingly important topic, both industrially and in research. In previous studies the suitability of nanocellulose papers for nanofiltration and adsorptive filtration was demonstrated. A main outcome of these studies was that a thin active filtration layer of nanocellulose was most effective. This drove the use of nanocellulose coatings for membranes or other applications to become closer to industrial relevance.

Still, one of the main shortcomings when using nanocellulose in industrial processes is that in order to achieve a homogeneous distribution of nanocellulose, the nanocellulose
suspension needs to be very dilute (water content > 99%). Thus, consolidation of coatings requires the removal of large amounts of water. In addition, realizing high flux membranes or filters while maintaining high retention remains challenging when applying tight nanocellulosic structures.

Our solution to this challenge is to replace water by air and utilize cellulose foams rather than dilute suspensions in cast coating processes. We applied nanocellulose foams to coat cellulose based filter substrates, for the use as high flux water filters. Furthermore, this approach was pushed toward industrial production by foam coating negatively charged TEMPO-CNF onto a porous viscose substrate on a pilot line (continuous roll-to-roll process) to prepare filters capable of rejecting metal ions.

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Chitosan/cellulose fibrous composite as efficient adsorbent for Co^{2+} removal

Shuting Zhuang, zhuangst16@mails.tsinghua.edu.cn, Jianlong Wang. Tsinghua University, Beijing, Beijing, China

Adsorbents with high surface area are vital for the exposure of more adsorption sites, leading to higher adsorption capacity. In this study, chitosan/cellulose fibrous composite was prepared using wet-spinning method to improve its specific surface area and mechanical properties. Results showed that fibrous composites had homogeneous fiber structures (88±16 μm) and high surface area (2.5 m² g⁻¹). Its surface area and adsorption capacity towards Co^{2+} were greatly enhanced, increasing more than three times compared to pure chitosan beads (2-3 mm). Its maximum adsorption capacity was determined to be 23.6 mg-Co^{2+} per g-chitosan using the Langmuir isothermal model, which was one order of magnitude higher than pure chitosan beads/microbeads reported. Additionally, the adsorption kinetic behavior of Co^{2+} by chitosan-based fibers followed the pseudo-second-order kinetic model. The optimal pH for Co^{2+} removal was about 6. Furthermore, FTIR and XPS analysis demonstrated the participation of amino groups (dominant role) and hydroxyl groups in the coordination of Co^{2+}, leading to its adsorptive removal. Possible interaction configurations were also given in this study. Above all, the chitosan-based fibers with high surface area were promising biosorbents for Co^{2+} removal.
Zwitterionic functionalized nanolignocellulose for removal of metalloids from industrial effluents

Dimitrios Georgouvelas¹, dimitrios.georgouvelas@mmk.su.se, Ulrica Edlund², Aji Mathew³. (1) Environmental and Materials chemistry, Stockholm University, Stockholm, Sweden (2) Fiber and Polymer Technology, KTH Royal Inst of Technology, Stockholm, Sweden (3) Dept. Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

During the last decades, the increased awareness towards the protection of the environment has resulted in very strict regulations and legislations regarding the treatment of industrial wastewater and effluents. Consequently, the development of new, more efficient, more sustainable, and cheaper filters with tunable smart functionalities has become of high interest.

In this study, we aim to develop hybrid nanolignocellulosic materials functionalized with zwitterionic polysulfobetaine grafts for the treatment of industrial wastewater. Nanolignocellulose was isolated from the residue of pilot scale wood bioethanol production, partially delignified to maintain some residual lignin (ca. 6 wt%), and subsequently mechanically defibrillated. The nanolignocellulose was further functionalized by grafting zwitterionic polysulfobetaine, with single electron transfer living radical polymerization (SET-LRP). Effects of lignin content and zwitterionic
grafting on the morphology, crystallinity, surface chemistry, and thermal stability were evaluated. The presence of residual lignin as well as the zwitterionic grafting enhanced the antimicrobial activity and thermal stability of the system. The adsorption capacity of the nanoparticles was evaluated with respect to copper ion capture.

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Bioinspired concepts for clean water and air

Tekla Tammelin, tekla.tammelin@vtt.fi. VTT, Espoo, Finland

The presentation elaborates how inherent features of plant-based building blocks and cell wall functions can be exploited in biobased materials engineering. The inherent response of plant components towards water (e.g. high hygroscopicity and water transport functions) are harnessed to develop novel materials for water and air purification purposes. The concrete solutions will draw the inspiration from structure, property and function of plant-based components perfected by nature. Material structuring is carried out using highly hydrophilic and hygroscopic 2D and 3D architectures of cellulose nanofibrils which simultaneously provide nanoscaled porosity. In the presence of water, strong capillary forces and diffusion (transport functions) convey ions, molecules and particles including even microplastics inside the 2D/3D structure. The mechanisms playing a key role are based on water interactions and water transport mechanisms in plant cell wall, and capturing of constituents on the fibril surface takes place via specific attractive surface interactions. Furthermore, by exploiting the hygroscopicity of the nanocellulosic materials, water vapour can be used as a carrier for emissions in the form of aerosols, gases and nanoparticles.

CELL 344

Fuel contamination in renewable energy production: Demands of materials development for sustainably reducing of emissions to air, water and soils

Jinying Yan1,2, jinying@kth.se, Anna Karlsson2, Carl Nordenskjöld2, Ulrica Edlund3. (1) Chemical Engineering, KTH Royal Institute of Technology, Stockholm, Sweden (2) Vattenfall AB, Stockholm, Sweden (3) Fiber and Polymer Technology, KTH Royal Inst of Technology, Stockholm, Sweden

Recycled woods and combustible municipal solid waste have been considered as important fuels used for renewable energy generation (district heating and cooling as well as power) in Sweden and EU countries due to improved recycle/separation of sources for waste-to-energy, the mitigation of CO2 emission and relatively low fuel costs. In comparison to conventional biomass fuels, the recycled wood and waste fuels are often enriched with certain contaminants e.g. acidic components, heavy metals and metalloids. Sustainable reducing the impacts of acidic components and heavy metals is an essential environmental issue for this bioenergy conversion. The results of comparative characterization and statistical analysis are given to identify the main
features of the contaminations. Sustainable emission reduction is developed based on a closed water loop, which is implemented in the thermal energy conversion processes of the combined heat and power (CHP) plants and waste incineration (WI) units. A better water-energy-environment nexus could be improved by (1) optimisation of cross-media effects in a closed water loop of the energy conversion processes to eliminate the heavy emissions to water streams, to enhance internal water utilisation and to minimise wastewater discharge, and (2) integration of new separation process to achieve energy- and cost-effective separation process for metal and salt recovery. Cost-effective solutions of emission reduction and material recovery/utilisation are highly dependent on the physicochemical properties of materials used in the emission control processes. A comprehensive analysis of the demands on material improving and new material development will be given based on the following aspects:
- better functional adsorbents to improve flue gas cleaning and recuing solid waste generation (sustainable emission reduction to air and soils),
- suitable membrane materials and technology for cost- and energy-effective water recovery, recycling and purification (reducing emissions to waters, wastewater generation, and enhancing internal water reuse), and
- smart materials and processes for recovering of metals and metalloids (reducing heavy metal contamination and recovering valuable materials).

CELL 345

Structural and surface properties of CMC-CNf based membranes for purification and chromatographic separation of lysozyme as a model biopharma protein

Vanja KOKOL¹, vanja.kokol@um.si, Vera Vivod¹, Simona Vajnhandl¹, Tina Simčič², Urh Černigoji². (1) Institute of Engineering Materials and Design, Univeristy of Maribor, Maribor, Slovenia (2) BIA Separations doo, Ajdovščina, Slovenia

The usage of low-cost readily-available or even disposable single-use filter or membranes in biopharma applications are becoming an attractive alternative for large-scale manufacturing, eliminating the need for the development and validation of intermediate cleaning cycles. In this frame, fiber-based membranes are also becoming of particular significance, where, however, beside of high-enough adsorption-specific sites and tailored pore size distribution, efficient regeneration together with no/low swelling, which directly impacts on the filtration performance in terms of permeability and retention, is still the main challenge.

The aim of this work was to ascertain the morphological (SEM, Mercury), surface (charge/potentiometric titration, hydrophobicity/ZP), swelling/shrinkage and mechanical (strength, pressure stability) properties of membranes prepared from carboxymethyl cellulose (CMC) acting as an anionic adsorbent and cellulose nanofibrils (CNFs) as strengthening filler, both supported with simultaneous citric acid mediated cross-linking. The effects of operating parameters (filtration pressure and velocity, feed concentration) on the performance of dead-end filtration in terms of permeate flux (flow rate) as well as the adsorption (binding capacity) of Lysozyme/Lys as a model protein, will be shown. In addition, the Lys binding capacity and permeability/recovery, evaluated by a
chromatographic mode, will be presented, showing their potential for biochromatography.

CELL 346

Cellulose nanocrystals as a tunable component of pervaporation membranes for ethanol recovery

Aristotelis Kamtsikakis¹, aristotelis.kamtsikakis@unifr.ch, Gwendoline Delepierre¹, Justin O. Zoppe²,¹, Christoph Weder¹. (1) Adolphe Merkle Institute, University of Fribourg, Fribourg, Fribourg, Switzerland (2) Omya International AG, Oftringen, Switzerland

Driven by sustainability concerns, processes that allow the fermentation of biomass into biologically produced fuels, such as bioethanol, are receiving considerable scientific attention. A major challenge of these processes is to recover the biofuels from the aqueous fermentation broths. In this context, pervaporation through dense membranes has emerged as a potential alternative to distillation.

A common design strategy to tailor the permeation properties of pervaporation membranes is to employ (nano)fillers to tune the diffusion of the permeating species and the sorption properties of the composites. Recently, bio-based cellulose nanocrystals (CNCs) have attracted significant interest for membrane applications, due to their high specific surface area and tunable surface chemistry. Interestingly, however, CNCs were so far not used in the context of ethanol recovery via pervaporation, perhaps because they are difficult to incorporate into non-polar polymers.

In this work, we prepared nanocomposite membranes of a hydrophobic poly(styrene)-b-poly(butadiene)-b-poly(styrene) (SBS) matrix and surface-modified CNCs isolated from cotton linters with oleic acid (OLA-CNCs) of varying concentration (0, 8, 15 and 22 % w/w) by solvent-casting from tetrahydrofuran. In order to study the effect of the surface modification on the pervaporation performance, we also used membranes with unmodified CNCs. The SBS/CNCs membranes displayed improved mass fluxes compared to the neat SBS. However, this improvement in fluxes appeared to come at the expense of a lower separation factor and membrane selectivity towards ethanol. Conversely, the SBS/OLA-CNCs membranes offered increased net fluxes of ethanol, while the separation properties were similar as for the neat SBS. Thus, we demonstrate that by tuning the surface chemistry of CNCs the pervaporation performance of ethanol-selective polymers can be tailored to achieve higher fluxes and/or improved selectivity using a renewable nanomaterial.
Schematic showing qualitatively the permeation of ethanol and water through SBS, SBS/CNCs and SBS/OLA-CNCs nanocomposite pervaporation membranes.

**CELL 347**

**Novel method to prepare hemicellulose nanocrystals**

**Zhuojun Meng**, zhuojun.meng@aalto.fi, Daisuke Sawada¹, Christiane Laine², Yu Ogawa³, Nishiyama Yoshiharu³, Tekla Tammelin², Eero Kontturi¹. (1) Aalto University, Espoo, Finland (2) VTT, Espoo, Finland (3) CERMAV—CNRS, Grenoble, France

Xylan is a major hemicellulosic component of hardwoods and plays an important role in physiological process and overall mechanical strength. As the most abundant noncellulosic polysaccharides in hardwood and annual plants, xylan accounts for 20%–35% of the total dry weight and can be produced from different kinds of wood and agro-based materials using various extraction methods. It has drawn considerable interest due to the potential for packaging films, coatings and its use in biomedical products. Although the structure and role of xylan at the molecular level have been revealed, xylan nanocrystal has not been reported so far. Meanwhile, the soft amorphous structure has limited the functional research and application of xylan in, for example, cytoskeleton and reinforcing biomaterials area.

In this contribution, we have successfully produced self-seeded xylan nanocrystals. They differ from cellulose nanocrystals (CNC) in several key aspects: they have controllable length and uniform width distribution, and they are prepared by a bottom-up approach from dissolved xylan, for example. Moreover, the structure of this new hemicellulose nanocrystal and its interaction with solvents within the crystal morphology are uncovered, through which we can better understand and discover the potential
application of hemicellulose in general. Since hemicellulose is biologically compatible, it could open possibilities in biomimetic toughening, drug delivery, membranes, biosensors and bioactive systems.

CELL 348

Mercerized cellulose nanocrystals: From structure to interface organization

Isabelle Capron¹, isabelle.capron@inra.fr, SOMIA haouache¹,², Clara Jimenez-Saelices¹, francois jerome². (1) INRA, Nantes, France (2) 86000 Poitiers, Institute of Chemistry of Environments and Materials of Poitiers, Poitiers, France

Cellulose I can undergo an irreversible transition into a more thermodynamically stable crystalline form, cellulose II, by two distinct processes; regeneration and mercerization. Mercerization involves intracrystalline swelling of the cellulose in concentrated aqueous NaOH followed by reorganization. During that transition, cellulose chains change their orientation from original parallel chains of cellulose I into antiparallel chains of cellulose II.

In that work, native microfibrils MFC-I are mercerized into MFC-II. They are both hydrolyzed using the same classical acid hydrolysis using sulfuric acid leading to CNC-I and CNC-II as demonstrated by X-ray diffraction. A combination of several technics is used to characterize precisely their morphology by electronic microscopy (TEM), AFM and neutron scattering (SANS), showing a noticeable decreasing thickness from 6 nm to 3.5 nm. Chromatographic fractionation of chains solubilized in DMAc-LiCl (SEC-MALLS) or in water (A4F-MALLS) show that the treatment with NaOH doesn’t change the chain length of the fibers but clearly the CNC dimensions. The affinity of the surface of CNCs for oil is also investigated by preparing oil-in-water Pickering emulsions. Both systems show highly stable emulsions. However, the interface thickness measured by SANS is increased for CNCs-II, whereas their dimensions are much lower, which reveals a change in orientation at the interface.

CELL 349

Combining properties of ordered cellulose nanocrystals and mobile silk proteins to facilitate orientation in flow

Ilona A. Leppänen¹, ilona.leppanen@vtt.fi, Suvi Arola², Grysofie Nissen², Juha Salmela³, Stéphanie Lesage³, Tekla Tammelin⁴. (1) VTT Technical Research Center of Finland, Helsinki, Finland (2) Biomass processing and products, VTT Technical Research Centre of Finland Ltd., Espoo, Finland (3) Oxford Biomaterials Ltd, Oxford, United Kingdom (4) Spinnova, Jyväskylä, Finland

Natural materials, such as silk and cellulose, have an inspiring set of properties, which have evolved over hundreds of millions of years. Taking inspiration from these materials, novel functionalized materials mimicking aquamelts are constructed by combining cellulose nanocrystals (CNC) and regenerated silk fibroin (RSF) from
An aquamelt is a water-polymer complex that can transition from a soluble liquid state to an insoluble fiber through a stress input. CNCs are negatively charged colloidal particles with high crystallinity and they were surface modified via amination to enhance the attractive interactions with silk. CNCs are expected to bring order and alignment along with reinforcing ability whereas RSF provides soft and more mobile regions to further facilitate the alignment of the final fiber structure. Interactions and compatibility between CNCs and silk were studied using a quartz crystal microbalance with dissipation monitoring (QCM-D). The aim was to determine whether ionic interactions between CNC and RSF are enough for sufficient binding or whether covalent crosslinking is needed. RSF was successfully adsorbed on CNCs with different surface charges; however, ionic interactions were not strong enough to hold all the adsorbed RSF on the surface. For this reason, covalent crosslinking of the two components is needed, which was achieved by bioconjugation, and again the interactions between the components was determined by QCM-D. Rheological properties of the different CNC-RSF mixtures was studied to determine their suitability for fiber spinning. Under shear, due to the rod-like morphology, CNCs naturally align along the shear direction, exhibiting three distinct regions, which is a typical rheological behavior for a lyotropic liquid crystal polymer. RSF as such does not possess this type of property and does not show orientation. Due to the verified interactions between CNC and RSF it was hypothesized that CNC would induce alignment of silk under shear. The steady shear rheology measurements and simultaneous polarized light imaging showed orientation of some of the mixtures in flow. This was confirmed by the appearance of the Maltese cross due to birefringence. Ionic interactions were observed to be more favorable for inducing alignment of RSF than covalent crosslinking. In conclusion, the CNCs are able to induce alignment of RSF, and could lead to materials that can be spun into fibers with good mechanical properties.

**CELL 350**

**Cellulose based devices based on thin film composites**

*Gregor Trimmel, Stefan Spirk,* stefan.spirk@tugraz.at. Institute of Paper, Pulp and Fiber Technology, Graz University of Technology, Graz, Austria

The use of cellulose in complex devices and composites is very often hampered by the processing of the materials. Here, we discuss our latest findings in the manufacturing of cellulose thin film composites involving different types of nanoparticles. The composites either contain active nanoparticles inside a cellulose matrix or are formed as a thin coating. We will present several examples of optoelectronic devices that are based on such composites, e.g. in optoelectronic devices.

**CELL 351**

**Mechanisms controlling mobility of cellulose nanofibers in the dilute to semi-dilute regime: Influence of semi-flexibility?**
Spinning of cellulosic filaments is far from a novelty, viscose filaments could be spun already in the late 19th century. Today there is a wide variety of filament materials originating from cellulose that are spun under industrial conditions using well-understood spinning processes. Furthermore, significant efforts have been made aimed at the fabrication of filaments from cellulose nanofibrils (CNF) during the last decade, and they typically apply conventional spinning processes and aim at achieving favorable properties by developing spinnable liquids that allow the use of these processes. However, given the nature of CNF, being very slender particles, the application of existing knowledge on macroscopic fiber suspension flows provides insights that offer new routes process routes that give improved mechanical performance, which also have been applied to proteins. The ideal process would align CNF in the direction of the formed thread and by some means preserve this controlled structure during drying.

In order to achieve nanostructure control in the flowing dispersion during spinning, there are a set of parameters that need to be tuned. Examples are the macroscopic time-scales connected to the flow and geometry, gelling by diffusion of salts or protons, as well as mechanisms on the nanoscale such as e.g. Brownian motion. If alignment is to be achieved by tuning the flow-fields, Brownian motion would quickly force nanoscale rod like particles to return to an isotropic state assuming that the suspension is dilute. The time-scale for Brownian return-to-isotropy of a nanorod with a diameter of 10 nm and aspect ratio of 100 would be of the order $10^{-5}$ s, and an increase in concentration would slow down return-to-isotropy about one order of magnitude. These time-scales assumes dilute to semi-dilute suspensions and, in principle, that the nanoscale rods are perfectly stiff. However, if the rods have some flexibility and friction-like forces are present at contact points, the rods may form what we can be described as a loose network. Although the suspension is clearly below the percolation threshold, entanglement still allows flow-field based alignment but with a marked reduction in Brownian effects, allowing the fabrication of e.g. CNF-based filaments with exceptional properties.

**CELL 352**

**Interaction of cellulose nanocrystals with lipid bilayers**

_yotam navon_1,2, yotamon@gmail.com, Bruno R. Jean1, Anne Bernheim2, Laurent Heux1. (1) CERMAV-CNRS, Grenoble Cedex 9, France (2) Ben Gurion University of the Negev, Beer sheva, Israel

Using elementary building blocks to mimic and reconstruct biological structures is intriguing both from fundamental aspects, providing a simple model to study a complex environment, as well as from the applicative point of view, opening the possibility of utilizing such constructs for the creation of new functional materials. Understanding the
key parameters governing the interaction between the building blocks of such systems is highly important.

In the framework of bio-inspired materials, the plant cell wall provides an interesting platform, since its basic components are abundant, eco-friendly and possess outstanding properties. In plant kingdom, one of the first steps of cell wall constitution is the deposition of cellulose microfibrils on top of the plant plasma membrane. In model systems, cellulose nano crystals (CNCs), prepared by acid hydrolysis of the natural fiber, are an attractive building block since they possess similar properties to the native fiber and have excellent colloidal stability.

In this work we have investigated the interaction between CNCs and lipid membranes using 2D and 3D architectures. Quartz crystal microbalance with dissipation, total internal reflection fluorescence microscope, atomic force microscopy and neutron reflectometry were used for the investigation of the 2D system, in which CNCs were deposited on top of supported lipid membranes (SLBs). The interaction between lipid vesicles and CNCs was studied in suspension using isothermal titration calorimetry, light scattering and transmission electron microscopy. Key parameters governing the interaction were elucidated and the results are discussed in the context of plant cell wall inspired materials.

Cell 353

Phase separation and viscoelasticity of aqueous suspensions of colloidal chitin nanocrystals

**Emily Facchine**1,2, efacchi@ncsu.edu, Johanna Majoinen2, Long Bai3, Saad A. Khan1, Orlando Rojas2,1,4. (1) Department of Chemical & Biomolecular Engineering, NC State, Raleigh, North Carolina, United States (2) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (3) Aalto University, Espoo, Finland (4) Departments of
Chitin is a renewable biopolymer with the potential to add value to a vast number of applications as society shifts away from petroleum-based products. Colloidal nanochitin is a particularly promising material due to its nanoscale dimensions and water dispersibility, among other advantages. One of the attractive features of nanochitin is its liquid crystalline behavior, which can be advantageous for uses in optics and mechanical reinforcement. Like many liquid crystal-forming nanoparticles, (such as cellulose nanocrystals), nanochitin has a propensity to phase separate into an ordered and an isotropic phase above a critical concentration (c*). For many such materials, as concentration is increased beyond this threshold the volume fraction of the ordered phase increases accordingly. In this work, however, we observe a complex behavior which results in a very narrow range of concentrations (1.5% - 3% w/w) where phase separation of nanochitin can be observed. Using rheology, the self-assembly behavior and interparticle interactions of aqueous colloidal nanochitin suspensions is investigated to elucidate the dominant mechanisms in structure formation and phase separation or lack thereof. It is shown that entanglement, kinetic arrest, and gelation all play a part in the sensitive phase diagram of colloidal chitin nanocrystals, where the viscoelastic behavior of the suspension is highly dependent on subtle changes in the particle morphology.

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Microstructure arrays of cellulose nanocrystals in liquid crystal bubbles via topographical control

Wenchao Xiang1, wenchao.xiang@aalto.fi, Guang Chu1, Orlando Rojas1,2. (1) Aalto University, Espoo, Finland (2) Departments of Chemical & Biological Engineering, The University of British Columbia, Vancouver, British Columbia, Canada

Cellulose nanocrystals (CNC) have been used as building blocks for producing structures with intriguing photonic features. The photonic responses derived from CNC are due to the fine feature size and liquid crystalline phase. Recent studies have shown that manipulating CNC under confinement causes topological defects. The defects are unique features that can be controlled via topological methods. In the design of complex architectures with liquid crystals, bulk materials, such as droplets, have been widely used. However, the direct and main utilization of the air/water interface, for instance, bubbles, is rare and hard to control.

We will demonstrate the controlled generation of liquid crystal bubbles under different confinements. The structural transition across the air/water interface within confinements both at equilibrium and dynamic states will be discussed. The results are expected to contribute to the design of complex hierarchical architectures.

CELL 355
Cost effective and ultra-low density cellulose based hybrid aerogel from waste biomaterials towards sustainable super thermal insulation

Pragya Gupta, Chhavi Verma, Pradip K. Maji, pradipmaji@gmail.com. Polymer and Process Engineering, Indian Institute of Technology Roorkee, Saharanpur, Uttar Pradesh, India

The environmental friendly aerogel for thermal insulation application is beneficial to minimize energy consumption by shielding the heat flow between the system and surroundings. Depletion of non-renewable sources, waste disposal as well as high thermal conductivity of existing insulating material motivates us to develop biobased insulation materials to reduce the energy utilization for heating or cooling the buildings. The most efficient way towards sustainable development is the utilization of most abundantly available naturally gifted biomaterial i.e. cellulose. It is a naturally occurring biopolymer available in the earth, which is the key component of the plant and formed by linking together β-d-glucose. In this particular study, nanofibrillated cellulose aerogel based on major agricultural waste residue (i.e. wheat straw, rice straw) were prepared by low energy consumption chemo-mechanical method followed by freeze-drying technique. Nanofibrillated cellulose aerogel was modified by sepiolite and methyltrimethoxysilane to enhance flame resistivity, hydrophobicity, and compressibility. Synthesized aerogel demonstrated ultrahigh hydrophobicity (contact angle-159°), incredibly low density (~8kg/m³) and high porosity (~99.76%). The thermal conductivity of aerogels was determined by the transient plane source method. The resultant thermal conductivity of aerogel was demonstrated by about 18.26 mW/mK, which is below the thermal conductivity of air (25.5 mW/mK). The insulation R-value was calculated as 4.8 per inch. Significant reduction of thermal conductivity is beneficial to minimize the requisite space for construction as well as insulation materials per unit area hence; it would permit retrofitting of old buildings exclusive to their architectural design. Initial thermal degradation (5%) of aerogel was around 265°C, and the vertical burning test shows excellent fire retardant property of the material with limiting oxygen index (LOI) 38.9%. The compression modulus of aerogel was determined by cyclic compression stress at 75% strain, resultant ~627 kPa. Considering the unique properties of aerogel, nanoscale engineering is a significant opportunity for its exploration towards energy efficiency building applications

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Water-stable aerogel particles made of enzymatic CNF and alginate

Magnus Gimåker¹, magnus.gimaker@ri.se, Hjalmar Granberg¹, Sara Bacaicoa García³, Hugo Françon², Lars Wagberg². (1) Bioeconomy Division, RISE Research Institutes of Sweden AB, Stockholm, Sweden (2) Fibre and Polymer technology, KTH Royal Institute of Technology, Stockholm, Sweden (3) Public University of Navarre, Pamplona, Spain
By spraying a mixture of 1.6% w/w enzymatic CNF, 0.4% w/w alginate and 10mM CaCl₂ into flaxseed oil, small droplets were obtained. Everything was then frozen at -24°C and kept frozen for 18 hours. After thawing and oil removal by filtration, the formed particles were transferred to a beaker filled with 0.5 M CaCl₂-solution to improve the physical cross-linking between the alginate polymer and possibly also the nanocellulose. The particles were then solvent exchanged to acetone via ethanol and allowed to dry at ambient conditions. The result was a coarse flaky powder with particle diameters ranging from 100-1000 µm and an approximate pore size diameter was estimated to be in the range between 2 and 15 µm, see figure 1. These pores will need time to be filled with water and this might also explain why the particles initially showed a floating behavior when dispersed in water.

The water-stability of the formed particles was investigated by placing particles in water and stirring at 500 rpm for 4 hours. Image 1 shows the result of this process with photos taken at 0, 1 and 4 hours after stirring start and SEM images of corresponding dried powders. Even after 4 hours all particles are intact and the SEM images of a typical particle before and after stirring in water shows that they look qualitatively similar. (see figure 1). With this non-complicated procedure, it is hence possible to create rather well-defined submillimeter sized particles with a high water holding capacity and fine pores, and all this starting with a rather coarse CNF raw material. The particle dimensions and their internal structure are very interesting for a variety of applications, e.g. air and water filtration, catalyst support, controlled release of active components in biomedicine, just to mention a few examples. The enzymatic CNF is cost-efficient, which paves the way for an industrial up-scaling of these type of particles.
Tuning the thermal conductivity of phonon-engineered cellulose nanomaterial-based foams by modifying the surface chemistry

Varvara Apostolopoulou Kalkavoura1, varvara.apostolopoulou@mmk.su.se, Tahani Kaldéus2, Pierre Munier1, Lukasz Dlugoza1, Eva E. Malmstrom2, Lennart Bergstrom1.
(1) Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden (2) Dept of Fibre and polymer technology, KTH Royal Institute of Technology, Stockholm, Sweden

Cellulose nanomaterials (CNMs) combine low thermal conductivity, multiple interfaces, low density and high strength that are of interest in the design of phonon-engineered materials for thermal management. Anisotropic foams based on TEMPO-oxidized cellulose nanofibrils (TCNF) made by ice-templating exhibit very low radial – perpendicular to the columnar pores– thermal conductivity, paving the way to reduce the current energy consumption due to insufficient insulation.

The thermal conductivity of hygroscopic CNM-based foams and aerogels depends on the moisture uptake, the alignment of the fibrils or rod-like nanocrystals, the porosity and fibril-fibril separation distance. Here, we will show how anisotropic ice-templated foams and aerogels can be phonon-engineered by tuning the surface properties of cellulose nanofibrils (CNF) and nanocrystals (CNC). We will determine how the thermal conductivity of anisotropic CNM-based foams depends on the relative humidity (RH), the porosity, and fibril alignment in the pore walls and discuss how the surface chemistry of the fibrils is related to the moisture-induced swelling and the thermal conductivity and the phonon scattering of the foam walls. Preliminary results show that ice-templated foams made from CNC, instead of TCNF, displayed a reduced moisture uptake and a significantly improved toughness but the degree of alignment is influenced by the formation of liquid crystals above the critical concentration. Foams produced from hydrophobically modified fibrils, e.g. carboxymethylated cellulose nanofibrils (CM-CNF) having alkene or alkyn surface groups, exhibited a relatively low moisture uptake and a radial thermal conductivity that was much lower than the radial thermal conductivity of unmodified CM-CNF.

Utilizing cellulose nanofibril-polyampholyte interactions for preparation of hydrogels, films and aerogels

Johan Erlandsson1, jerland@kth.se, Tobias Ingverud1, Lars Wagberg2, Michael Malkoch3. (1) Fibre and Polymer technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) KTH Fibre Polymer Techn, Stockholm, Sweden (3) Royal Inst of Technology KTH, Stockholm, Sweden
The preparation of nanocomposites of cellulose nanofibrils (CNFs) and other materials such as polymers and nanoparticles naturally involves a mixing step. This is often a challenging task due to the sensitivity of CNF gels and dispersions that is coupled to pH and ionic strength but also due to their interaction with polymers and nanoparticles which often induces aggregation of the CNFs. This aggregation makes it difficult to prepare homogeneous materials and the desired properties associated with the CNFs’ nano-size and mechanical properties is also lost. A common route to prepare nanocomposites with CNFs is to mix electrostatically stable CNF dispersions with water dispersible or soluble materials having the same net charge. For example, anionically charged CNFs have been successfully mixed with anionic clays and polymers to form composite films and aerogels. Polyampholytes are polyelectrolytes with both cationic and anionic charges and if the charges emanate from weakly charged groups they will have a tuneable net charge density rendering the polymer net anionic or cationic depending on the pH. This opens up the field for CNF-polymer composites where the mixing without aggregation can be carried out at favourable conditions while at the same time opening up for a greater variety of chemical compositions of the polymer to be used for CNF composites. The present work focuses on Helux, a polyampholyte, and its fundamental interactions with CNFs in order to be able to prepare composite materials where an ideal mixing of the components can be achieved and allowing for tuning the final interaction between the components by simple changes in for example pH. The CNF-Helux composites prepared included films, aerogels and hydrogels. Based on the chemical functionality of Helux and the CNFs it was possible to prepare both physically and chemically crosslinked hydrogels. The chemical crosslinking was achieved by heat treatment and could also be applied to dry materials and wet-stable films and aerogels were prepared. These composites could also be subsequently further chemically functionalised utilising the functional groups of the Helux polyampholyte in the composites.

CELL 359

Time-dependent behavior of cellulose nanofiber networks: Effect of grammage on creep properties and strain-rate dependency

Alba Santmarti, as15713@ic.ac.uk, Hon Liu, Koon-Yang Lee. Imperial College London, London, United Kingdom

Cellulose nanofiber networks in the form of cellulose nanopaper are emerging as an important material structure for various industries. Numerous sectors in which cellulose nanopapers could be used rely on high-speed processing machines to achieve high productivities. Hence, studying the viscoelastic properties, strain-rate dependency and creep of cellulose nanopaper is crucial to assess its performance in many potential applications. Even though many researchers have studied the tensile properties of cellulose nanopaper, the range of testing speeds employed were quite limited and the fracture mechanisms proposed were rather speculative.

In this study, we prepared bacterial cellulose (BC) nanopaper to study the mechanical
Performance of 2-D cellulose nanofibers networks free of non-cellulosic compounds such as hemicellulose or pectin. We investigate the time-dependent behavior of cellulose nanopaper and the influence of grammage on its mechanical properties. Model BC nanopapers with grammages of 20, 40, 60 and 80 g m\(^{-2}\) were produced and the influence of strain rate on their tensile properties are investigated. The viscoelastic behavior and creep properties of BC nanopaper are also discussed in this work. Our results hint that BC nanopaper is not significantly sensitive to time-dependent deformations due to its mostly elastic behavior. It is hypothesized that strong hydrogen bonding between the BC fibers and the lack of amorphous hemicellulose in BC nanopaper might prevent significant deformation mechanisms such as fiber slippage from happening.

**CELL 360**

Effects of hydrothermal treatment on cellulose nanocrystal properties

Oriana M. Vanderfleet\(^{1,2}\), vanderom@mcmaster.ca, Jaclyn Winitsky\(^3\), Julien Bras\(^4\), Akira Isogai\(^5\), Jazmin Godoy\(^6\), Mohan K. Pangà\(^6\), Valerie Lafitte\(^6\), Emily D. Cranston\(^2,3,1\). (1) Chemical Engineering, McMaster University, Hamilton, Ontario, Canada (2) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (3) Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada (4) Grenoble INP Pagora - CNRS, St Martin d’Hères, France (5) Univ Tokyo, Tokyo, Japan (6) Schlumberger Technology Corporation, Sugar Land, Texas, United States

The thermal stability of cellulose nanocrystals (CNCs) is most often evaluated via thermogravimetric analysis, in which dried CNCs are heated in an inert atmosphere. While this can be relevant for applications which use dried CNCs, it cannot predict the performance of aqueous CNC suspensions at high temperatures. To further understand these aqueous systems, CNCs with varying surface chemistry, surface charge density, counterion and size were subject to hydrothermal treatment and subsequently analyzed. Changes in suspension properties such as colour, turbidity, colloidal stability and aggregate size, as well as CNC properties including chemical structure, degree of crystallinity and degree of polymerization, were evaluated before and after heat treatments. CNC surface chemistry, which is generally a function of the production route, heavily influenced the performance of the suspensions at high temperatures. CNCs with sulfate half-ester groups underwent rapid desulfation at temperatures as low as 150 °C. Without electrostatic stabilization, CNCs formed large aggregates and their suspensions became turbid. Despite the loss of colloidal stability, the physical structure of the CNCs remained intact and virtually no depolymerization of cellulose chains occurred. Conversely, by performing an oxidation and imparting carboxyl groups on the surface of the CNCs, significant changes in thermal stability were observed. Carboxylated CNCs maintained colloidal stability at high temperatures due to continuous electrostatic repulsion; however, heated suspensions were heavily discoloured and cellulose chains were degraded. Overall, this study provides insights into the ability of CNCs to withstand hydrothermal treatments and describes the
suspension properties which can be expected after such treatments. Additionally, models have been generated which can predict the behaviour of CNC suspensions for a wider temperature range than has been tested in this study. These new insights and prediction models can be used to expand the use of CNC suspensions in industrial processes with high operating temperatures.

**CELL 361**

**Structuration of hard materials using cellulose nanomaterials**

*Johan Foster, johanf@vt.edu. Virginia Tech, Blacksburg, Virginia, United States*

We present our work on structuration of hard materials (ceramics and metals), using biobased bioproducts. Multi-scale nanostructured porous ceramics exhibit porosity at different length scales. These materials are necessary for the next generation components for a wide range of applications, including, electronic devices, bioimplants, catalysts, aerospace and energy harvesting. Titanium and its alloys are versatile materials that are used primarily because of the materials' high strength, low density, and high corrosion resistance. Despite these very favorable characteristics, titanium is known to have poor mechanical wear behavior. Cellulose nanomaterials are fibers much smaller than a human hair and are available from trees and cotton and compatible with most materials. We present our ongoing work, looking at the structuration of ceramics and metals using cellulose nanocrystals (CNCs). The simplicity of our approaches can potentially lower manufacturing cost for these types of materials, resulting in cheaper (and better) computers, solar panels, airplanes and even implants.

**CELL 362**

**Surface modified CNF systems for composite and coating applications**

*Maria Rosella Telaretti Leggieri¹, roset@kth.se, Tahani Kaldéus¹,², Per-Erik G. Sundell³, Mats K. Johansson¹,², Eva E. Malmstrom¹,². (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden (3) SSAB EMEA, Borlänge, Sweden*

In light of the urgency to design novel functional materials derived from renewable and sustainable sources, cellulose has attracted significant interest over the past decades as a high value biopolymer, partly due to its mechanical properties. Among the varieties of cellulose-based nanomaterials that have been developed, cellulose nanofibrils (CNFs) have proven to be promising bio-based reinforcing nanofillers for composite materials. However, given the hydrophilic nature of native cellulose, surface modification is often essential to ensure compatibilization in hydrophobic matrices such as polymers commonly employed for industrial applications. Hence, in the present project various approaches for modifying the CNF surface are explored. Grafting polymer brushes and hydrophobic biomolecules is investigated, via
covalent and non-covalent attachment of functional and compatibilizing moieties on the CNF surface. Surface-initiated ARGET ATRP (activators regenerated by electron transfer, atom transfer radical polymerization), esterification and transesterification reactions are employed, in aqueous systems or in bulk, aiming for green and scalable processes. Surface modification is investigated as a tool for tuning the properties of polymeric nanocomposites and enhancing the dispersibility performance of modified CNFs in resin formulations.

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Bio-based carbon aerogels with anisotropic porous structure prepared from lignin and nanocellulose for high-performance supercapacitors

bony thomas¹, bonyalappattu6237@gmail.com, Shiyu Geng², Mohini Sain³, Kristiina A. Oksman⁴,odied (1) Department of Engineering Sciences and Mathematics, Luleå university of technology, Sweden, Luleå, Sweden (2) Department of Engineering Sciences and Mathematics, Luleå University of Technology, Luleå, Sweden (3) Department of Mechanical and Industrial Engineering, Centre for Biocomposites and Biomaterial Processing, university of Toronto, Toronto, Ontario, Canada (4) Div. Materials Science, Lulea University of Technology, Lulea, Sweden (5) Fibre and Particle Engineering Research Unit, Faculty of Technology, University of Oulu, Oulu, Oulu, Finland

Developing suitable energy storage systems which are clean, sustainable and efficient has become the primary focus for researchers around the world in the current search for sustainable energy materials to mitigate environmental concerns. In this perspective, lignin-derived carbon materials have already attained great attention as potential supercapacitor electrode materials, because lignin extracted from renewable resources, is low in cost, and generates high carbon yield. In the current study, we have used mechanically fibrillated cellulose nanofibers (CNFs) along with different types of lignin including kraft and soda lignin, for the preparation of the carbon aerogels. The lignin-CNf precursors were prepared using ice-templating followed by freeze drying, which were further carbonized at 1000 °C to obtain the carbon aerogels. The effects of lignin type and lignin to CNF weight ratios on the properties of the carbon aerogels, such as carbon yield, volume shrinkage, density and porosity, elemental compositions, surface area, microstructure and electrochemical properties, have been investigated. The carbon aerogels derived from kraft lignin had higher surface area compared to those derived from soda lignin with the highest value of 715 m² g⁻¹ for the one with 80:20 composition. Surprisingly, the best electrochemical performance has been achieved by the carbon aerogel with 60:40 composition from kraft lignin with a specific capacitance of 163.4 F g⁻¹ at a current density of 0.1 A g⁻¹, with a BET surface area of only 436 m² g⁻¹. A possible reason for the rather unusual observation could be the presence of hierarchical porous structure with more mesopores in the materials. The later benefits electrochemical performance, while providing a large but primarily inaccessible microspores for electrolyte ions and further enhances to the electrochemical properties.

CELL 364
Biomass-based active materials for redox-flow batteries

Werner Schlemmer¹, werner.schlemmer@tugraz.at, Wolfgang Kern², Marlene Kienberger³, Stefan Spirk¹. (1) Institute of Paper, Pulp and Fiber Technology, Graz University of Technology, Graz, Austria (2) Chair of Chemistry of Polymeric Materials, Montanistic University Leoben, Leoben, Austria (3) Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Graz, Austria

The increasing share of renewables such as solar and wind in energy supply challenges the grid stability since the generation often does not match demand. Redox flow batteries (RFBs) are considered as highly promising candidates for large-scale buffering systems to tackle the supply/demand imbalance. However, comprehensible sustainability in the energy system should also be based on renewable materials rather than the currently used non-renewable and often even toxic ones in commercial RFBs. Recent research deals with the synthesis of quinones as active materials for RFBs in order to tune price, stability and redox-potentials. Here, we present our latest results of the investigation of bio-based active materials with applications in stationary energy systems in redox flow batteries. The electrochemical properties of the battery as well as its performance under real conditions will be presented. Using bio-based active materials, coulomb efficiencies between 94 and 99% per cycle can be retained for 250 cycles.

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Lignin-derived electrospun carbon nanofiber networks for high-performance energy storage devices

Jiayuan Wei¹, jiayuan.wei@ltu.se, Lisa J. Carne¹, Shiyu Geng¹, Mohini Sain², Kristiina A. Oksman¹,². (1) Luleå University of Technology, Luleå, Sweden (2) University of Toronto, Toronto, Ontario, Canada

High carbon aromatics rich and naturally abundant biopolymers, such as lignin and their derivatives, show promising future as a carbon source for energy storage applications. In recent time, electrospinning of lignin-based solutions and their carbonization in the form of nanofibers have drawn a great interest among researchers because of their high conductivity and large specific surface area. The later characteristics render them suitable for their use in energy storage devices. There are several industrial methods to extract lignin from various types of biomass, resulting in a diverse array of chemical structures and compositions. These differences can significantly influence the behavior of lignin-based solutions during the electrospinning process as well as the structure, elemental composition, and electrochemical performance of the final lignin-based carbon nanofibers. Therefore, in this study, different types of lignin, such as kraft, lignoboost, soda lignin as well as lignin extracted from bioethanol production are electrospun by using poly(vinyl alcohol) as a binder polymer. The spun fiber networks as such were directly carbonized at 1000 °C for 1 h under the nitrogen atmosphere. Images from the scanning electron microscopy show that all fibers are intact and they
Hierarchical anisotropic carbon aerogels derived from lignin and cellulose nanofibers toward CO₂ capture and energy storage applications

Shiyu Geng¹, shiyu.geng@ltu.se, Jiayuan Wei¹, Simon Jonasson¹, Jonas Hedlund², Kristiina A. Oksman¹,³. (1) Department of Engineering Sciences and Mathematics, Luleå University of Technology, Luleå, Sweden (2) Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, Luleå, Sweden (3) University of Toronto, Toronto, Ontario, Canada

Nowadays, CO₂ capture and energy storage are two important application areas because of the environmental issues and the growing market in electronic devices. Porous carbon materials have great potential toward these areas, which are attributed to their high porosity, large surface area, and good electrical conductivity. However, currently developed carbon materials still have several limitations or drawbacks, such as using non-renewable resources, complex and costly processing and lack of adjustable structure. In this work, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-oxidized cellulose nanofibers, which can be isolated from various renewable resources, and currently under-utilized lignin, which is a primary byproduct of pulp and paper industry, are used as precursor materials to develop a new type of multifunctional carbon aerogels with an adjustable, anisotropic pore structure. By carefully tuning the weight ratio of lignin to cellulose nanofibers in the precursors, the porosity and surface area of the carbon aerogels can be controlled, resulting in different CO₂ adsorption and electrochemical properties. The best results are achieved by the carbon aerogel derived from the precursor with 12 wt% of TEMPO-oxidized cellulose nanofibers, which shows a CO₂ adsorption capacity of 5.23 mmol g⁻¹ at 273 K and 100 kPa, and a specific electrical double layer capacitance of 124 F g⁻¹ when assembled in a two-electrode setup and tested at a current density of 0.2 A g⁻¹. This indicates that the developed carbon aerogels have great potential in the sustainable, next-generation relevant application.

Design of friction, morphology and wetting by cellulose blend thin film composition

Tiina Nypelo¹,³, tiina.nypelo@chalmers.se, Caterina Czibula⁴,⁵, Gundula Teichert², Maximilian Nau⁶, Mathias Hobisch², Chonnipa Palasingh¹, Markus Biesalski⁸, Stefan
Film formation, roughness, wetting, and patterning from polymer blends are often investigated, but frictional properties are less extensively studied. We extend the fundamental understanding of spin coated complex cellulose blend films via revealing their surface friction using Friction Force Microscopy (FFM). Two cellulose derivatives were transformed into two-phase blend films and adjusting the volume fraction of the spin coating solution resulted in variation of the surface fraction of hydrophilic and hydrophobic film component. The film morphology was affected by lateral and vertical separation resulting in roughness variation of the blend films from 1.1 to 19.8 nm depending on the film composition. Friction analysis revealed that the friction coefficient of the films could be tuned and the blend films exhibited lowered friction force coefficient compared to the single-component films.

CELL 368

Xylan additive for cellulose films: Interactions in solution and at surfaces

Chonnipa Palasingh¹, chonnipa@chalmers.se, Anna Ström¹, Hassan Amer³, Tiina Nypelo¹,². (1) Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden (2) Chalmers, Wallenberg Wood Science Center, Gothenburg, Sweden (3) Department of Chemistry, University of Natural Resources and Life Sciences, Vienna, Vienna, Austria

The unfolding bio-based materials revolution demands for new materials grades and this has brought wood hemicelluloses into the spotlight. Molecular interactions with solvents (solubility) and substrates (adsorption) are critical for developing new materials. We have elucidated characteristics of oxidized xylan grades in water solutions and at cellulose surfaces. The experimental approach has been to investigate affinity between cellulose and oxidized xylan and interaction with other compounds, for example amines. Cellulose nanofibrils (CNF) and TEMPO oxidized cellulose nanofibrils (TEMPO-CNF) were used in this study. Investigating the interactions at the hydrated interfaces demands for a combination of analytical techniques and Surface Plasmon Resonance (SPR) and Quartz Crystal Microbalance with dissipation monitoring (QCM-D) were used here. Determination of refractive index in dilute and semidilute solutions were also performed to facilitate molecular analytics. We have so far found out that the oxidized xylans have affinity towards CNF and TEMPO-CNF film. High molecular weight oxidized xylan adsorbed preferably on CNF films while amounts of xylans adsorbed on TEMPO-CNF film were quite similar regardless the size of oxidized xylan. Incorporation
of xylans in TEMPO-CNf film enhanced fibrils network and expelled water molecules from the layer. Oxidized xylan inhibited amine interactions of the cellulose films. The findings are essential for future development of wood hemicellulose materials engineering.

CELL 369

In situ adsorption studies of industrially relevant chemicals on cellulose

Carina Sampl\textsuperscript{1,2}, carina.sampl@tugraz.at, Stefan Spirk\textsuperscript{1,2}, Ulrich Hirn\textsuperscript{1,2}. (1) Institute of Paper, Pulp and Fibre Technology, Graz University of Technology, Graz, Austria (2) CD-Laboratory for Fibre Swelling and Paper Performance, Graz University of Technology, Graz, Austria

The industrial production of paper-based products is always accompanied by controlled inclusion of different types of additives. Cationic polyelectrolytes such as poly(diallyldimethyl)ammoniumchloride (PDADMAC) and cationic starches are introduced in order to manage the paper manufacturing process and increase paper strength. Others are dedicated to change surface properties and optical appearance such as sizing agents and optical brightening agents. The intricate interaction behaviour between the mentioned compounds and paper depends on various factors such as \textit{e.g.} pH, temperature, additive concentration, presence of ions (ion species and concentration). As experiments on pulp fibres and papers are difficult to accomplish, cellulose thin films can give a valuable insight into interaction potential with small and large molecules. Here we employ cellulose thin films derived from trimethylsilylcellulose (TMSC) and cellulose xanthate (CX) prepared via spin-coating. Surface plasmon resonance spectroscopy (SPR) was employed to study the interaction potential of industrially relevant compounds (\textit{e.g.} cationic polymers) in real time. All the thin films were analysed with complimentary surface sensitive techniques.

CELL 370

Birch extract as emulsifier: Interplay of hemicelluloses, pectin and lignin

Maarit H. Lahtinen, maarit.lahtinen@helsinki.fi, Venla Junitti, Kirsi S. Mikkonen. Department of Food and Nutrition, University of Helsinki, Helsinki, Finland

Pressurized hot-water extraction (PHWE) of wood saw meal produces water-dispersible extracts composed of hemicelluloses as main constituents and lignin as a minor component. The main hemicelluloses in birch wood are glucuronoxylans (GX, 28-30\%) and galactoglucomannans (GGM, 1-2\%). Using wood extracts as stabilizers of oil-in-water emulsions is a highly potential application for this material stream, which has been underexploited in traditional pulping processes.

We have recently demonstrated that partial fractionation of lignin from wood extracts is fairly simple by using centrifugal forces. By this approach, we showed that the presence
of lignin increases the long-term physical and oxidative stability of emulsions. We also showed that certain carbohydrate fractions are highly associated with lignin.

The emulsion stabilization capacity of birch extract is complex, as the droplet size distribution in emulsions is clearly bimodal, but on the other hand, the emulsions are extremely stable over storage. The aim of this study was to examine the role of carbohydrates and phenolic compounds of birch extract at the emulsion droplet interface. For this, the oil phase, representing the emulsion droplet interfaces, and the continuous phase of emulsions were separated by centrifugation. The carbohydrate composition and phenolic content of each phase were characterized and quantified, and compared to the previously obtained data for fractionated birch extract (carbohydrate- and lignin-rich fractions).

According to the carbohydrate composition analysis, especially galactouronic acid, which indicates the presence of pectins, was concentrated in the oil phase of emulsions. Quantification of phenolic compounds vanillin and syringaldehyde, which indicate the presence of lignin, were also concentrated in the oil phase. On the other hand, methyl glucuronic acid, which concentrates with lignin in the centrifugal separation of the birch extract, was slightly more associated with the continuous phase of emulsions. However, separation of oil and continuous phases of emulsions by centrifugation enhances sedimentation of lignin and associated methyl glucuronic acid.

The results show that the pectin-rich fractions of birch extract adsorb at emulsion droplet interface. Thus pectin-rich structures may be partially responsible for the excellent emulsion stabilizing capacity of birch extract, in association with hemicelluloses and lignin.

CELL 371

Process innovation for lignin retention and aligning microstructures to strengthen lignin-based fibers

Ericka Ford1, enford@ncsu.edu, Charles Blackwell2, Hannah Dedmon2. (1) Textile Engineering, Chemistry & Science, NC State University, Raleigh, North Carolina, United States (2) Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina, United States

The textiles industry will become more environmentally sustainable as it embraces the use of biopolymers in its processes and products. Lignin is an ideal candidate for sustainable fiber production due to its natural abundance and low cost for production in comparison to synthetic resins. However, there remains a challenge to manufacturing lignin-based fibers at more than 30% lignin to polymer, while maintaining mechanical performance comparative to that of industrial textile fibers (> 30 g/den for specific modulus). Through innovations in lignin-based fiber spinning, we have improved the modulus of polyacrylonitrile (PAN) fibers, upon the addition of lignin by 66%!
Adaptations to the gel-spinning technique- a process for drawing high strength, high
modulus fibers from vinyl polymers- were investigated to improved lignin retention among solution-spun fibers and to achieved microstructures of highly aligned molecules. Using the solubility parameters of lignin and matrix polymer, coagulations baths were tuned to retain lignin within drawn as-spun fiber. Circumstances leading to highly drawable as-spun fiber caused lignin molecules to exhibit the characteristics of an anti-plasticizer. As a result, molecular adhesion between both polymers lead to reinforcement for stiffer fibers. Furthermore, ancillary additives were spun with lignin and vinyl polymer to enhance the thermal properties of PAN fibers. The implications of these results show lignin-based fibers have potential use as low cost precursors for carbon fiber

CELL 372

Lignin based structural biocomposite containing organic phase change material for thermal energy management in buildings

Yunsang Kim¹, yunsang.kim@msstate.edu, Xuefeng Zhang¹, Gulbahar Bahsi Kaya¹, Iris B. Vega Erramuspe², Brian Via², Heejin Cho³. (1) Sustainable Bioproducts, Mississippi State University, Mississippi State, Mississippi, United States (2) Auburn University, Auburn, Alabama, United States (3) Mechanical Engineering, Mississippi State University, Starkville, Mississippi, United States

A substantial portion of the energy produced in the world is consumed by buildings. In 2018, the energy consumption in residential and commercial buildings occupied about 40% (or about 40 quadrillion British thermal units) of total U.S. energy. Given rapidly growing global energy demand and the amount of nonrenewable fossil fuels required to meet such energy demand, enhancing the efficiency of energy consumption in buildings has become critically important. In this work, a lignin based biocomposite containing a phase change material (PCM) is presented. PCM can serve as a source to store and release thermal energy with its latent heat upon phase transition. Specifically, a paraffin based organic PCM, whose melting temperature ranges in room temperature, is confined in a lignin-based rigid polyurethane (RPU) foam. Lignin-RPU foam serves as a porous three-dimensional template with tens-of-micrometer pores that allow for the impregnation of PCM. A vacuum-assisted impregnation method is used for the incorporation of PCM into RPU. The formation of a PCM-containing biocomposite is confirmed by weight and density gain, visual inspection, Fourier-transform infrared spectroscopy, and scanning electron microscopy. Thermogravimetric analysis quantifies the level of PCM incorporation in RPU. Compressive strength of the RPU with and without PCM is tested. Differential scanning calorimetry is used to estimate the amount of thermal energy that can be stored and released in the temperature range relevant to residential and commercial buildings. A custom-made test rig with heating and cooling sides separated by the PCM-RPU composite will evaluate the potential impact of the biocomposite on the thermal resistance, heat transfer, and energy-saving potential in buildings. With the combined experimental results, I will show that the PCM biocomposites have potential for serving as an energy management component in buildings.
CELL 373

Characterization of lignin for preparing lignin modified phenolic resin as wood adhesives

Archana Bansode, asb0062@tigermail.auburn.edu. Chemical Engineering, Auburn University, Auburn, Alabama, United States

The first objective of this study was to characterize lignin macromolecule by various characterization technique such as FTIR (Fourier-transform infrared spectroscopy), Py-GCMS (Pyrolysis–gas chromatography-mass spectrometry), 2D HSQC (Heteronuclear Single-Quantum Correlation), $^{31}$P NMR (Phosphorus-31 nuclear magnetic resonance spectroscopy) and Gel permeation chromatography (GPC). After that, 50% of the phenol by weight in phenol-formaldehyde (novolac) resin is replaced by lignin in addition and condensation reaction between phenol and formaldehyde. The bionovolac is an integrated network of phenol and lignin which is fully cross-linked by common curing agent such as hexamethylenetetramine (HMTA). Further, the lignin and prepared novolac converted to bioepoxy resin. In epoxidation, the hydroxyl group in the structure shows reactivity towards epichlorohydrin. The synthesized bioepoxy cross-linked with amine hardener. The wood composite adhesive strength is measured using the lap-shear test.

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Bio-based polyurethane materials from lignin, cellulose and their derivatives

Elisabete Frollini, elisabete@iqsc.usp.br. Sao Carlos Chemistry Institute, Sao Paulo University, Sao Carlos - SP, Brazil

Cellulose, lignin, and their derivatives have been used as "polyols macromonomers" in the synthesis of polyurethanes aiming at the simultaneous formation of films or composites. Castor oil has been used as an additional polyol, also acting as cellulose or lignin dispersant. Sisal or rayon fibers mats, as well as other components, such as microcrystalline cellulose, have been used as reinforcements of the polyurethane matrices, aiming at obtaining hierarchically reinforced composites. Films with good properties, as the tensile ones and high thermal stability, have been formed in the absence of solvent and catalyst. Hierarchically reinforced composites exhibited exceptional impact properties as they have not fractured when subjected to various conditions. To our knowledge, the approach of this study, and the reported result set (films and composites) are unprecedented.

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Sustainable rice hull pretreatment for bioproducts
Rice hulls are an underutilized and highly available resource in our world. Since the hull or husk constitutes 20% of rough rice, vast quantities of rice hulls are disposed of as waste, or burned in open fields, polluting the environment. Separation of individual lignocellulosic biomass components into cellulose or lignin can increase their value dramatically. However, the recalcitrant nature of the lignocellulosic biomass package prevents easy separations. Dissolution in ionic liquid-glycerol mixtures, hydrothermal carbonization, and combustion for use as a pozzolan have been investigated. The valuable bioproducts from these procedures have been analyzed.

**CELL 376**

**Composite preparation: Exploring the dissolution of flax fibres in an ionic liquid**

_James E. Hawkins¹, jehawkins@live.com, Michael E. Ries², Peter J. Hine²._ (1) Physics, University of Leeds, Leeds, United Kingdom (2) Physics and Astronomy, University of Leeds, Leeds, United Kingdom

Green composite materials can be created from a wide range of textile waste products. This work explores the underlying physics of composite preparation when using linen as a base material in the form of flax fibers. A multiphase all cellulose composite consists of a high stiffness reinforcement and a low modulus yet high failure strain matrix phase. Tailoring the amount of each requires an understanding of the dissolution process. In this work, flax fibers were dissolved in the ionic liquid 1-ethyl-3-methylimidazolium acetate for a range of exposure times and temperatures. Post dissolution analysis consists of both optical microscopy and X-ray diffraction in order to quantify the changes in fibre dimensions and crystalline fractions. Results show that as the fibers are processed, they are surrounded by a regenerated matrix layer which continually increases in size. This layer is found to be a combination of cellulose II and an amorphous cellulose. Optical analysis shows that the time-temperature dependence of this matrix volume follows an Arrhenius dependence with a single activation energy of 90kJ/mol. The reduction in the fraction of cellulose I in the original flax fibres can also be modelled by an Arrhenius type equation and thus an activation energy required for the dissolving of flax fibres is determined. All the data form time-temperature superposition master curves.
A partially dissolved fiber, displaying both the inner core and emergent outer matrix layer.
Valorization of cocoa shells: Effect of two different chemical treatments on physical and chemical properties of cellulose nanofibers

Catalina Gomez Hoyos\textsuperscript{1}, catalina.gomezh@upb.edu.co, Jorge A. Velasquez\textsuperscript{2}, Paulina Mazo\textsuperscript{2}, Lucas Penagos\textsuperscript{4}, Robin Zuluaga Gallego\textsuperscript{3}. (1) ENGINEERING, Universidad Pontificia Bolivariana, Medellin, Colombia (2) Universidad Pontificia Bolivariana, Medellin Antioquia, Colombia (3) New Materials Research Group, Pontificia Bolivariana University, Medellin, ANT, Colombia (4) Centro de Investigación de Desarrollo y Calidad-CIDCA, Compañía Nacional de Chocolates, Medellín, Colombia

During the last 10 years, cocoa fruit has been promoted as a social and economic alternative to substitute illicit crops in Colombia. This trend increased the harvested area in the country nearly 40\%, significantly enhancing the production of its by-products. The valorization of these by products is economically and environmentally relevant for the chocolate industry. This work proposes new alternatives to exploit this biomass, by evaluating two different chemical treatments to isolate cellulose nanofibers- an insoluble dietary fiber which can be used to stabilize fat and reduce the caloric content of cocoa products. For this purpose, cellulose nanofibers were isolated from cocoa shells by two different chemical treatments. A long chemical treatment (LCT) that involves four stages with KOH, NaClO\textsubscript{2}, KOH, and HCl; and a short chemical treatment (SCT) that requires two stages with KOH and NaClO\textsubscript{2}. Each sample was passed through a grinder equipment (Masuko Sangyo, Supermasscolloider MKCA6-2) to deconstruct the hierarchical structure of the isolated cellulose (LCT or SCT). In order to study the effect of these chemical treatments on the physical and chemical properties of the final product, both nanocelluloses were characterized by Fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA), X-ray diffraction (X-ray), fluorescence microscopy and atomic force microscopy (AFM). Results showed that cellulose type I was isolated by both chemical treatments. Fluorescence microscopy, TGA and FTIR showed a higher presence of non-cellulosic components such as cocoa fat and hemicelluloses in cellulose isolated by SCT (holocellulose nanofibers) than in cellulose isolated by LCT. Finally, larger diameters and lower crystallinity index were observed in cellulose isolated by SCT than in cellulose obtained by LCT, associated to a higher presence of non-cellulosic components.

Surface characterization of honeycomb porous films obtained with algae residue cellulose–polystyrene mixtures by breath figure technique

Roxana Lopez-Simeon\textsuperscript{3}, roxanasimeon@gmail.com, Maribel Hernandez-Guerrero\textsuperscript{1}, Hiram I. Beltran\textsuperscript{4}, Jose Campos-Teran\textsuperscript{1,2}, jcampos@correo.cua.uam.mx. (1) Procesos
Cellulose obtained from algae residues (algae-Cell) from a Mexican agar industry with a basic treatment was extracted in a continuous solid-liquid reaction/extraction system. This algae-Cell showed particular physicochemical characteristics (crystallinity, molecular weights and polydispersity) and yield of 74%. In this work, algae-Cell was used mixed with polystyrene (PS) to produce honeycomb porous films using the breath figure technique (see Figure 1). Two different ways to mix the components was considered. In the first one, PS was added to a cellulose suspension (CS₂ or THF) until a final concentration of 10 mg/mL. The second way consisted in the incorporation of algae-Cell during styrene polymerization process. The deposits were performed in glass surfaces at 95% relative humidity and the membranes were characterized with optical microscopy, SEM, fluorescence microscopy and contact angle measurements. A thermo stability study of the films was also performed. The films obtained with the first PS-cellulose mixture had areas with hexagonal arrays of pores and different levels of structure. On the other side, films from the second way showed a highly structured hexagonal array. According to fluorescence microscopy images of the films, cellulose was scattered without any preferential ordering for either the surface or the interior of the pores. Compared to non-porous films, an increase in the contact angle was observed for all the porous films.
Figure 1: Porous membrane films fabrication process

CELL 379

Atomic force microscopy as a tool to probe nanocellulose interactions with water pollutants

Aji Mathew, aji.mathew@mmk.su.se. Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden
The use of nanocellulose based membranes in the adsorption of metal ions, dyes, nitrates and humic acid as well as antifouling coatings well documented. However, the mechanisms of adsorption of contaminants on biobased nanoparticles, surface interactions forces between nanocellulose and water pollutants and surface property changes due to adsorption at micro, nano to molecular scale are largely unknown. Atomic force microscopy (AFM) being a surface sensitive technique is used as a tool to study the surface interactions of nanocellulose with water pollutants. New methodologies for advanced topographical imaging with micro to sub-nanometer resolution and force measurements with pico-newton sensitivity using micro/ nanocellulose modified colloidal probes both in air and liquid medium were developed successfully to understand nanocellulose-pollutant interactions. Liquid phase AFM opened up the possibility for the in situ study of interaction of nanoparticles, ions, dyes etc with nanocellulose in aqueous medium where as PF-QNM nanomechanical measurements on single cellulose nanofiber confirmed the adsorption of metal ions on tempo oxidised nanocellulose. AFM studies provided evidence on the phenomenon as adsorption, self-assembly, mechanical reinforcements and metal ion clustering or stacking related to interactions of nanocellulose with water contaminants. These results are further supported by advanced spectroscopy and modelling tools.

CELL 380

Thin films of nanocellulose: Interactions with water, vapor, and gases

Eero Kontturi, eero.kontturi@aalto.fi. Department of Bioproducts and Biosystems, Aalto University, Aalto, Finland

Nanocellulose networks often exhibit high surface areas with tunable porosity which can be useful for capturing solute and gas molecules as well as other discrete particles. Water and water vapor present challenges for such usage because it affects the porosity of any cellulose network and their excessive presence may, in the worst case, destroy the integrity of the whole network. Yet water molecules in the nanocellulose network can also be seen as an advantage, in very much the same way as water acts as an integral component in plants, modifying the mechanical properties, and altering the adsorption performance, for example. The utilization of water in artificial cellulose constructions, however, requires careful fundamental research on cellulose/water interactions and the influence of water on gas adsorption. This contribution presents a collection of fundamental results on precisely such phenomena. The experimental template consists of ultrathin films of nanocellulose where the morphology has been reduced to the level of a 2D network and changes due to water and vapor sorption are effortless to monitor with various surface sensitive analytical tools. The results constitute the first steps towards understanding the role of water in a cellulose network that is deliberately built for particle capturing purposes.

CELL 381
Unravelling the spontaneous formation of metal oxide nanoparticles on cellulose nanofibrils during adsorption of metal ions: Green alternative towards multifunctional hybrid materials

Luis A. Valencia, luis.alexandro@mmk.su.se, Aji Mathew. Department of Materials Chemistry, Stockholm University, Stockholm, Sweden

Nanocellulose, derived from the most abundant polymer on earth, is known to act as a universal substrate for the in-situ growth of diverse nanoparticles, among them metal oxide nanoparticles. However, typical mineralization reactions require hydrothermal conditions or addition of toxic reducing agents which reduce the environmental friendliness of the hybridization procedures or increase the energy consumption. In this work, we demonstrate the capacity of carboxylated cellulose nanofibrils to spontaneously form functional metal-oxide nanoparticles in operando during the adsorption of heavy metal ions in water, occurring at room temperature. This phenomenon provides great value to nanocellulose as the multiple components act synergistically towards an optimal expression of their properties. Moreover it allows the upcycling of materials through multi-stage applications, increasing their sustainability through the optimal use of resources. The resultant hybrids materials exhibit great potential towards dye-removal from water and superior antimicrobial properties. Furthermore, we mechanistically unravel this phenomena by means of a combination of cutting-edge in situ techniques which allow us to propose a plausible mechanism of the intermediate pathways of assembly of the in-situ growth metal oxide nanoparticles.

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Design of nanoscaled environmental scavengers from biomass: Descriptive and predictive computational modelling as support to the experimental strategies

Susanna Monti1, sapeptides@gmail.com, Aji Mathew2. (1) Institute of Chemistry of Organometallic Compounds, National Research Council, Pisa, Tuscany, Italy (2) Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

The need to create smart ecofriendly scavengers to remove pollutants from water and wastewater has urged scientists to develop new antipollution materials with improved properties from biobased resources.

In our laboratory, we have chosen cellulose as a promising target for scaling, engineering, functionalizing, doping, decorating interfacial portions and bulk regions, at the nanoscale, on purpose (on the basis of the required action), and used a combination of experimental techniques and computational materials modeling, at different scales and levels of accuracy, to characterize and optimise the final compounds and their performance.

Modeling could provide us with structural and dynamical scenarios at the atomic/nano/micro level and molecular dynamics simulations based on reactive force fields, parametrized against quantum chemistry (QC) and experimental data, were
capable of depicting not only structure and dynamics of the hybrid materials, but also bond breaking and formation, interactions with various type of pollutants (i.e. dyes, metal ions, etc.) with an accuracy comparable to QC but at a reduced computational cost. The simulations provided possible pictures of the molecular assemblies inside the biohybrid membranes explaining the formation of different porous structures in solution or dry conditions and demonstrated the ability of these scavengers to capture both metal ions and dye pollutants dispersed in solution. Focusing on (TEMPO)-mediated oxidized cellulose nanofibers (TOCNF)-graphene oxide (GO) biohybrids (Figure 1) it was found that the modulation of the porosity of the material depended on the degree of bending of the GO basal planes, the action of the solvent, GO sheets self-assembly, and location of GO inside the fibers. It was also shown that the matrix network efficiently entrapped metal ions through cooperative coordination of the hydroxyl and carboxyl groups of both the TOCNF and GO components. The formation of copper clusters on the fibers was also reproduced in agreement with the experimental findings.

(TEMPO)-mediated oxidized cellulose nanofibers (TOCNF)-graphene oxide (GO) biohybrid model in solution. Captured copper ions are represented by orange spheres.

CELL 383

Toward smart and safe engineered materials and devices for clean air and water

Ulrica Edlund, edlund@kth.se. Fiber and Polymer Technology, KTH Royal Inst of Technology, Stockholm, Sweden

Water issues are high on the political agenda worldwide, such as the lack of access to safe water and sanitation. Also, emissions to air and insufficient cleaning technologies pose threats to social, economic, and environmental sustainability. Improved and new filter techniques and materials are needed to address current and future challenges.

In our transdisciplinary research program – Mistra TerraClean – partners come together across academia, research institutes and industry in developing smart, safe and sustainable material systems for managing air and water quality in industrial and municipal operations. The smart materials respond and perform in a controlled fashion based on operating stimuli by changing e.g. voltage, pH, illumination, pressure, salt, temperature, or ion strength. We study material candidates derived from
functionalization and hybridization of lignocellulose, activated carbons derived from biomass, amorphous carbonates and/or zeolitic structures. In addition to technical performance, material systems are also assessed with respect to life cycle analyses (LCA) and toxicological appraisal of material production, application in case studies, post-consumer fate, and management. Screening assessments of material performance in relation to national environmental and human health standards help prioritize and guide further materials development in an iterative manner.

CELL 384

Capturing nano- and microplastics with nanocellulose networks

Suvi Arola¹, suvi.arola@vtt.fi, Ilona Leppänen¹, Tia Lohtander²,¹, Christopher Jonkergouw², Minna Hakalahti³, Benjamin Wilson⁴, Hannes Orelma⁵, Tekla Tammelin³.

¹Biomass processing and products, VTT Technical Research Centre of Finland Ltd., Espoo, Finland (2) Bioproducts and Biosystems, Aalto University, Espoo, Finland (3) VTT, Espoo, Finland (4) Department of Chemical and Metallurgical Engineering, Aalto University, Espoo, Finland (5) Department of Forest Products Technology, Aalto University, Espoo, Finland

Microplastic pollution entering our environment at an increasing rate is a major problem in especially the aquatic environment where it cause health issues and mortality to living creatures. Microplastic particles (µPp) are omnipresent found in even the most remote corners of our planet such as the deep sea, they have been reported in human food and raise now concerns to human health. Plastic materials are persistent and degrade over hundreds or thousands of year while at the same time eroding in the environment to smaller µPp (size >1µm) and nanoplastic particles (nPp, size <1µm). To date there are no means to recover nPp or the smaller regime µPp from the environment for quantitation or qualitative analysis as the proposed methods for µPp recovery are based on different filtration and elutriation techniques suited only for the larger regime of the µPp, namely 50µm and above.

Due to limited methods for nPp and smallest µPp extraction very little is known about their abundance in the environment. Studies showing nPp accumulation in aquatic organisms have been done and clearly show their presence in the environment. By using synthetic plastic particles of size below 1µm, it has also been shown, that the nPp accumulate and effect drastically the quality of life and health of several aquatic organisms. Our work tackles the problem of capturing the µPp smaller than 50µm and offers a promising material for their capturing for research purposes as well as at the site of production to mitigate their release to the environment.

In this study, we show that an extremely hygroscopic and amphiphilic large surface area nanomaterial, cellulose nanofibrils (CNF), in different formulations acts as an ideal capturing element for colloidal regime nano- and microplastics. Due to hygroscopic, amphiphilic nature of cellulose driving water diffusion induced capillary forces in the network and cohesion and large surface area of nanocellulose enhancing the cohesion with the particles, CNF captures efficiently the colloidal regime particles. We use fluorescence techniques to verify and quantify capturing of µPp and nPp from flowing
and still media, and we study the capturing mechanisms by using a surface sensitive methods, QCM-D. Using SEM we image the surfaces and quantify the particle amounts after adsorption.

**CELL 385**

*In situ* fermentation derived micro-nano composites with contrast wettabilities and application in oil-water filtration

Siju C R, sijucr@iith.ac.in, anju P. Veedu, Mudrika Khandelwal, mudrika26@gmail.com. Department of Materials science and Metallurgical Engineering, IIT Hyderabad, Hyderabad, TELANGANA, India

We present the preparation of a unique composite comprising of fibres with a combination of contrasting wettability and length scale. A polystyrene - cellulose composite was obtained by in situ growth of nanofibrous cellulose by bacteria inside a matrix of polystyrene macrofibres. These composites were used for oil-water separation and were found to have better efficacy than polystyrene or cellulose alone.

**CELL 386**

Fabrication of aerogels from β-cyclodextrin grafted-cellulose nanofibrils for capture of microcystin-LR for water remediation

Diego Gomez-Maldonado¹, dzg0023@auburn.edu, Autumn M. Reynolds¹, Leena-Sisko Johansson², Matthew Waters³, Iris B. Vega Erramuspe¹, Maria S. Peresin¹,4. (1) School of Forestry and Wildlife Science, Auburn University, Auburn, Alabama, United States (2) School of Chemical Technology, Aalto University, Aalto, Finland (3) Department of Crop, Soil and Environmental Sciences, Auburn University, Auburn, Alabama, United States (4) Technical Research Centre of Finland, VTT, Espoo, Finland

Microcystin-LR found in algal blooms is increasing year by year, so that concentrations already exceed by several hundred-folds the safe level of 1 µg/L recommended by The World Health Organization. High levels of this toxin increase possibility of liver damage, fatalities in domestic animals and wildlife; and promotes bioaccumulation in fish, rice and other food sources. The need to develop environmentally friendly adsorbents to capture this toxin is pressing.

β-cyclodextrin (CD), a cyclic oligosaccharide consisting of 7 anhydroglucose monomers, with a hydrophobic cavity at its center, has been reported to form strong complexes with this toxin. However, the low molecular weight of neat CD limits its use for simple capture and filtration of toxin.

In this work, CD was immobilized in solution onto bleached softwood cellulose nanofibrils that were used to generate high surface aerogels. Charge density titration, Fourier Transform Infrared (FTIR), X-Ray Photoelectron Spectroscopy (XPS) Thermogravimetric Analysis (TGA), and Atomic Force Microscopy (AFM) characterization techniques were used to confirm modification of the fibrils; Inductive
Coupled Plasma Mass Spectroscopy (ICP-MS) was used to determine the presence of trace chlorine in the material, while Scanning Electron Microscopy (SEM) and Dynamic Vapor Sorption (DVS) were used to determine porosity and surface area of the aerogel. The removal of microcystin-LR by the formed aerogels was followed by High-Performance Liquid Chromatography with an UV detector (HPLC-UV).

**CELL 387**

**Aerogels from pulps: Influence of pulp composition and non-solvent type on aerogels’ properties**

Lucile Druel¹, Lennart Salmen², Elisabet Brännvall², Fernando Alvarado², Tatiana Budtova¹, Tatiana.Budtova@mines-paristech.fr. (¹) CEMEF/Mines ParisTech, Sophia Antipolis, France (²) RISE/Bioeconomy, Stockholm, Sweden

Cellulose aerogels are lightweight materials with specific surface area around 200 – 300 m²/g; they can be used as delivery matrices, for absorption and adsorption and in electro-chemical applications when pyrolysed. In most cases cellulose aerogels are made from “pure” cellulose (microcrystalline cellulose or cotton) and coagulation is performed in water which is then replaced by acetone or ethanol in order to perform drying with supercritical CO₂. The goal of this work was to answer two questions: what is the influence on aerogels’ properties, of 1) non-cellulosic components in dissolving pulps (hemicellulose, lignin) and 2) the first coagulation bath? Pulps with various amounts of lignin and hemicellulose were dissolved in 8%NaOH-water or 8%NaOH-0.8%ZnO-water, coagulated in different non-solvents (1 M HCl, distilled water, ethanol) and dried under supercritical conditions. The composition of aerogels, organic (lignin, sugars) and inorganic (Na, Zn) components, was determined and correlated with the solubility of each component in cellulose non-solvents. Aerogels’ density, specific surface area and morphology were studied. We demonstrated that the type of non-solvent has a significant influence on aerogels’ properties in terms of the presence of non-dissolved metals and cellulose crystallinity. Hemicellulose leads to a slight decrease of aerogels’ specific surface area.

**CELL 388**

**Aerogels directly from whole biomass: Fabrication and mechanistic study**

Yang Liao¹, Zhiqiang Pang¹,², Xuejun Pan¹, xpan@wisc.edu. (¹) Biological Systems Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States (²) State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Jinan, Shandong, China

Lignocellulosic aerogels, including or excluding lignin, were fabricated directly from ground Douglas fir wood without prior removal of hemicellulose and lignin using lithium bromide (LiBr) molten salt hydrate (lithium bromide trihydrate – LBTH) as a cellulose
solvent via a procedure of cellulose dissolution, gelation, and regeneration. The fabricated aerogels had homogeneous and continuous porous structure, extremely high porosity, large surface area and very low density. The lignin-excluding aerogel had a density as low as 4.6 mg/cm³ and a porosity larger than 99%, while the lignin-including whole biomass aerogel retained almost all lignin and more than 90% of the starting biomass and had 24.9 mg/cm³ density and 98.3% porosity. Mechanistic study revealed that different from those in other cellulose solvent systems, cellulose gelation and regeneration in the LBTH system occurred in two independent steps. The weak crosslinking through coordination effect between cellulose hydroxyl group and Li⁺ cation led to the gelation of cellulose solution in the LBTH, while the exchange of the solvent LBTH with non-solvent water during washing resulted in the cellulose regeneration via precipitation/aggregation to form a 3D fibrous network of cellulose.

CELL 389

Air-dried, ultralight nanocellulose-based aerogels with tunable functionalities

Jowan Rostami², jowan@kth.se, Korneliya Gordeyeva¹, Goksu Cinar Ciftci², Ekeram Lahchaichi², Lars Wagberg². (1) Fluid Mechanics, KTH Royal Institute of Technology, Stockholm, Sweden (2) Polymer and Fibre Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Aerogels can be used in a wide range of applications, for example in lightweight construction materials, thermal insulation, water and air purification, and biomedical applications. Aerogels made from cellulose nanofibrils (CNFs) have many high-performing characteristics such as low density, good mechanical performance, and the amenability to surface modification for tuning material functionality. However, the preparation of CNF-based aerogels, analogously with conventional silica-based aerogels, commonly involves tedious and energy-demanding drying processes. Furthermore, to facilitate use in water, crosslinking protocols are needed to obtain wet-stable structures. Although several methods to chemically crosslink CNF structures have been reported, these processes generally require mixing of the CNFs with a crosslinking reagent, often with a post activation of the reaction that facilitates the crosslinks. In this work, we propose a multicomponent supramolecular mixture in which CNF and sodium alginate form strong complexes with multivalent cations for structure stabilization, that is, no covalent crosslinking chemistry is needed. The fabrication approach is based on ice-templating of the multicomponent gel-network in a conventional freezer, generating structures strong enough to withstand subsequent solvent exchange and drying under ambient conditions. The resulting aerogels have densities ranging from 3.4–20 kg/m³ and exhibit exceptional mechanical properties under both dry and wet conditions. The prepared aerogels also have a unique shape recovery from a fully compressed state under wet conditions and excellent water-holding capacity, which makes them highly suitable as absorption materials.

CELL 390
Amphiphilic to hydrophobic nanocellulose aerogels via ice-templating, sol-gel and organogel

You-Lo Hsieh, ylhsieh@ucdavis.edu. Biological & Agricultural Engineering, University of California, Davis, California, United States

Aerogels are unique ultra-porous and super-light materials with density close to air (1.2 mg/cc at 20 °C). Structural engineering and properties of aerogels depend on the chemical nature of precursors as well as structural formation processes. Whereas silica aerogels are hydrophilic and carbon aerogels are hydrophobic, amphiphilic aerogels can be facilely structured from nanocelluloses. Highly crystalline Iα nanocelluloses can be efficiently derived by combined chemical and shear force approaches into either nanocrystals or nanofibrils of controlled geometries and surface chemistries. The nanoscale lateral dimensions and specific surface chemistry allow 3D structural formation. This presentation will give examples of distinctively different functional aerogels by engineering the structural formation processes involving ice-templating, chemical crosslinking and sol-gel synthesis processes as amphiphilic super-absorbent, hydrophobic separators, CO2 capturing, strain sensor, energy storage, etc.

CELL 391

Crosslinked cellulose nanocrystal aerogels and hydrogels with hierarchical structure for tissue engineering

Kevin J. De France4, Daniel A. Osorio1, Ariana L. Hurley6, Jaclyn Winitsky6, Kathryn Grandfield6, Todd Hoare4, Jose Moran-Mirabal5, Emily D. Cranston2,3, emily.cranston@ubc.ca. (2) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (3) Chemical and Biological Engineering, University of British Columbia, Vancouver, British Columbia, Canada (4) Chemical Engineering, McMaster University, Hamilton, Ontario, Canada (5) Dept Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario, Canada (6) Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada

Cellulose nanocrystals (CNCs) are promising renewable nanoparticles with unique properties including high mechanical strength and a large aspect ratio. As such, CNCs form strong hydrogels and aerogels either by being crosslinked to each other or to a networked polymer matrix. This work will first look at “CNC-only” aerogels which are 3D structures with bimodal porosity and shape recovery features that make them ideal to fill bone defects and promote bone regeneration. Next, CNC-poly(oligoethylene glycol methacrylate) (POEGMA) nanocomposite hydrogels with controlled orientation of CNCs and structure in 2.5D and 3D will be demonstrated. Directional freeze casting, magnetic alignment, and biaxial and uniaxial shrinking of hydrogel disks, films and electrospun fibres were used to obtain novel structured biomaterials. Electron microscopy and X-ray microcomputed tomography allowed for visualization of the favorable interactions that occur between CNC structures and cells. Shrinking CNC materials on pre-strained substrates not only provides new structures but also elucidates their mechanical
properties. In vitro and in vivo results with CNC aerogels and hydrogels will be presented including cell compatibility, cell and protein adherence, tissue differentiation, hydroxyapatite nucleation and biodistribution of fluorescently labelled CNCs in an animal model. These studies highlight the potential of CNC-based materials in a variety of biomedical applications and allow us to gain a better understanding of CNC toxicity, biodegradation and clearance.

CELL 392

Cellulose nanofibril based gels for 3D printing of scaffolds for use in tissue engineering

Kristin Syverud1,2, kristin.syverud@rise-pfi.no, Ellinor Heggie3. (1) Paper Fibre Research Inst, Trondheim, Norway (2) Chemical engineering, NTNU, Trondheim, Norway (3) RISE PFI, Trondheim, Norway

Cellulose nanofibrils (CNFs) are promising candidates in several material applications like for e.g. substitute for fossil plastic, in coatings, in wound healing and tissue engineering. Cellulose is generally known for high strength and stiffness but also by being brittle. Thus, combining cellulose with other polymers in hybrid materials could improve the properties of the combined materials. The combination of CNFs with alginate and gelatine is studied, with focus on mechanical properties of hydrogels. 3D printing of CNF based gels is a promising technique for production of personalized products, like scaffolds for tissue engineering. Properties of composite inks of CNFs and either CNCs or alginate for 3D printing will be presented. Furthermore, results from in vivo studies of TEMPO oxidized, carboxymethylated CNF and gelatine scaffolds will be presented. The inflammatory responses after 4, 30 and 180 days will be presented.

CELL 393

Cactus mucilage as a material for nanofibrous membranes for scaffolding and wound healing applications: Cell viability study

Dominika Borakiewicz, borakiewicz@mail.usf.edu, Norma Alcantar, Diane Allen-Gipson, Zhi Tian, Sylvia Thomas. University of South Florida, Tampa, Florida, United States

In recent years, natural biomaterials have been functionalized to mimic the body’s own extracellular matrix for wound healing and tissue scaffolding. Mucilage, from the Opuntia ficus-indica, is responsible for promoting nutrient transport, wall healing, and water replenishment; all of which are needed to maintain and restore integral tissue functions. Therefore, cactus mucilage should be investigated as a credible, natural, plant-based biomaterial for direct applications in the area of wound dressing and tissue regeneration.

In this study our goal is to analyze the structure and cell viability of electrospun
polymeric biomembranes of two different forms of cactus mucilage (gelling and non-gelling) and copolymers, polyethylene glycol (PEG) and polymethyl methacrylate (PMMA).

By electrospinning a polymeric solution to fabricate a nanofiber biomembrane, a topography is created that promotes cell adhesion, migration and proliferation as in the body’s own ECM. In addition, the high surface area to volume ratio of the nanofibers and porosity of the nanofiber membrane are advantages for regenerative and healing processes.

PEG and PMMA are examined and tested as potential copolymers for electrospinning mucilage biomembranes suitable for cell viability. Investigations explore cactus mucilage and PEG/PMMA polymeric concentrations suitable for biomembrane formation and testing viability effects on NuLi cells. A 50/50 w/w % of PEG and PMMA solution was prepared and used to fabricate valid and sustainable membranes, including non-mucilage polymer membranes (PM), gelling mucilage membranes (GEM), and non-gelling mucilage membranes (NGM). Solutions were electrospun at predetermined parameters (flow rate, voltage, distance, and concentration) to create detachable nanofiber biomembranes for analysis. The trials resulted in the formation of nanofibers, and the Scanning Electron Microscopy (SEM) scans revealed fibers with a diameter range of 1 micron to 150 nanometers.

Experimental results show that GEM and NGM membranes had more cell viability around the edges of the membrane, which could be due to the membrane taking away the medium nutrients at the more dense membrane center or the membrane’s weight pushing the cells to the outer edges. Further testing of the GEM and NGM membranes needs to be conducted, but the results suggest that the cactus nanofiber biomembranes could create a stable environment for cells and beneficial conditions for regenerative and healing processes.

CELL 394

Anisotropic nanocellulose gel membranes for drug delivery: Tailoring structure and interface by sequential periodate: Chlorite oxidation

Sven F. Plappert¹, Falk Wolfgang Liebner¹, falk.liebner@boku.ac.at, Johannes Konnerth², Jean-Marie Nedelec³. (1) Dept of Chemistry, Boku University Vienna, Tulln an der Donau, Austria (2) Institute of Wood Technology and Renewable Materials, University of Natural Resources and Life Sciences Vienna, Tulln, Austria (3) CNRS, SIGMA Clermont, ICCF, Université Clermont Auvergne, Clermont-Ferrand, France

This study investigates periodate – chlorite oxidation as a pretreatment to tailor the surface charge density of cellulose nanofibers employed in open-porous anisotropic hydrogel membranes for transdermal drug delivery. The obtained materials feature high specific surface (≤500 m²g⁻¹, BET), small average pore size (ca. 40 nm) and tunable surface charge, which are key properties for adsorption and slow release of charged
drug molecules. Loading of the non-steroidal anti-inflammatory drug (NSAID) piroxicam (PRX) into the membranes confirmed that the extent of loading is governed by surface charge density and carboxylate group content, respectively, which can be controlled by the oxidation procedure within the range of 0.74–2.00 mmol g⁻¹. Prolonged release of PRX over several hours was observed upon exposure of the loaded membranes to simulated human skin fluid demonstrating the applicability as drug delivery patches.

**CELL 395**

**Reinforcement of guayule and natural rubber latex using nitro-oxidized jute nanofibers**

*Priyanka R. Sharma, prsharma195@gmail.com, Sunil Kumar Sharma, Benjamin Hsiao*. StonyBrook University, STONY BROOK, New York, United States

Synthetic polymers produced from non-renewable fossil fuel requires high energy cost and are dependent on the presumed unstable petroleum price. Guayule rubber latex is known to be a potential alternative rubber source since it is derived from arid adapted, low input shrubs. It is also known to be hypoallergenic which makes it suitable for personal use and competitive with other rubber sources in the medical device market. Our study primarily focuses on integrating sustainably processed carboxycellulose nanofibers from untreated jute biomass into guayule and natural rubber latex to enhance the mechanical strength of the material for various applications. The carboxycellulose nanofibers extracted using the Nitro-oxidation method possessed carboxyl content of 0.94 mmol/g and integrated into its deprotonated form (-COONa) for its higher dispersion in water to increase the interfacial interaction between latex and nanofibers. The TEM analysis of carboxycellulose nanofibers shows the dimensions of nanofibers are (L) > 1000 nm and diameter (D) 4-6 nm. Furthermore, FTIR analysis of carboxycellulose nanofibers depicted the presence of the carboxyl group. However, the polydispersity and the effective diameter of natural rubber latex is measured by DLS. The DLS measurement shows the narrow polydispersity value of 0.005 with the effective diameter in the range of 643 nm. Tensile and expansion mechanical strengths are tested to observe the enhancement effects at various concentrations of carboxycellulose nanofibers in the latex.

**CELL 396**

**TEMPO oxidized cellulose-reinforced composites: Pulp or nanofibrillated-cellulose?**

*Andre Gaduan, a.gaduan17@imperial.ac.uk, Koon-Yang Lee*. Department of Aeronautics, Imperial College London, London, United Kingdom

The utilization of cellulose as reinforcement in polymer composites have received tremendous interest during the past few decades. This was motivated by regulations and the increase of public’s awareness which led to the demand of environmentally
friendlier products in various applications. In the automotive industries especially, cellulose is an attractive material to manufacture green lightweight parts. It is highly abundant and cheap in comparison to other types of reinforcing materials such as carbon fiber. In terms of its mechanical properties, cellulose has high specific modulus; up to 128 GPa for cellulose originating from natural plant fiber. Further fibrillation of cellulose to its nanoscale form (10-20 nm) would produce fibre with even higher specific surface area and superior mechanical properties. Nanocellulose is therefore favoured to produce composites with great performance. However, the isolation of highly individualized nanocellulose from their plant celluloses requires a high energy consumption and must be done separately prior to composites production.

In this study, we report the mechanical and thermal properties of polypropylene (PP) reinforced with (i) TEMPO oxidized pulp and (ii) nanofibrillated cellulose. PP composites containing 5 wt.% of the cellulose reinforcements were compounded using a twin-screw extruder and fabricated into test specimens using an injection moulder. Results showed that the tensile modulus and fracture toughness of PP reinforced with TEMPO oxidized pulp were higher (18 % and 17 %, respectively) than those reinforced with nanofibrillated cellulose. In addition, the onset degradation temperature of PP reinforced with TEMPO oxidized pulp was also 11 degree Celsius higher. TEMPO oxidation promotes good dispersion of pulp in PP, however further nanofibrillation of the cellulose resulted in agglomeration and thermal degradation during melt-processing of composites. This was further supported by the dynamic mechanical analysis (DMA) and the fracture surfaces morphology of the composites.

CELL 397

Catalytic surface engineering for highly functionalized and water-resistant nacre-mimetic cellulose nanofibrils/clay nanocomposites

Armando Cordova¹, armando.cordova@miun.se, Rana Alimohammadzadeh¹, Rana.Alimohammadzadeh@miun.se, Lilian Medina², Lars Berglund³. (1) Mid Sweden University, Sundsvall, Sweden (2) KTH Royal Institute of Technology, Stockholm, Sweden (3) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

The versatile catalytic surface-modification of nacre-mimetic nanocomposites is disclosed. The utilization of metal-free catalysis allows for designing tailor-made surfaces of cellulose nanofibrils/clays nanocomposite with different functional groups and properties (hydrophobicity). The catalytic surface-engineering is mild and no significant structural changes were observed after the functionalization of the nacre-mimetic nanocomposites, which also kept their important mechanical properties. Several functional groups (e.g. allyl, phenyl, allyl, aminopropyl, alkyl) were attached. The contact angles of the corresponding modified nanocomposites were high and when constructing the surface with thiapropyl groups it became as high as when fabricating the surface with perfluoroalkyl groups.
**In situ** Modification of beads from regenerated cellulose: Creating all-cellulose composites

*Katarzyna Mystek¹, mystek@kth.se, Michael Reid¹, Per A. Larsson², Lars Wagberg³.*

(1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (3) KTH Fibre Polymer Techn, Stockholm, Sweden

Regenerated cellulose materials have been utilized for more than a century as films, textiles and composites. Traditionally, these materials have been produced using chemically aggressive, and potentially hazardous processes, which has led researchers to explore more benign dissolution routes. Non-derivatizing solvents, specifically, have gained significant attention due to the relatively mild conditions in which cellulose can be dissolved.

Previously, our group has utilized N,N-dimethylacetamide/lithium chloride (DMAC/LiCl) to produce regenerated cellulose beads as a platform for fundamental cellulose studies and as capsules for a variety of applications, such as extended release and lightweight materials, as well as capsules from partly modified cellulose that can expand upon exposure to a proper stimuli. However, modification of these materials must be performed prior to or following regeneration, creating additional processing steps such as rinsing or dialysis. In this work we demonstrate that regenerated cellulose beads can be modified in situ using nanoparticle dispersions in the precipitation media. Specifically, we utilize cellulose nanocrystals (CNCs) to create all-cellulose composite beads with tunable properties. Characterization of the composite beads via atomic force microscopy, scanning electron microscopy and energy dispersive x-ray spectroscopy revealed that CNCs are incorporated in the material. Moreover, the structural and mechanical properties can be readily tuned by altering the concentration of CNCs in the precipitation media. In summary, this work demonstrates a novel way to tune the structure properties and functionality of regenerated cellulose materials, potentially facilitating applications ranging from water treatment and drug delivery to advanced textiles and membranes.

**CELL 399**

Molecular mobility and structure of cellulose nanofibrils composites as revealed by broadband dielectric spectroscopy and fast scanning calorimetry

*Anna M. Elert¹, anna-maria.elert@bam.de, Paulina Szymoniak¹, Muhammad Farooq², Juan Jose Valle-Delgado², Monika K. Osterberg², Heinz Sturm¹, Andreas Schoenhals¹.*

(1) Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany, Berlin, Germany (2) Dept. of Forest Products Technology, Aalto University, Espoo, Finland

Advanced materials based on renewable resources gain more and more attention for application in high technology. To design materials with tailored properties the
sustainable natural products must be modified. For this process, in-depth understanding of molecular interactions between the composite phases is crucial and of fundamental interest. It is already known that the properties of the interface in composites might be different from that of the bulk matrix. This is of considerable importance especially for nanocomposites because, due to the small size of the nanoobjects, the amount of interfacial area is large and determines the properties of the composite to a large extent. Here a Cellulose Nanofibrils (CNF) film and CNF modified with 10 % colloidal lignin particles (CLPs) were investigated by a combination of different experimental techniques. Besides Thermogravimetric Analysis (TGA), Infrared Spectroscopy (IR) and X-ray scattering, mainly a combination of Broadband Dielectric Spectroscopy (BDS) and Fast Scanning Calorimetry (FSC) was employed because these methods provide different perspectives on the structure-property-relationships of CNF and its composites. It should be noted that FSC, by using heating and cooling rates up to $10^4$ K/s, was applied for the first time to the best of our knowledge to such a novel system. In principle high heating rates will allow to investigate the melting and crystallization behavior of the cellulose because degradation can be suppressed by decoupling the time scales corresponding to phase transition and decomposition. The dielectric relaxation spectra show several relaxation processes indicated by peaks in the dielectric loss. Some of them depend sensitively on the water content in the system, which is discussed in detail, and can be of great importance in further understanding of water interactions in studied systems. Moreover, the glass transition phenomena of CNF and its composites is addressed by BDS and advanced calorimetry.

CELL 400

Diffusion-softening of a mechanically adaptive cellulose nanocrystal polyurethane composite

Cailean Pritchard1, cqpritch@vt.edu, Jake Fallon3, Cody Weyhrich2, Katherine V. Heifferon2, Boer Liu2, Timothy E. Long3, Michael Bortner4. (1) Chemical Engineering, Virginia Polytechnic Institute and State University, Lexington, Virginia, United States (2) Chemistry, Virginia Tech, Christiansburg, Virginia, United States (3) Virginia Tech, Blacksburg, Virginia, United States (4) Chemical Engineering, Virginia Tech, Blacksburg, Virginia, United States

Cellulose nanocrystals (CNCs) are an exciting filler for emerging bio-renewable nanocomposite systems. CNCs provide mechanical reinforcement through the development of a strong hydrogen bonding network within the matrix, when loaded above a critical percolation threshold, greatly enhancing the storage modulus. Upon the introduction of water, competing interactions consume hydrogen bonding sites thereby reducing the mechanical reinforcement provided by CNCs.

We explore the dynamics of the mechanical softening upon exposure to water, focusing on the role of CNC-water interactions on water transport in nanocomposites. Additionally, we provide insight into this process through a relationship between storage modulus and water diffusion as functions of filler loading. Dynamic mechanical analysis
(DMA) coupled with a relative humidity accessory enabled direct evaluation of the mechanical adaptivity in response to the water stimulus and thermogravimetric analysis – sorption analysis (TGA-SA) was implemented to evaluate the diffusivity of water in a high relative humidity environment. Following a hindered diffusion model, the ratio of bound-unbound water was characterized for its impact on mechanical softening providing new insight into the softening kinetics. Finally, local water transport was evaluated through Fourier transform infrared – attenuated total reflectance (FTIR-ATR) spectroscopy and compared to bulk transport phenomenon.

**CELL 401**

**Composites of HDPE and cellulose nanocrystals: Exploring properties of materials containing sustainable polymers**

Anastasia Volokhova¹,³, nastya95@vt.edu, Kyle Arrington⁴, Keith Hendren²,³, Johan Foster²,³, John B. Matson¹,³. (1) Chemistry, Virginia Tech, Christiansburg, Virginia, United States (2) Materials Science Engineering, Virginia Tech, Blacksburg, Virginia, United States (3) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (4) Intel, Chandler, Arizona, United States

The synthesis and investigation of physical properties of an ABA triblock copolymer of polyethylene (PE) and cellulose triacetate (CTA) for dispersion of cellulose nanocrystals (CNCs) in HDPE is described herein. Structural similarity between CTA and CNCs was hypothesized to improve CNC dispersion in HDPE and afford reinforced HDPE with improved barrier properties. A three-step synthesis involving functionalization, polymerization, and hydrogenation afforded a CTA-b-PB-b-CTA triblock copolymer which may act as a dispersing agent for the composite. Initially, the CTA was monofunctionalized with a pendant olefin substituent on the reducing end through basic solvolysis. The olefin-terminated CTA behaved as a macro chain transfer agent (CTA) in cross-metathesis ring-opening metathesis polymerization (ROMP) of cyclooctadiene, yielding a triblock copolymer containing CTA and polybutadiene (PB). The CTA-b-PB-b-CTA copolymer was subject to hydrogenation, which converted the PB midblock into PE and produced the final dispersing agent CTA-b-PE-b-CTA. This triblock copolymer was added to coprecipitated and melt-mixed composites of CTA and PE in 1, 2.5, and 5 wt. % quantities and the resulting mixtures were melt pressed to form films. Mechanical analysis of composite films showed significant reinforcement of PE, both with and without the dispersing agent. This system provides a cost-effective alternative to conventional PE with greater sustainability, enhanced strength, and improved oxygen barrier properties.
Tailoring the surface of cellulose nanocrystals for thermoset composites

Douglas Fox¹, dfox@american.edu, Emilio Cano¹, Wanofe Wideska¹, Christie Sayes⁴, Jeremiah W. Woodcock², Jeffrey W. Gilman³. (1) American University, Washington, District of Columbia, United States (2) MML, National Institute of Standards and Technology, Gaithersburg, Maryland, United States (3) MS 8541, NIST, Gaithersburg, Maryland, United States (4) Department of Environmental Science, Baylor University, Waco, Texas, United States

Cellulose nanomaterials offer great potential for lightweighting fiber reinforced plastics and improving the stiffness and strength of polymer composites. However, their hydrophilicity often leads to aggregation, water absorption, and embrittlement of the polymer. Modification of the cellulose surface can reduce the aggregation and improve interfacial adhesion with the polymer. However, over modification can reduce the stiffness and strength enhancements originally desired. In this study, we examine the use of cellulose nanomaterials to enhance the properties of epoxy and vinyl ester thermosets. A number of surface modifications (ion exchange, physisorption, and covalent attachment) are used to improve the dispersion and distribution of cellulose within the matrix. Changes in the surface properties are monitored using zeta potential and inverse gas chromatography. Distribution of the cellulose is monitored using fluorescence and electron microscopy. Composites will be characterized for mechanical, viscoelastic, and water adsorption properties. Measured surface properties will be correlated to both cellulose dispersion / distribution and physical properties of the composites.
Case study tuneable wood: Transfer of bioinspired concepts into bio-based materials

*Tobias Keplinger*, tkeplinger@ethz.ch, *Marion Frey*. ETH Zurich-Wood Materials Science, Zürich, Switzerland

Nature provides numerous examples of elegant material design principles including for example stiffness gradients, fibre flow adaptations or specifically tailored interfaces. However, when natural materials such as wood are directly used, we cannot entirely profit from these strategies because they are not specifically designed for man-made applications but for the living tree. There are two main strategies to bypass this limitation and to develop the materials according to our needs. First, biological materials can act a role models for new materials design approaches, and their basic design principles are replicated within a synthetic system. This strategy, however, often comprise rather complex bottom-up processes that may face limitations in scalability and it remains challenging to reach the structural complexity of the biological material. The second strategy, is the modification of biological materials in a top down approach that allows for retaining the hierarchical structure and incorporating bioinspired concepts.

Here, we present a top-down approach of increasing interest based on structure retaining delignification of wood, which results in a light-weight cellulose scaffold that is equipped with enhanced mechanical properties upon densification. Beyond rather simple densification treatments, we processed delignified wood into a novel material characterized by fibre flow adaptations within 3D shapes, mechanical gradients and tuneable functionality. These characteristics are inspired by the tree and plants ability to locally tune their macro- and micro structure along with their chemistry. A detailed focus will be given on the moisture triggered reversible interlocking between neighbouring fibres, which allows for shaping in wet state and endows the material with high strength and stiffness in dry condition. These materials represent a promising alternative for less sustainable materials such as glass fibre reinforced composites.

Super strong anisotropic cellulose-based films from wood by a cellulose DP protection strategy

*Zhiqiang Fang*1,3, mszhqfang@scut.edu.cn, *Yu Liu*1, *Jie Zhou*2, *Xueqing Qiu*2,1. (1) State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, Guangdong, China (2) School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong, China (3) South China Institute of Collaborative Innovation, South China University of Technology, Dongguan, Guangdong, China
Ever-increasing environmental issues and continuous depletion of fossil fuel reserves demand an emerging quest for lightweight materials with superior mechanical properties and economic production from sustainable resources. Natural cellulose, in the form of wood, paper, and clothing, has long been used by human beings for thousands of years as engineering materials for building, tools, furnish, and textiles. However, its mechanical properties fail to fulfill the rising needs of modern society for high performance materials that are currently dominated by nonrenewable materials, for example, glass, metal, and plastics. We demonstrate super strong yet lightweight anisotropic cellulose-based films from wood by a strategy of protecting the degree of polymerization (DP) of cellulose, which not only exhibited a tensile strength as high as 1.13 GPa, but also reached a record high specific strength of 820 MPa g⁻¹ cm³. To the best of our knowledge, these are the highest mechanical properties reported so far for any known natural polymers and some strong metals (such as aluminum, cast iron, carbon steel, Mg2Zn, monel, and GrNbTiVZr). Besides, the underlying mechanism for the exceptional mechanical properties of the resulting cellulose-based film is investigated in detail. Such superior mechanical properties enable the lightweight cellulose-based films to use in novel areas where are traditionally dominated by nonrenewable materials such as plastics, glass, and metals. Meanwhile, this work will give a crucial clue to design novel strong and lightweight materials.

CELL 405

Advanced wood technologies for energy efficient buildings

Tian Li, mytian1211@gmail.com. Materials Science and Engineering, University of Maryland, College Park, College Park, Maryland, United States

Wood is a sustainable building material due to its relatively low carbon footprint and low embodied energy, though there is still much room for improvement, especially towards the goal of net zero energy consumption in buildings. A radiative cooling wood was directly made from natural wood, realizing sub-ambient cooling continuously during day and night. The porous backbone of the cellulose framework largely reflect sunlight while the molecular vibration/stretching facilitates a strong emission in the IR range. The emission within the 8 to 13 um goes through the atmospheric transparency window into our ultra-cold universe. When the emission energy overwhelms the absorbed energy from Sunlight, the sub-ambient cooling can be obtained. Another example is the continuous development of transparent wood. Transparent wood shows intrinsically lower thermal conductivity than that of glass with largely tunable optical properties, which can be used towards energy efficient windows.

CELL 406

Wood nanotechnologies

Liangbing Hu, binghu@umd.edu. Materials Science and Engineering, University of Maryland College Park, Hyattsville, Maryland, United States
I have been investigating wood materials for a range of emerging technologies towards sustainability since I joined at University of Maryland at 2011, such as lightweight structural material, energy storage and conversion, environmental remediation, green electronics, and energy-efficient building, with the following inventions. (1) **Superstrong and supertough wood (super wood)** as a replacement of steel that exhibits a similar strength but 6-times lower density to steel, a comparable specific strength to carbon fibers and metal alloys but nearly 10-times lower cost, at the meantime, showing much lower carbon footprint with a better sustainability prospect. (2) **Various advanced wood technologies** for green building applications, including Transparent wood for replacing glass, Super insulating nanowood for thermal insulation in buildings with a low thermal conductivity (~0.06 W/mK,), and Radiative cooling wood (Science, 2019). (3) *Transparent paper as a replacement of plastic.* (4) *A tree-inspired wood membrane for solar desalination toward clean water.* (5) **Wood-water batteries for low-cost energy storage.**

**CELL 407**

**Lytic polysaccharide monooxygenases (LPMO) promote cellulose defibrillation: New tool for cellulose nanofibril production**

*Céline Moreau*¹, *Amani Chalak², Ana Villares¹, Isabelle Gimbret², Sacha Grisif², Sandra Tapin-Lingua³, Valérie Meyer³, Michel Petit-Conil³, Jean-Guy Berrin², Bernard Cathala¹, bernard.cathala@nantes.inra.fr. (1) BIA, INRA, Nantes, France (2) BBF, INRA-AMU, Marseille, France (3) CTP/FCBA, InTechFibres, Grenoble, France

Cellulose is the most abundant naturally occurring polymer and it is mostly obtained from wood. During the last decades, research efforts have been focused on a new class of cellulose-derived products, the nanocelluloses which comprise semi-crystalline cellulose nanofibrils (CNF). Preparation of CNF consists in a mechanical delamination of cellulosic fibres that requires high energy, limiting industrial production of CNF. In order to face this challenge, innovative pre-treatments of the fibres are still required to meet cost-effective, environmentally-friendly and sustainable production of CNF. Lytic polysaccharide monooxygenase (LPMO) enzymes are recently-discovered fungal enzymes possessing a type II copper active center coordinated by a histidine brace. Their interest arises from their observed “boosting effect” on the enzymatic polysaccharide degradation. In this work, kraft pulp fibres were treated with a fungal LPMO from the AA9 family that harbors a carbohydrate binding module (CBM) and homogenized without prior mechanical treatment. Untreated pulps cannot be processed while pulps treated with the LPMO enzyme allowed the production of good quality nanocelluloses. Cellulose structure modifications induced by the LPMO were investigated by SEC, AFM and TEM. A high degree of defibrillation was observed down to nanoscale while the chains cleavages remained limited. Solid state $^{13}$C NMR demonstrates that LPMO creates nicking points that trigger the disintegration of the cellulose fibrillar structure and the release of elementary nanofibrils. Investigation of LPMO action using solid-state NMR provides direct evidence of modification of accessible and inaccessible surfaces surrounding the crystalline core of the fibrils. The
importance of the CBM module was also demonstrated using complementary approaches. On the basis of these results, the mechanism of action of fungal LPMO on cellulose will be discussed.

CELL 408

Nanocellulose reinforcement for hyperthermia phantoms

Saül J. Llàcer Navarro¹,³, saul@chalmers.se, Tiina Nypelo²,³, Anna Ström¹, Hana Dobsicek Trefna⁴. (1) Chalmers University of Technology, Göteborg, Sweden (2) Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden (3) Wallenberg Wood Science Center, Göteborg, Sweden (4) Department of Electrical Engineering, Chalmers University of Technology, Göteborg, Sweden

Phantoms are used as tissue-mimicking materials in the field of radiotherapy. We employed nanocellulose and its derivatives: cellulose nanofibrils, and several grades of cellulose nanocrystals, including sulfated, desulfated, and their oxidized derivates, to transform gelatin phantoms suitable for hyperthermia fat phantoms. Nanocellulose forms entangled fiber networks with water holding capacity, which works as reinforcement in the preparation of hydrated oil- gelatin composites. The mentioned phantoms require a thermal and dielectric equivalence of the mimicked tissue. A successful fat phantom has low permittivity (ε=11) and low conductivity (0.08 S/m, within the frequency band of 100MHz and 2GHz) coupled with mechanical strength enabling a self-standing and cuttable phantom body.

Determination of storage and loss moduli as a function of temperature in small deformation, rheometry, and large deformation, Young modulus, proved physical and chemical crosslinking of nanocellulose and its derivatives in the gelatin matrix to be vital to facilitate the thermal stability and adequate resistance to deformation. Without the oxidative modification, the gel interactions were non-covalent. The tuning of the crosslinking type and rate is an additional controllable for stabilizing the system. Oil/water composition is used to adjust the permittivity and conductivity to the target level.

We will discuss the approaches for achieving successful phantom as well as the role of the morphology of the oil droplets in the dielectric properties of the phantom.

CELL 409

Poly(ethylene glycol) as a coating agent to prevent hornification of cellulose nanofibres

Alba Santmarti, as15713@ic.ac.uk, Koon-Yang Lee. Imperial College London, London, United Kingdom

Cellulose nanofibres (CNF) are emerging as an important material for various industries due to their outstanding chemical and physical properties. Despite the advances in CNF
production, wet storage and transportation of nanocellulose is still one of the biggest challenges to make CNF commercially viable. This is due to the irreversible formation of hydrogen bonds between cellulose fibers during drying known as hornification. Even though various authors have come up with solutions to prevent CNF agglomeration and enhance their redispersibility, some of the methods proposed are energy-intensive or use additives that are inadequate in the food and pharmaceutical industry.

In this study, we propose the use of low molecular weight poly (ethylene glycol) (PEG) to control the moisture content in CNF films and to prevent CNF fiber hornification. Various CNF to PEG ratios were used to produce dehydrated CNF-PEG films with varying moisture content. The manufactured CNF-PEG films exhibited constant moisture contents for long periods of time (> 1 week). PEG was easily removed by washing with distilled water and filtrating the recovered CNF. The percentage of PEG was found to affect the redispersibility of CNFs as well as their physical and mechanical properties. The properties of redispersed CNF prepared at CNF: PEG ratios equal or higher to 1:2 closely resemble the properties of never-dried CNF.

CELL 410

Fabrication and properties of electrospun cellulose nanofibres from ionic liquid

**Simona Sriubaite**¹, simona.sriubaite@ktu.lt, **Mindaugas Bulota**¹, **Edvinas Krugly**², **Darius Ciuzas**¹, **Dainius Martuzevicius**¹. (1) Department of Chemical Technology, Kaunas University of Technology, Kaunas, Lithuania (2) Environmental Technology, Kaunas University of Technology, Kaunas, Lithuania

During past decades, biocomposite research has been focused on cellulose based materials due to its mechanical properties and abundance. Nonetheless, in order to compete with synthetic counterparts in composite applications cellulose has to be often modified. Herein, we present a method to modify cellulose in ionic liquid and produce electro-spun fibres with special properties. Two types of modification have been employed in order to showcase the possibilities to achieve different properties. Firstly, modification of cellulose in ionic liquid (1-Butyl-3-methylimidazolium acetate) with benzophenone as an immobilized initiator, followed by acrylamide grafting. Dissolved and modified cellulose was electro spun in special conditions and then post-treated in order to induce cross-linking. Secondly, hydroxymethyl methacrylate grafting followed by polymerization.

Degree of substitution was evaluated using FT-IR and Raman Spectroscopy. Nanofibres have been successfully formed, having median diameters in the range of 500-800 nm. Morphology of fibres was studied using scanning electron microscopy.

CELL 411

Safer-by-design approach for the elaboration of versatile nanocellulose-based hybrid particles for photocatalytic applications
Hugo Voisin, hugo.voisin@gmail.com, Isabelle Capron. INRA, Nantes, France

There is a strong dynamic to design tomorrow’s nanomaterials that will be safer both for humans and the environment. The global objective is to develop products made of nanomaterials or nanostructured materials taking into account socio-environmental constraints (exposure and risk) throughout their whole life cycle. In this context, the safer-by-design strategy consists in developing innovative processes to characterize and minimize the materials environmental impact from their synthesis to the end of their lifetime. Nanoparticles are a class of nanomaterials that have received especial attention in this regard. We will present here how the immobilization of TiO$_2$ nanoparticles on cellulose nanocrystals (CNCs) limits their mobility and size related risks. It simultaneously improves their photocatalytic properties in suspension due to an increased dispersability, leading to a lower TiO$_2$ content in the targeted application. The particular case of photocatalytic paints is followed on the complete life cycle. New TiO$_2$ synthesis method leads to the homogeneous covering of CNC by TiO2 nanoparticles with an optimal anatase/rutile ratio of 80/20 as demonstrated by X-ray absorption near edge structure (XANES) and with a tunable grafting percentage up to 45 wt. % (determined by ICP-MS). As a result, grafting TiO2 on a biobased material such as nanocellulose in a controlled way increased their photocatalytic efficiency compared to ungrafted TiO$_2$ NPs. This has been demonstrated by the degradation of a water soluble dye. Furthermore, it improved the ageing of the final material and led to a lowered release of larger nanoparticles. Finally, the functionalization of surface-active CNC with the TiO$_2$ allows the scalable degradation of organic pollutants through the preparation of Pickering emulsions and the derived photocatalytic materials.

CELL 412

Robust poultry feather fibre preform: Upcycling waste feathers with (nano)cellulose

Victoria Vilchez$^1$, Elena Dieckmann$^2$, Christopher Cheeseman$^3$, Koon-Yang Lee$^4$, koonyang.lee@imperial.ac.uk. (1) Department of Aeronautics, Imperial College
Commodity plastics and their composites are of high interest for many semi-structural applications, yet the current environmental issues urge to reduce plastic waste and better manage our resources. To address this challenge, research has turned to the upcycling of waste material such as poultry feather waste. Poultry meat is one of the most consumed meat on the planet, with over 122 million tons produced worldwide in 2018. Due to increasing global population and demand, the poultry industry produces significant feather waste, which is in major part incinerated or sent to landfills. In the current context of over-exploitation of natural resources and poor management of waste, it is crucial that we transform our economic model into a more sustainable solution, which uses smarter materials and gives more added value to waste. Feathers are low-cost, abundant, natural fibres, which makes them ideal candidates towards circular economy.

In this presentation, we will discuss the production of whole feather composites that are fully biodegradable, easy to manufacture and to recycle. (Nano)cellulose fibres were used as a binder to go from loose feathers to 2-dimensional easy-to-handle fibre preforms. Our study demonstrates the possibility of converting loose chicken feathers fibres to a rigid and robust polymer-free chicken feather fibre preform that possessed a tensile strength up to 1.56 N/mm (defined in non-woven testing standard). Using a wet layup technique, the dry preforms were impregnated with a gelatin matrix to produce chicken feather-reinforced gelatine composites with fibre weight fractions of up to 47%wt. The resulting composites possess a tensile modulus and strength up to 2.10 GPa and 18.6 MPa respectively, which are comparable to that of commodity plastics such as high-density polyethylene, polypropylene, polyvinyl chloride or polyethylene terephthalate. These biocomposites provide a sustainable alternative to the plastic industry, with a better control of the lifecycle and better potential to fit into a circular economy. The influence of different types of (nano)cellulosic fibres on the mechanical properties of the fibre preform, as well as the resulting biocomposites will also discussed.

CELL 413

Combining tannins with cellulose biocolloids towards functional materials

Bruno Mattos1, bruno.mattos@aalto.fi, André Missio2, Eric Hahnert1, Blaise Tardy1, Orlando Rojas1,3. (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Wood Technology, Federal University of Santa Maria, Santa Maria, Brazil (3) Departments of Chemical & Biological Engineering, Chemistry and, Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

Tannins are plant-based polyphenolic molecules with high antioxidant, light adsorption, binding and chelating properties that can be exploited toward advanced materials. Due
to their high solubility and reactivity, embedding tannins into a matrix is the best strategy to fully explore their functions. Cellulose nanofibrils (CNF) – biocolloids derived from plants or bacteria – can form highly interconnected fibrillar networks that mirror the supramolecular cohesion of the cellulose biopolymer. Such architecture has shown upper boundaries in terms of mechanical strength when assembled into aerogels, filaments and films. Therefore, in this work we utilized the nanonetworking capability of CNF and the versatile chemical features of tannins to form high-performance packaging and fireproof materials. A one-step method was designed to strongly embed tannins within the primary cellulose fibrils forming the nanofibrillar network. The process involves the addition of condensed tannins – neat or purified – or tannic acid into cellulose pulp that is further mechanically processed by either Masuko’s Supermasscolloider or microfluidizer. The resulting tannin-embedded CNF suspensions contain up to 19 wt.% of strongly adhered polyphenolics. Active films and anti-flame aerogels could be prepared from such composite biocolloidal suspensions by taking different processing routes. Condensed tannin-CNF films were prepared through simple filtering. Such films presented high density, hydrophobic character, high air-barrier, and tuned antioxidant properties. Tannic acid-CNF anti-flame aerogels were prepared by first complexing the protonated phenolic molecules with Fe$^{+3}$ ions to create a metal-phenolic network (MPN) strongly anchored to the CNF nanonetwork. The gelled suspensions could be ice templated or simple freeze dried into aerogels. Such materials presented the flexible characteristic of pure CNF aerogels with high anti-flame, and most importantly self-extinguish properties deriving from the creation of an embedded MPN within the CNF matrix.

CELL 414

On the Interaction of Softwood hemicellulose with cellulose surfaces in relation to molecular structure and physicochemical properties of hemicellulose

Polina Naidjonoka¹, polina.naidjonoka@fkem1.lu.se, Gunnar K. Pállson², Frank Heinrich⁴, Henrik Stålbrand³, Tommy Nylander¹. (1) Physical Chemistry, Lund University, Lund, Sweden (2) Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden (3) Biochemistry and Structural biology, Lund University, Lund, Sweden (4) Stop 6102, NIST Center for Neutron Research, Gaithersburg, Maryland, United States

The water-soluble hemicellulose fraction obtained during wood processing has so far been discarded. Softwood contains up to 20% of hemicellulose which makes it an abundant and underutilized resource. The aim with this work is therefore to explore the interfacial properties of hemicellulose for new applications. Previously it has been demonstrated that hemicellulose has high affinity towards cellulose and alter the properties of cellulose based products like paper and wood resin in emulsions. Here we focus on the interactions between softwood hemicellulose (galactoglucomannan, GGM) and cellulose at the surface on a molecular scale. We have revealed how two structurally different GGM samples as well as two galactomannans adsorb to silica, hydrophobized silica and cellulose surface by using a combination of ellipsometry,
QCM-D and neutron reflectometry. The solution structure of the GGM samples had been characterized with SAXS, SANS and light scattering to establish how branching and molecular weight affect the conformation of these polymers in bulk. A correlation between the molecular weight of polysaccharides and the adsorbed amount on cellulose was found, whilst the adsorption to the hydrophobic surface was fairly constant. The obtained layer thickness was compared with the hydrodynamic radius, $R_H$, and radius of gyration, $R_G$, from bulk scattering data.

**CELL 415**

**Visual appearance of chiral nematic cellulose-based photonic films: Angular and polarization independent color response with a twist**

Chun Lam Clement Chan$^1$, clc80@cam.ac.uk, Mélanie M. Bay$^1$, Gianni Jacucci$^1$, Roberto Vadrucci$^1$, Cyan A. Williams$^1$, Gea T. van de Kerkhof$^1$, Richard Parker$^1$, Kevin Vynck$^2$, Bruno Frka-Petesic$^1$, Silvia Vignolini$^1$. (1) Chemistry, University of Cambridge, Cambridge, United Kingdom (2) Laboratoire Photonique, Numérique et Nanosciences (LP2N), CNRS, IOGS, Univ. Bordeaux, Talence, France

Hydroxypropyl cellulose (HPC) is a biocompatible and renewable resource derived from cellulose. In aqueous solution, it is capable of self-assembling into a lyotropic chiral nematic phase, which reflects right-handed circular polarized light of a particular wavelength and can thereby exhibit structural color. The specific color reflected can be tuned through various parameters, including temperature, ionic strength and most importantly, HPC weight fraction.

In this study, we demonstrate that, by introducing a crosslinking agent, we can drastically alter the visual appearance of the HPC mesophase. Not only can we control the reflected color, we are able to tune the scattering properties of the chiral nematic system, resulting in solid-state films with a matte appearance. Furthermore, the polarization response is now altered in such a way that the system can now reflect both right and left-handed light.
Such angular and polarization dependence is a highly demanded property within the pigment industry, and one which is difficult to achieve via structural coloration. As a result, developing a robust methodology towards such a system is an important step towards the development of HPC as a real-world photonic colorant.

**CELL 416**

**Integrated process to recover extractable, starch- and cellulose-derived sugars from food waste**

Qing Jin, jin622@vt.edu, Nick Poe, Hengjian Wang, Haibo Huang. Department of Food Science and Technology, VIRGINIA POLYTECHNIC INSTITUTE, Blacksburg, Virginia, United States

Sugar is an essential component for the production of biofuels, pharmaceuticals, and other value-added chemicals by fermentation or chemical process. Sugar is normally produced from three types of feedstock: sugar-containing (e.g., sugarcane), starch-based (e.g., corn), and cellulose-based (e.g., wheat straw) biomass. However, sustainable and economical sugar production is currently hindered by the high feedstock cost of sugar- and starch- based biomass and the high operating cost of pretreatment and enzymatic hydrolysis of cellulose-based biomass. Food waste, the single largest component of municipal solid waste, represents a significant source of carbohydrates (free sugars, starch, and cellulose). Sugar production from food waste would potentially provide a cost-effective and sustainable sugar source.

In this study, a cascading process was designed and optimized to recover sugar from food waste collected from university dining halls. In details, different sources of food waste (vegetables-, fruits-, and bakery-based wastes) were ground and mixed to get a slurry. The slurry was first centrifuged to obtain free glucose, fructose, and sucrose. After centrifugation, the solid residue was liquefied and saccharified to hydrolyze starch to glucose, which was then recovered by hot water wash. The leftover rich in fiber was pretreated with dilute acid followed by enzymatic hydrolysis to obtain cellulose hydrolyzed sugars. Critical process parameters including enzyme dosage and solid loading were optimized to achieve the highest sugar recovery from food waste.

As a result, 62.3 g/L free sugar was obtained with a recovery rate of 81.8% after centrifugation; a maximum starch hydrolysis efficiency of 93.3% was achieved with the sugar concentration of 150.6 g/L in the hydrolyzed slurry; after three times hot water wash of the slurry, 85.1% of residual sugar was recovered; and finally, a total of 72.5 g/L sugar was obtained after cellulose hydrolysis. As to the mass balance of the designed process, 43.5, 50.1, and 9.3 kg of sugars could be obtained from one MT of food waste after free sugar separation, starch hydrolysis, and cellulose hydrolysis, respectively. The high amount of sugar obtained from food waste can be used in various industries and help reduce economic loss and environmental burdens caused
by food waste disposal. A detailed techno-economic analysis will be conducted to estimate the cost of sugar production from food waste.

CELL 417

Carboxylated cellulose nanofibrils (R-CNFs) as an additive in water based drilling fluids (WBMs) applied to shale formation

Yurany Villada Villada¹, yvillada@santafe-conicet.gov.ar, María C. Iglesias², Junyong Zhu³, Natalia Casis¹, Maria S. Peresin⁴,², Diana Estenoz⁵. (1) Universidad Nacional del litoral, Santa FE, Santa Fe, Argentina (2) Auburn university, Auburn, Alabama, United States (3) USDA Forest Service, Madison, Wisconsin, United States (4) Technical Research Centre of Finland, VTT, Espoo, Finland (5) INTEC (UNL-CONICET), Santa Fe, Argentina

Drilling fluids are used during petroleum exploitation to cool and lubricate the drill bit, clean the hole bottom, carry cuttings to the surface, and control formation pressures, among others. An efficient drilling fluid must exhibit desired rheological and filtration properties, stability under operating conditions (high temperature and pressure), and stability against contaminating fluids. According to the nature of the continuous phase, fluids are classified into two groups, water based drilling fluids (WBMs) and oil based drilling fluids (OBMs). OBMs are known to provide unequaled performance. However, they are subjected to strict environmental regulations. The WBMs present low environmental impact but exhibit some disadvantages associated to shale inhibition, lubricity, and thermal stability. To overcome these deficiencies, specific additives are added, such as natural and synthetic polymers, and inorganic nanoparticles.

In this study, a sustainable alternative for the application of carboxylated cellulose nanofibrils (R-CNFs) obtained through maleic acid hydrolysis was proposed. Specifically, the use of R-CNFs as an additive in WBMs formulations as a replacement of xanthan gum (XGD) was studied. The effect of R-CNFs on the main functional properties of WBMs and their performance was evaluated and compared with the corresponding to XGD. To this end, interactions between R-CNF and bentonite (BT), as well as between R-CNF and polyanionic cellulose (PAC) were evaluated using Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) technique. The rheological analyses showed a shear-thinning behavior of WBMs containing XGD similar to WBMs with R-CNF, while filtration properties and thermal stability improved by the presence of R-CNF. The results obtained by QCM-D indicated higher interaction between PAC and R-CNF observed by the frequency changes. The Sisko model was used to determine the rheological parameters. On the other hand, it was found that by replacing XGD by the double concentration of R-CNF in a special WBM for Argentina shale, similar rheological properties were obtained.

CELL 418

Wet stable nanocellulose-based materials with tannins
The applications of nanocellulose-based materials, such as films and foams, are limited by their inherent sensitivity to humid and wet conditions. In this contribution, we present nature-inspired routes to render nanocellulose films and foams more resistant towards water by utilizing the chemistry and interactions with tannins. Tannins, which are found in the bark and leaves of many plants, are able to precipitate proteins, an ability that is utilized in leather tanning to make hide collagen less water-soluble. Films with high wet strength were prepared by vacuum filtration where gelatin, which was grafted onto dialdehyde-modified nanocellulose, was complexed with a water-soluble tannin. The tensile strength of tannin-treated hybrid films was 18 times higher than unmodified nanocellulose films after immersing the material in water for one hour. The addition of tannins also inferred the hybrid films with antioxidant and UV-blocking properties. Given time, we will also present recent work on crosslinking of amine-modified TEMPO-oxidized nanocellulose foams with different catechol-containing compounds.

CELL 419

Production and surface characterization of biopolymeric films from tomato cuticle, starch and glycerol mixtures

María del Carmen Romero-Saavedra¹, mariichinita.dark@gmail.com, Alberto S. Luviano², Dolores Reyes-Duarte², dreyes@correo.cua.uam.mx, Jose Campos-Teran²,³. (1) Licenciatura en Ingeniería Biológica, UAM-Cuajimalpa, Mexico, Mexico (2) Procesos y Tecnología, UAM-Cuajimalpa, Mexico, Mexico (3) Lund Institute of Advanced Neutron and X ray Science, Lund, Sweden

Nowadays the use of agro-industrial residues to obtain products with high added value is of great importance. In Mexico, tomatoes are one of the main agricultural export products which have a high residue rate, as is the case for potatoes. Because of this we have used components such as tomato cuticle and starch to make films with interesting characteristics of resistance and biodegradability that could have potential use in the industry. The tomato cuticle was obtained from tomato residues using a solvent extraction method in combination with an enzymatic process. For the formation of the films, the tomato cuticle, starch and glycerol were dissolved in water at 80 °C to avoid the use of organic solvents. To this solution, glycerol was added as an integrator and flexible film former. The mixtures were evaluated by modifying the concentration of each component. After a previous study the selected concentrations were 5% for starch and 3% for glycerol and subsequently the percentage of tomato cuticle was evaluated, between 0.2% and 2%. Surface morphology and roughness of films were studied by AFM and their surface wetting characteristics with surface angle measurements.
Non-destructive imaging of lignin chemistry in plant cell wall using hyperspectral stimulated Raman scattering microscopy

Shi-You Ding, SDing@msu.edu. Plant Biology, Michigan State University, East Lansing, Michigan, United States

Lignin is a major impediment in the deconstruction of plant biomass to its soluble monomeric constituents. Modification of the lignin biosynthetic pathway has proven to be an effective means of reducing biomass recalcitrance but can often result in impaired growth. Successful examples of “designer” biomass include introducing monolignol ferulate conjugates into lignin backbone to allow readily breakdown under mild alkaline condition. Genes, such as feruloyl–coenzyme A (CoA) monolignol transferase (FMT) and p-Coumaroyl-CoA monolignol transferase (PMT), have been introduced into poplar or Arabidopsis and further confirmed the incorporation of monolignol ferulates into the lignin polymer in the FMT and PMT transgenic plants by a series of analytical methods. In order to evaluate the deconstructibility of the lignin-modified biomass, it is critical to understand the fine chemistry changes in situ, as well as the location and concentration of these conjugates in the cell walls of these transgenic plants. To this end, we have developed hyperspectral stimulated Raman scattering (hsSRS) methods using femtosecond or picosecond laser systems, which allow us to map the chemical changes in planta using lignin conjugated α–β carbon double bonds as the proxy. We found unique shifts between 1400 – 1750 cm⁻¹ in their Raman spectra due to the conjugation of the double bond and an associated ester carbonyl group, and we are able to quantify the chemical concentration in situ at the nanometer scale in the cell walls of both FMT and PMT mutants. In addition, imaging of the cell wall ultrastructure in the transgenic plants have shown significant increase of accessible areas to the cellulases, which may be beneficial to the chemical penetration during pretreatment and substrate accessibility during enzymatic hydrolysis. Our study suggests that both physical and chemical
modification of the plant cell wall could contribute to the observed improvements in sugar yields during biomass conversion processes.

CELL 421

Deformation and imaging of cellulose using Raman spectroscopy

Stephen J. Eichhorn, s.j.eichhorn@bristol.ac.uk. Bristol Composites Institute, University of Bristol, Bristol, United Kingdom

This talk will review work both done by the group over the years into measuring the micromechanical deformation of cellulose using Raman spectroscopy in a variety of forms (e.g. fibres, composites and nanocellulose), and how this technique has allowed better understanding of structure-property relationships. With the advent of improved optics and detector systems imaging of cellulose nanocomposites has also been made possible, giving unique insight into how thermoplastic polymers interact with the reinforced phase. The talk will review some of these developments, and also compare these imaging techniques to other approaches using confocal microscopy, Time of Flight Secondary Ion Mass Spectroscopy and X-ray Photoelectron Spectroscopy.

CELL 422

Application of Raman spectroscopy on the structure-performance of polyacrylonitrile/cellulose nanocrystals precursor and carbon fibers

Huibin Chang¹,², huibindan@gmail.com, Satish Kumar¹,². (1) School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States (2) Renewable Bioproducts Institute, Georgia Institute of Technology, Atlanta, Georgia, United States

For polyacrylonitrile (PAN) based carbon fiber production, the precursor fiber property, stabilization, and carbonization will significantly affect the resulting carbon fiber’s properties. Nowadays, due to the environmental concerns, the biorenewable materials such as cellulose nanocrystals (CNCs) have been proposed as precursors for carbon fibers. Thus it requires insightful understanding the structure-performance of PAN/CNC composite fibers to make high performance carbon fibers. In our studies, the change of orientation and interfacial stress transfer of CNC in PAN fibers, and the carbon structure development of the resulting carbon fibers were systematically investigated by Raman spectroscopy as well as other techniques. The 1095 cm⁻¹ Raman band associated with C-O ring stretching of the cellulose backbone could be used to quantify the orientation and interfacial stress transfer of CNC, which helps to understand structure-performance of PAN/CNC precursor fibers. For the stabilized and carbonized PAN/CNC fibers, Raman spectroscopy is a powerful tool to measure the carbon structure including ordered and disordered carbon structure. The structure-performance of the carbonized PAN/CNC fibers will also be discussed.
Raman spectra of Valonia and Tunicata: Questions they raise about the structures of celluloses Iα & Iβ

Rajai H. Atalla1,2, rhatalla@wisc.edu. (1) Cellulose Sciences International, Madison, Wisconsin, United States (2) Chemical and Biological Engineering, University of Wisconsin, Madison, Madison, Wisconsin, United States

The Raman spectra of Valonia, which is approximately 65% Iα and Tunicate, which is almost all Iβ are nearly identical, differing only in regions of cellulose spectra associated with hydrogen bonding or with the orientation of the methylene group at C6. Their similarities indicate that the conformations are nearly identical, and their structures differ only in patterns of hydrogen bonding.

The keys to understanding the implications of the spectra are a number of normal coordinate analyses we have carried out. They included analyses, in sequence, of the series: the 1,5 anhydropentitols; the pentitols and erythritol; the pentoses; the hexoses; the inositols; cellobiose and the cello-oligodextrins. The core issue in all of their spectra is that the majority of their bands in the fingerprint and the low frequency regions are associated with vibrations of C-C and C-O bonds. For such bonds the reduced masses and bond energies are quite close, so in molecules consisting primarily of such bonds they are very highly coupled. Thus, differences in observed frequencies are primarily consequences of differences in skeletal geometries, which in turn determine the patterns of coupling between the very similar vibrational modes and their corresponding frequencies.

The near identity of the Raman spectra of celluloses Iα & Iβ leaves little question that their skeletal geometries do not differ significantly from each other. They differ significantly from the Raman spectra of highly crystalline native celluloses from other sources, and even more dramatically from those of other polymorphic forms.

Another important consideration is that the Raman spectrum of cellulose Iβ shows no evidence of correlation field splitting in any of the bands. Thus it cannot have two molecules per unit cell.

The major conclusion arrived in this study is that the published structure of Iα is likely the closest approximation to the structures of both Iα & Iβ. The rationale for this conclusion will be presented.

New insights into wood-based nanocomposites by Raman spectroscopy imaging

Tobias Keplinger, tkeplinger@ethz.ch. ETH Zurich-Wood Materials Science, Zürich, Switzerland
Within recent years there has been tremendous progress in the development of functional wood based materials. Their successful development requires high precision and control over the distribution and location of the modifying agents within the wood scaffold and necessitates detailed analysis by high resolution analytical techniques. Raman spectroscopy imaging has been proven an excellent tool to provide detailed insight into novel wood based nano-composites. In contrast to other diffraction limited techniques such as UV- and fluorescence microscopy, Raman spectroscopy is not limited to specific constituents but enables a simultaneous analysis of the main natural constituents (lignin, cellulose) in addition to modifying agents, such as polymers, minerals, and nanoparticles.

We highlight here the potential of Raman spectroscopy to map the distribution of minerals and polymers within the wood structure. Using confocal Raman microscopy we investigated the mineralogy and exact distribution of CaCO₃ after artificial calcification of wood and proved the deposition of the minerals deep inside the wood structure. Regarding polymer functionalization we proved by Raman spectroscopy imaging a locally controllable functionalization within wood cell walls with hydrophobic polymers. In addition, we show how Raman spectroscopy is not only capable of visualizing components but also offers the possibility to follow conformational changes of modifying agents. This is of great importance when it comes to the development of stimuli responsive composites. As example we present the possibility to follow the hydrophilic/hydrophobic change of stimuli responsive poly(NIPAM) hydrogel within the wood structure.

Furthermore, specifically highlighted is the capability of utilizing Raman spectroscopy to gain insight into the wood inherent transport pathways by following the infiltration behaviour of ultra-small europium doped HfO₂ nanoparticles.

CELL 425

Raman spectral study of the effects of temperature and degree of polymerization on the structure of regenerated cellulososes

Rajai H. Atalla¹,², rhatalla@wisc.edu, Bruce Dimick³. (1) Cellulose Sciences International, Madison, Wisconsin, United States (2) Chemical and Biological Engineering, University of Wisconsin, Madison, Madison, Wisconsin, United States (3) Institute of Paper Chemistry, Appleton, Wisconsin, United States

The supermolecular structure of cellulose precipitated from solution is quite sensitive to the temperature of regeneration and the degree of polymerization (DP). The effects of temperature have been explored in studies of regeneration from solutions in phosphoric acid as well as from solutions in the dimethylsulfoxide-paraformaldehyde (DMSO-PF) solvent system. When the cellulososes are characterized by x-ray diffractometry the samples regenerated at or below room temperature appear predominantly of the cellulose II form. As the temperature of regeneration is elevated above room temperature increasing proportions of cellulose IV are indicated. At higher temperatures (100-150°C) the IV polymorph is the dominant form, the degree of order varying with DP and the time scale of the precipitation process. Ultimately at 160°C and for relatively low
DP, the regenerated form is in the native or cellulose I polymorph. In sharp contrast, Raman spectral studies of the same samples show them all to contain varying proportions of cellulose molecules in the conformations typical of celluloses I and II, hereinafter referred to as conformation I and conformation II. Conformation II is dominant in samples precipitated at or below room temperature. As the temperature of precipitation increases, a greater proportion of cellulose separates from solution in conformation I. In the samples precipitated above 100°C, which by x-ray diffractometry appear to be cellulose IV, the Raman spectra indicate similar proportions of conformations I and II. These two conformations were earlier thought to coexist in mixed lattice forming the cellulose IV polymorph, as may occur in block copolymers. Recent developments in the field of nanocelluloses suggest that they may be composites within which nanocrystals of cellulose I and II coexist in a composite form. That would be consistent with the evolution of the x-ray diffraction patterns.

CELL 426

Challenges in lignin band assignment

Peter Bock, peter.bock@boku.ac.at. Department für Nanobiotechnologie, Universität für Bodenkultur, Wien, Austria

Plant cell wall is the barrier to the outer world, as it consists of a compact architecture made up of cellulose, polyoses and lignin. Next to cellulose, lignin is one of the most abundant polymers on earth which renders the wall hydrophobic, provides additional mechanical support and makes it highly resistant to microbial decay. Today, while much is known about the biosynthesis and chemical structures of lignin, aspects like transport of the building blocks to the sites of lignification remain poorly understood.

Raman microscopy is a spectroscopic technique, where a laser is directed on the sample and inelastic scattering is recorded. This gives a microscopic image of the sample and also provides chemical information of tissues at high resolution. It can be taken as a dynamic staining where the user decides what he wants to see. Every pixel of the image has its own Raman spectrum which contains all the molecular information at this position. The challenge is then to extract this information from the spectrum. In the case of lignin, the following issues are encountered when interpreting the spectrum: The exact structure of lignin is not known. While the chemical structure of subunits is known, their spatial arrangement remains unknown. Since orientation of molecules or their parts in space can drastically affect the Raman spectrum, this is the major source of uncertainty for spectroscopists. Furthermore, π-conjugated substructures like cinnamaldehydes cause stronger Raman signal and mask unconjugated moieties. The cause for this signal enhancement is related to resonance scattering, electron delocalizations extending over a specific normal coordinate and charge transfers. This means that lifting this “shining cloak” from the main body of lignin requires different strategies, each of which will make different features visible. Apart from this, research is heavily based on reference structures. Unfortunately, most of them are not properly substituted from the vibrational point of view, as frequently OH-groups are in position 4 of the ring. The associated spectral changes are most evident for modes showing...
Keküle-type ring stretchings. Looming on the horizon are the advances with the tip-enhanced-Raman-spectroscopy (TERS). This high-resolution technique allows band assignment based on individual atom movements, which perfectly complements the traditional way of recording spectra from reference compounds and comparing them to quantum-chemical calculations.

CELL 427

Exploring developing nutshell tissues with 3D Raman imaging

Jessica C. Huss$^{1,3}$, jessica.huss@boku.ac.at, Nannan Xiao$^2$, Sebastian J. Antreich$^1$, Notburga Gierlinger$^1$. (1) Nanobiotechnology, University of Natural Resources and Life Sciences, Vienna, Austria (2) Department of Nanobiotechnology, Institute of Biophysics, Vienna, Austria (3) Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

Many seed plants rely on lignocellulosic shell structures to protect their seeds during development, maturation, dispersal and germination. Nutshells, such as walnuts and macadamias, represent some of the most common examples of these lignocellulosic shell structures. During development and maturation, the shell tissues undergo a transformation from soft to hard – a process that involves geometrical and chemical changes on the cell wall level. To track these changes in developing walnut shells, we used serial section-based Raman imaging to produce 3D images of individual cells. In this presentation, we show the cell wall composition in 3D and identify the chemical changes in the developing cell wall. We also briefly discuss the advantages and disadvantages of 3D Raman imaging when compared to other 3D imaging methods, such as x-ray micro-tomography and serial block face electron microscopy.

CELL 428

From the soft to the hard: Changes in microchemistry during cell wall maturation of walnut shells

Nannan Xiao, nannan.xiao@boku.ac.at, Notburga Gierlinger. Department of Nanobiotechnology, University of Natural Resources and Life Sciences, Vienna, Austria

The walnut shell is a hard and protective layer that provides an essential barrier between seed and environment. The shell is based on only one unit cell type: the polylobate sclerenchyma cell. For a better understanding of the interlocked walnut shell tissue, we investigate the microstructural and compositional changes during the development of the shell from the soft to the hard state by Confocal Raman microscopy. Walnut shell development takes place beyond the outer green husk, which protects and delivers components during the development of the walnut. Our results show that in the developing shell (July) the cells towards this outer green husk are the thickest and most lignified cell walls and across the shell a gradient in cell wall thickness and lignin content pictures the ongoing development, but pectin distribution shows opposite pattern.
Raman imaging also shows that lignin is deposited first into the pectin network between the cells and cell corners, at the very beginning when the secondary cell wall is added onto the primary cell wall. Furthermore, Raman imaging of fluorescence visualized numerous pit channel within every cell, connecting all the interlocked polylobate walnut shells with each other and enabling transport during development. In the final mature stage (October) thick-walled highly lignified cells were found across the entire shell and fluorescence was increasing throughout the cell wall, but also a remarkable fluorescent layer towards the lumen was detected in the inner part. This final sealing of the microspaces with aromatic components reminds on heartwood formation of trees and is suggested to improve protection properties of the mature walnut shell.

Our results clearly indicate the potential of Confocal Raman spectroscopy to gain new insights into chemical changes of the walnut shell microstructure of different development stages. In the long term, it will inspire biomimetic material design and packaging concepts, but is also important for utilizing nutshells in terms of food waste valorization, considering that walnuts are the most widespread tree nuts in the world.

**CELL 429**

**Bioinspired thermo-responsive hydrogels composed of xyloglucan and cellulose nanocrystals**

Malika Talantikite¹, Taylor C. Stimpson², Antoine Gourlay¹, Nadege Beury¹, Céline Moreau¹, Emily D. Cranston²,³, Jose Moran-Mirabal², Bernard Cathala¹, bernard.cathala@inra.fr. (1) BIA, INRA, Nantes, France (2) Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada (3) Department of Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

Xyloglucan (XG) is an hemicellulose that has a cellulose-like backbone composed of 1,4-linked, β-glucopyranosyl residues and displays high affinity for cellulose surfaces. The XG backbone is typically arranged in blocks of four successive glucose units, three of which carry a flexible α-(1,6) linked D-xylosyl decoration, either as a single sugar or as a β-D-Gal-(1,2)-α-D-Xyl side chains. It has been reported that the removal of galactose residues results in degalactosylated XG (DG-XG) with thermo-responsive behaviour. Inspired by the entropically-driven interactions between XG and cellulose and the thermo-responsiveness of DG-XG, we have combined DG-XG and cellulose nanocrystals (CNCs) to produce thermo-reversible hydrogels.

DG-XG fractions were prepared through enzymatic cleavage and their interaction with CNCs was studied through quartz crystal microbalance with dissipation (QCM-D). When compared to XG, it was observed that higher amounts of DG-XG bound to model cellulose surfaces. The gelation behavior of XG/DG-XG alone and in combination with CNCs was investigated over a range of CNC/XG:DG-XG ratios and temperatures to establish phase diagrams for the hydrogel systems. Furthermore, the mechanical properties of XG/CNC and DG-XG/CNC hydrogels were measured using buckling-based methods indicating that the modulus of DG-XG/CNC hydrogels was significantly higher than for unmodified XG with CNCs. Overall, the DG-XG/CNC hydrogels displayed thermo-responsive behavior, a high affinity for water absorption, and tunable...
mechanical properties. Based on the aggregated results, gelation mechanisms for XG/CNC and DG-XG/CNC mixtures are proposed.

CELL 430

**Pineapple aerogels from agricultural waste for engineering applications**

Nga H. Do¹, Thao Luu¹, Quoc B. Thai², Duyen K. Le², Phung K. Le¹, Hai Duong², mpedhm@nus.edu.sg. (1) Faculty of Chemical Engineering, Hochiminh City University of Technology, Ho Chi Minh City, Viet Nam (2) National University of Singapore, Singapore

Aiming to investigate the helpful solution to deal with the pollution of agricultural waste, multi-functional cellulose aerogels are developed successfully from biodegradable pineapple leaf fibers in combination with polyvinyl alcohol (PVA) as a cross-linker, followed by the cost-effective freeze drying process. Their highly porous 3D network with porosity of nearly 99% and remarkably low density of 0.013 – 0.033 g/cm³ give them the great capabilities of heat insulation and acoustic insulation. In fact, their thermal conductivities are valued between 0.030 to 0.034 W/m.K, indicating the abilities of PF aerogels to retain heat very well. In addition, with the same thickness, the noise reduction coefficient of PF aerogels can reach at 0.52, higher than that of acoustic absorber Basmel® in which implies their exceptional competitiveness with commercial products. The thermal jacket using PFs aerogel can keep water inside chilled below 0 °C for 6 hours and above 40 °C for 2.5 hours. Moreover, the PF aerogels coated with methyltrimethoxysilane (MTMS) exhibit excellent oil adsorption performance that they can absorb oil quickly up to nearly 40 g/g within 1 minute.
Polysaccharide-protein nanofibers reinforced hydrogels: Production, characterization and potential applications

Maria Teixeira, Manuel Coelho, Hélder Baptista, Nuno Silva, Ricardo Pinto, Carla Vilela, cvilela@ua.pt, Carmen Freire. CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal

Polysaccharide-based hydrogels are a particularly fascinating family of materials due to their singular properties such as low cytotoxicity, hydrophilicity and mechanical strength. Among the catalogue of polysaccharides, alginate, which is extracted from seaweed, has been clearly the most employed biopolymer in current biomedical applications. However, alginate hydrogels have some mechanical and biological restrictions, namely structural degradability and poor cell-adhesion. These limitations are usually overcome via blending with cell-adherent molecules or other biomaterials. An example of such materials includes protein nanofibrils that present excellent properties in terms of mechanical strength and stability, but also antimicrobial and cell-adherent activities, and their use as building nanoblocks in innovative functional nanocomposites has attracted increasing attention.

In this sense, the present study is focused on the development of new nanocomposite alginate-based hydrogels reinforced with protein nanofibrils, in order to produce hydrogels with improved mechanical performance and cell viability for application in the biomedical field, for example in tissue engineering and development of bioinks for 3D-bioprinting.

CELL 432

Self-healing and conductive double network hydrogel with enhanced mechanical property

Yang Zou, whzouyang@whu.edu.cn. Wuhan University, Wuhan, Hubei, China

Recent years have witnessed great developments in self-healing biopolymeric hydrogel. However, the applications of these hydrogels are limited due to that their mechanical properties are not enough for some special fields. In this article, a double-network (DN) hydrogel was fabricated by combining the first network formed between acrylamide-modified chitosan and oxidized alginate with the second network of hydrogen bond linkage from Polyvinyl alcohol (PVA). This double-network hydrogel could self-heal after incubating for 12 hours without external stimulus. In addition, This DN hydrogels showed enhanced mechanical properties compared with acrylamide-modified chitosan/oxidized alginate hydrogel and pure PVA hydrogels. The DN hydrogel can recover its original shape after a compression strain of 80 %, which exhibited great mechanical strength, tough and recoverability. Interestingly, the free ions in chitosan and alginate endued the DN hydrogels with electric conductivity of 4.6 S cm⁻¹. This self-healing and conductive hydrogels can be used as wires to light the LED bulb and be assembled into an electrochromic device. We anticipate that this DN hydrogels with
self-healing, conductive and enhanced mechanical properties can be applied in different engineering fields.

**CELL 433**

**UV-triggered on-demand thermoreversible and irreversible gelation of cellulose nanocrystals**

Olli T. Ikkala¹, olli.ikkala@aalto.fi, Christoph Hoerenz¹, Kia Bertula¹, Tony Tiainen², Sami Hietala³, Ville Hynninen¹. (1) Dept of Applied Physics, Aalto University, Espoo, Finland (2) Department of Chemistry, University of Helsinki, Helsinki, Finland (3) University of Helsinki, HU, Finland

We show ionically crosslinked, selectively thermoreversible or permanent hydrogels of anionic cellulose nanocrystals (CNCs) and methacrylate terpolymers by mixing them homogeneously in the initially charge-neutral state of the polymer, which was subsequently switched cationic by cleaving a side-group by UV-irradiation. The polymer is a random terpolymer poly(di(ethylene glycol) methyl ether methacrylate)-rnd-poly(oligo(ethylene glycol) methyl ether methacrylate)-rnd-poly(2-((2-nitrobenzyl)oxycarbonyl)aminoethyl methacrylate), i.e., PDEGMA-rnd-POEGMA-rnd-PNBOCAEMA. The PDEGMA and POEGMA repeating units lead to Lower Critical Solution Temperature (LCST) behavior. Initially, homogeneous aqueous mixtures are obtained with CNCs and no gelation is observed even upon heating to 60 oC. However, upon UV-irradiation of the homogeneous mixtures, the PNBOCAEMAs are transformed to cationic 2-aminoethyl methacrylate (AEMA) groups, as 2-nitrobenzaldehyde moieties are cleaved. The resulting mixtures of anionic CNC and cationic PDEGMA-rnd-POEGMA-rnd-PAEMA show thermoreversible ionic gelation for sufficiently high polymer fractions upon heating short times up to 60 oC. However, for long enough heating times, even permanent ionic gels can be obtained, indicating importance of kinetic aspects. The ionic nature of the crosslinking is directly shown by adding NaCl, which leads to gel melting. In conclusion, the optical triggering of ionic interaction allows a new way for ionic nanocellulose hydrogel assemblies.

**CELL 434**

**Carbon aerogels from Biochoice™ kraft lignin for production of supercapacitor electrodes**

Muzaffer A. Karaaslan¹, karaasma@mail.ubc.ca, Li-Ting Lin¹, Li-Yang Liu¹, Shabnam Sanaei², Bruno Marcoccia², Frank K. Ko³, Scott Renneckar¹. (1) Wood Science, University of British Columbia, Vancouver, British Columbia, Canada (2) Domtar, Montreal, Quebec, Canada (3) University of British Columbia, Vancouver, British Columbia, Canada

Carbon aerogels are mesoporous, three dimensional solid materials consisting of interconnected network of nanoscale carbon particles. Due to their unique network
structure, low density and high surface area, carbon aerogels are promising materials as thermal and acoustic insulators, adsorbents, filters, catalyst supports, desalination electrodes, and electrodes for hydrogen and energy storage. Current methods to produce organic aerogels and their carbon derivatives includes using resorcinol or phenol as phenolic precursors and formaldehyde as crosslinking reagent, but they are non-renewable, toxic and expensive. Lignin, as a renewable aromatic biopolymer with high carbon content and chemical functionality, is a sustainable abundant resource for carbon aerogel production. In this study, softwood kraft lignin isolated by LignoBoostTM process was used to produce lignin-based gels under mild conditions through sol-gel chemistry with various crosslinking strategies. The effects of processing conditions, lignin content and crosslinking density on gelation kinetics and chemical and physical properties of resulting gels were investigated. Rigid carbon aerogels were prepared by controlled removal of liquid phase from lignin gels with supercritical drying, and a final pyrolysis step. Carbon electrodes assembled from these aerogels were characterized with cyclic voltammetry, galvanostatic charge-discharge tests and electrochemical impedance spectroscopy. Electrochemical tests showed that lignin carbon aerogels are promising candidates for energy storage applications such as supercapacitor electrodes.

**CELL 435**

**Production of functionalized product-stream proteins: Towards sustainable absorbent materials**

*Antonio Capezza¹, ajcv@kth.se, William Newson², Eva Johansson³, Richard Olsson², Mikael Hedenqvist².* (¹) Fibre and Polymer Technology, KTH/SLU, Stockholm, Stockholm, Sweden (²) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (³) Swedish University of Agricultural Sciences, Alnarp, Sweden

Superabsorbent polymers (SAPs) consist of fossil-based cross-linked hydrophilic polymer chains, forming networks that are able to absorb high amounts of different fluids such as water, saline and blood. SAPs are heavily utilized in the daily-care industry due to their swelling capacities and some of the most important applications include disposable diapers and sanitary pads. Multiple and emerging uses of SAP materials lead to an ever growing production, the market is expected to reach ca. 12 million dollars by 2023, with SAP products corresponding to more than 2-3% of the today’s household waste production. It is therefore of importance to develop biobased sustainable SAPs to replace those that are petroleum-based. Here, proteins being natural polymers having high liquid uptake capacity and being harmless when degraded, may provide a sustainable raw material and an alternative to already existing SAPs. Porous structures based on wheat gluten (WG) proteins, available as a product-stream from the wheat starch industry, have shown potential to perform as water-absorbent materials. The absorption capacity of WG-based porous materials have reached up to 30 grams of water per gram of dry material (g/g), and ca. 10 g/g of saline
and defibrinated sheep blood. Such WG materials have also shown high non-polar liquid uptake and sponge effects. The swelling capacity and mechanical properties of the different materials produced were modified by adding a naturally-occurring crosslinker, genipin, and cellulose nanofibers. Moreover, WG and potato proteins have been functionalized to mimic the chemical structure of SAPs and increase their liquid absorbent properties. Different physical features have also been obtained by varying the drying process of our materials, i.e. from lyophilisation to ambient drying (no freeze-drying). Consequently, both porous structures and particles can be produced, resembling properties of existing SAPs in the market. The results indicate that the modification of these inexpensive and readily available product-stream proteins can be considered as a potential alternative to fossil-based absorbing materials in the future.

CELL 436

High-performance solar steam device constructed with chitin-based wrinkled hydrogels

Yumin Du1,2, duyumin@whu.edu.cn, Xiaojuan Lei3, Xiaowen Shi2, Lina Zhang4. (1) Center of Research on Biomass Resource, Wuhan University, Wuhan Hubei, China (2) College of Resource and Environmental Sciences, Wuhan University, Wuhan, Hubei, China (3) College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei, China (4) Wuhan University, Wuhan Hubei, China

Solar steam generation has emerged as a promising technology, for its potential in harvesting solar energy for water purification and desalination. The chitin-based materials have been demonstrated to be efficient solar steam-generation device, and for the first time, the high-performance chitin-based solar steam device was constructed by interfacially polymerizing dopamine (DA) on chitin-based wrinkled hydrogel. Due to enhanced area for vapor dissipation, the wrinkled structure improves the water evaporation rate by at least 13% to 1.57 kg m⁻² h⁻¹ from that of a planar structure and exhibits a solar-thermal energy conversion efficiency of 80.27% under 1 sun illumination. This capability of high solar steam generation was attributed to the highly porous structure and channels of the hydrogel. The concave-convex wrinkled surface with a large surface-projected area ratio enabled stronger intrinsic evaporation. These features not only provided efficient light absorption, water supply, and vapor escape, but also suppressed three components of heat losses at the same time. This work could inspire new paradigms toward developing sustainable high-performance solar-driven desalination technologies with abundant and renewable marine resource.

CELL 437

Drying induced brittle-to-ductile transition of bacterial cellulose nanofiber network

Wenzhe Song1, w.song15@imperial.ac.uk, Natalia Herrera-Vargas3, Joanne Li1, hong.li18@imperial.ac.uk, Koon-Yang Lee2. (1) Department of Aeronautics, Imperial
Bacterial cellulose (BC) has attracted growing interest due to its high chemical purity, crystallinity and innate nanoscale fibre network. Consolidated BC nanopaper has thus been exploited in many novel applications, such as in electronic display, energy storage and nanogenerator. In all applications, mechanical properties are of significant importance for BC nanopaper to maintain structural integrity so as to deliver advanced functionality, and the desired mechanical performance can vary greatly depending on specific situations. Herein, we present a chemical-free and energy-efficient route for tailoring the mechanical properties of bacterial cellulose nanopaper.

The BC nanopaper was obtained by direct consolidation of wet BC pellicle. It was found that the tensile elastic/inelastic behaviour of the resulting nanopaper can be well controlled by altering the consolidation temperature of the BC pellicle. BC nanopaper dried at 120 °C showed (pseudo-) elastic deformation until failure, whilst nanopapers consolidated at 90 °C and 60 °C showed a clear yield point with significant strain hardening and higher failure strain. The brittle-to-ductile transition was mainly attributed to the difference in hydrogen bond density of the nanopapers dried at different temperatures. The accessible hydroxyl group, characterised by dynamic vapour sorption (DVS) with deuterium, increased from 1.26 per glucose unit of 120 °C dried nanopaper to 1.65 per glucose unit of 60 °C dried nanopaper, indicating a decrease in hydrogen bond density. This decrease provided a more flexible BC nanofiber network, which then transferred to a more ductile deformation behaviour. Furthermore, with the assistance of various characterisations, we shed light on the fundamental mechanism relating the consolidation process and the physical/mechanical properties of the BC nanopapers.

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Understanding the mechanical performance of nanocellulose nanopapers and bioinspired nanocomposites

Andreas Walther, andreas.walther@makro.uni-freiburg.de. University of Freiburg, Freiburg, Germany

Cellulose and chitin nanofibrils (CNF, ChNF) as well as nanocrystals (CNCs) are emerging building blocks for advanced functional materials due their nanoscale dimensions, high crystallinity and excellent mechanical properties. Key aspects in translating their intriguing properties into high performance and functional materials are to manage their organization into higher level structures and exploit the differences in their chemical composition to an advantage in materials design. In this talk I will first discuss in detail how highest-performance self-assembling bioinspired nanocomposites, i.e. wood-inspired nanopapers and crustacean-inspired nanocomposites can be prepared by exploiting our concept of polymer-coated hard/soft
nanoparticles to prepare highly ordered structures at high fractions of reinforcements. I will discuss how engineering of thermomechanical properties of the tailor-made polymers need controls toughness, and how the implementation of supramolecular reversible bonds can be used for implementing sacrificial bonds. In the case of CNCs, single step assembly of tunable photonic reflectors complement the design of the mechanical property space in the direction of multifunctional material classes. Additionally, the merger of this bottom-up structuring with top-down 3D printing enables the preparation of mechanical gradient materials that can even be reprogrammed in a light-adaptive manner.

CELL 439

Self-fibrillation of cellulose fibres: From papers to films

Yunus C. Gorur, gorur@kth.se, Per A. Larsson, Lars Wagberg. Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden

Cellulose nanofibrils (CNFs) prepared from wood biomass is a promising candidate to replace oil-based materials in, for example, packaging applications. CNFs have very desirable properties, such as high aspect ratio and small dimensions, which enables them to be used not only in making strong and transparent barrier films for applications such as packaging, but also in advanced bottom-up engineering of more complex materials. On the other hand, CNFs’ affinity for water combined with their small size leads to very slow and energy-demanding procedures for removal of water, which to a large extent is what today prevents a feasible production of dry CNF-based materials on an industrial scale. This work involves a careful manipulation and balancing of the interactions keeping the fibre wall together. By careful chemical modification of the fibres, it was possible to prepare films via established papermaking techniques without sacrificing dewatering speed and with film properties comparable to CNF-films. The
formed films show substantial transparency, barrier properties and wet strength values that are comparable to those found in the literature. The process is simple, robust and fast (on a scale of seconds), which opens great research possibilities and also forms a base for an industrial scale up.

CELL 440

Conducting polymer infiltration in porous cellulose thin films

Stephan Roth\(^3,1\), stephan.roth@desy.de, Calvin Brett\(^3,1\), Lucas Kreuzer\(^2\), Tobias Widmann\(^2\), Ola K. Forslund\(^3\), Elisabetta Nocerino\(^3\), Lionel Porcar\(^4\), Daniel Soderberg\(^3,5\), Martin Mansson\(^3\), Peter Mueller-Buschbaum\(^6\). (1) DESY, Hamburg, Germany (2) Chair for Functional Materials, TU München, Garching, Germany (3) KTH Royal Institute of Technology, Stockholm, Sweden (4) ILL Institute Laue-Langevin, Grenoble, France (5) Wallenberg Wood Science Center, Stockholm, Sweden (6) Technische Universität München, Garching, Germany

Cellulose nanofibrils (CNF) have proven their strengths in conductive and transparent films. One very promising route for their implementation is the fabrication of porous CNF films in large-industrial scale by spray deposition using water-based technologies; the resulting porous CNF templates are excellent candidates to infiltrate conductive polymers for functionalization. We therefore used poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), widely applied in organic photovoltaics and electronics, to functionalize the porous CNF template. We studied the infiltration, resulting structural rearrangement within the thin CNF film of 400 nm thickness and their behavior under cyclic humidity changes by grazing incidence small-angle neutron scattering (GISANS). Cyclic humidification is reversibly changing the nanoscale structure within the pristine CNF film, which might be attributed to voids or coiling. When infiltrating PEDOT:PSS, the behavior under cyclic humidity changes. Our results indicate the absence of coiling. Hence, morphological changes within the film are inhibited, which might be due to the fact that the polymer completely filled any porous structure within the thin film. Furthermore, we observe selective swelling of the PEDOT:PSS component within the film.

To conclude, we are able to resolve in situ morphological rearrangements within pristine CNF thin films. We showed that this behavior is reversible over at least two humidification cycles. The CNF/PEDOT:PSS composite obtained by infiltration does not show any structural rearrangement, but rather a swelling process. As humidity is present in many device applications and especially during processing and fabrication of conductive CNF composites, our results help to understand the humidity’s nanoscale impact to the meso- or macroscale in a device application.

CELL 441

Tough bacterial cellulose films for transparent composite applications
**Natalia Herrera-Vargas**, n.herrera@imperial.ac.uk, **Koon-Yang Lee**. (1) Aeronautics, Imperial College London, London, United Kingdom (2) Department of Aeronautics, Imperial College London, London, United Kingdom

Bacterial cellulose (BC) is a biopolymer gel based on pure cellulose produced by the bacteria *Acetobacter xylinum*. BC gels have a nano-sized three-dimensional network structure with fibers ranging from 25–100 nm. BC has a variety of applications in biomedical fields, cosmetics, and food applications because it is translucent, biocompatibility, and has water-retention ability. BC network is also strong and stiff (Young’s modulus of ~12 GPa and tensile strength of ~110 MPa), and therefore has been used as a renewable reinforcing agent for nanocomposites. Its nanofiber structure will allow the use of BC in applications such as optically transparent flexible films or as reinforcement/functional additive for transparent polymers as PMMA or PLA. The toughness of BC films needs to be improved if the last mentioned application are of interest.

In the present study, plasticized BC films with remarkably high toughness were prepared by immersing wet BC pellicle in poly(ethylene glycol) (PEG) followed by drying process. PEG of 200 and 400 molecular weight were used and two different drying process were evaluated. Thermal gravimetric analysis results showed that plasticized BC contained between 25-30 wt.% PEG. Scan electron microscopy (HR-SEM) was used to analyze the effect of the PEG and dry process on the morphology of the BC pellicle. The toughness of the BC, calculated as the area under the stress-strain curve, was increased from 3 KJ/m$^3$ to 8 and 12 KJ/m$^3$ for the plasticized BC with PEG200 and PEG400, respectively. Results also showed that PMMA composites prepared with plasticized BC exhibit higher Charpy impact strength than neat PMMA and composites prepared with neat BC.

**CELL 442**

**Synthesis of microcapsules consisting of a hexadecane core and a cellulosic shell for thermal energy management**

**Gulbahar Bahsi Kaya**, gb834@msstate.edu, Yunsang Kim. Sustainable Bioproducts, Mississippi State University, Starkville, Mississippi, United States

Organic phase change material (PCM) has an ability to store and release a large amount of energy in a wide range of temperature by latent heat of fusion or vaporization. However, the encapsulation of PCM is necessary to stabilize PCM from undesirable reaction and leaching. A PCM microcapsule whose shell is made of cellulosic biomass could be an option for better utilization of low-value bioresources. This study aims to prepare microcapsules containing hexadecane (PCM) that is encapsulated by a cellulosic shell from cellulose nanofibrils (CNF) through a sonochemical technique. High intensity ultrasonication at the CNF-hexadecane interface created a paraffin-in-water emulsion, followed by the partial melting and possible crosslinking of CNF to form the cellulosic shell surrounding the hexadecane
The formation of PCM microcapsules was investigated by visual inspection, FT-IR, and fluorescence microscopy with a selective dyeing of the hydrophobic core. After freeze drying, the morphology and size distribution of the microcapsules were studied by SEM, which ranged from 4 to 10 µm. Among various weight percents of CNF in water and hexadecane-water ratios, the maximum loading of PCM was determined to be 90% from 0.3% CNF in water and 2:1 water-oil ratio, respectively, by thermal gravimetric analysis. The thermal energy capacity of the PCM microcapsules will be evaluated by differential scanning calorimetry. The incorporation of the PCM microcapsules in a biomass derived matrix will also be shown.

CELL 443

**Highly cross-linked carboxycellulose nanofiber-based sustainable membrane with high proton conduction and PEM fuel cell performance**

Sunil Sharma¹, sksharma.iitb@gmail.com, Priyanka Sharma¹, Songtao Li², George Cai², Songze Wu², Aniket Raut², Miriam Rafailovich², Benjamin S. Hsiao². (1) CHEMISTRY, STONY BROOK UNIVERSITY, NEW YORK, NEW YORK, UNITED STATES (2) Stony Brook University, Stony Brook, New York, United States

Carboxycellulose nanofibers (CNFs) have been proved to be a green, inexpensive alternative material for polymer electrolyte membrane compared with the expensive commercial synthetic polymer membranes. However, its practical applications have been limited by its relatively low power density and reduced mechanical properties under high relative humidity and temperature. In this study, citric acid cross-linked cellulose nanofiber (CA/CNF) membranes were prepared by a solvent casting method using a carboxy cellulose nanofiber suspension from TEMPO oxidation of wood pulp. Results of FT-IR spectroscopy, ¹³C NMR, and powder XRD reveal a chemical crosslink between the citric acid and the CNF, and the optimal fuel cell performance was obtained crosslinking 70 mL CNF suspension (0.32 wt%) with 0.3 mL of 1.0 M citric acid solution. The membrane electrode assemblies (MEAs), operated in oxygen atmosphere, exhibit maximum output power density of 27.7 mW/cm² and maximum current density of 107 mA/cm² at 80 °C for the CA/CNF membrane with only 0.1 mg/cm² Pt loading on anode and cathode, which is approximately 30 times and 22 times of the uncrosslinked CNF film. The morphologies of CA/CNF films are characterized via SEM, TEM, and AFM. Despite the large thickness of ~65 µm. In addition to the enhanced fuel cell performance and mechanical properties, the CA/CNF composite membrane is also green and environmentally friendly, making it a promising candidate for future research and application.

CELL 444

**Nanocelluloses as texturizers in industrial applications**
Ellinor Hegset, ellinor.heggset@rise-pfi.no, Kristin Syverud. RISE PFI, Trondheim, Norway

Texturizers are important in a variety of end-use applications, and nanocelluloses have the potential to take important market shares in this area. However, to understand how the rheological properties are affected when nanocelluloses are added can be difficult, and it is important to obtain further knowledge here. To use nanocelluloses in multicomponent systems, cause a knowledge need on the interactions between the nanocelluloses and the other product components.

Examples of multicomponent systems which will be described, are for use in industrial application areas, such as foodstuffs. Here, nanocelluloses are suggested to function as a texturizer and a fat replacer. The studies performed is on different foodstuffs e.g. bread and mayonnaise, and results from pilot tests will be given.

CELL 445

Hydrogen-bonding-induced assembly of aligned cellulose nanofibers into ultrastrong and tough bulk materials

Xiaoshuai Han, Yuhang Ye, Feng Jiang, feng.jiang@ubc.ca. Department of Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

Structural materials with exceptional strength and toughness are highly desirable in engineering applications. However, it remains a grand challenge to combine these two mutually exclusive mechanical properties into one body. Nature has excelled in designing such strong and tough structures (such as nacre and bone) without using complicated molecules and processes, which has intrigued us to design biomimetic materials by mimicking natural process. In this paper, we proposed a simple yet universal mechanism for making strong and tough structural materials out of cellulose nanofibers by water molecules induced hydrogen bonding. This method can convert natural wood into strong and tough bulk materials, by going through a three-step process of delignification, drying induced assembly, and water molecules induced hydrogen bonding under compression. A tough and strong cellulose nanofibers bulk material was derived, showing simultaneously enhanced tensile strength (352 MPa vs. 56 MPa for natural wood) and toughness (4.1 MJ×m⁻³ vs. 0.42 MJ×m⁻³ for natural wood). As a proof of our hypothesis, the mechanical properties and morphological characteristics are greatly affected by water molecules within the structure during both drying and compressing. It is proved that water molecules can assist the assembly of cellulose nanofibers by participating in hydrogen bonding as a structural molecule. Other than developing a strong and tough biomimetic structural material, this paper also provides important information for understanding the mechanisms that nature used to design structural materials, and is expected to guide the design of biomimetic materials.

CELL 446
Additive manufacturing of 3D structures composed of wood materials

Doron Kam1,2, doron.kam@mail.huji.ac.il, Michael Layani1, Oded Shoseyov2, Shlomo Magdassi1. (1) Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel (2) Plant Sciences and Genetics in Agriculture, The Hebrew University of Jerusalem, Rehovot, Israel

Wood is a natural organic material that is widely available in the form of wood residues, which can be milled into small particles or fine wood powder, and therefore can be added to 3D printing compositions. Additive manufacturing (AM), also known as 3D printing, is a process for production 3D objects from a digital model. The 3D printed object is achieved using an additive layer-by-layer deposition processes. The use of wood powder was reported while combined with conventional plastics, natural adhesives, or with gypsum, cellulose, sodium silicate, and cement as a binder. Making a 3D printed object which is composed mainly of wood powder, requires the use of suitable binders (resins) that eventually results in a composite material with the desired shape. Among the currently known resins in the wood industry, such as in wood composite panels (not for 3D printing), urea formaldehyde (UF) and phenol formaldehyde (PF) are the most widely used. However, the emission of harmful formaldehyde during the production and utilization of wood composite has been a severe concern in recent years. An alternative synthetic resins aiming to avoid the use of formaldehyde is methylene diphenyl diisocyanate (MDI). Nevertheless, MDI is an allergen and sensitizer. Furthermore, it is considered as a violently reactive material with water and other nucleophiles and therefore is not industrially appealing. In this research, we present 3D printing methods and ink compositions which are composed of wood chips/powder and plant-extracted natural binders, cellulose nanocrystals (CNCs) and Xyloglucan (XG), without the need of any additional synthetic resins, that results in 3D printed wooden objects.

CELL 447

Emerging water-energy applications of wood

Chen Chaoji, chencj@umd.edu, Liangbing Hu. Materials Science and Engineering, University of Maryland College Park, Hyattsville, Maryland, United States

Water and energy play important roles in modern society in various aspects such as for supplying water for all living creatures, powering the electrical devices, and maintaining a sustainable Earth environment. However, with the growing population on Earth, the shortages of clean water and energy have become more pressing.1,2 Wood is a natural water-energy system. For example, it can utilize solar energy, and carbon dioxide for chemistry synthesis. Wood’s unique hierarchical, cellular microstructure with abundant aligned multiscale pores plays an important role in the natural water-energy process in tree. Inspired by wood’s naturally occurred processes, we can directly use wood for man-made water treatment and energy storage/conversion devices and systems with properties, functions, and performances that go beyond
nature. These water and energy devices take full advantage of wood’s hierarchical, cellular, porous structure for multiscale mass/ions transport and selection and thermal/optical management. In particular, with rational chemical/compositional/structural modification of wood at various length scales, the transport of mass/ions can be well manipulated, as well as the multispectral energy (photon, phonon, electron, and so on) transfer behaviors accompanied with. With wood’s renewability, large abundance (there is three trillion trees on Earth), sustainability and facile/scalable manufacturing capability as additional advantageous features, wood-based water-energy applications are attractive in response to the water/energy shortage crises. We will discuss these progresses in this field with a focus on recent works from our lab, as well as challenges and future research opportunities of the field.

CELL 448

Wood-like biodegradable polybutylene succinate / nanocellulose composites with controlled interface properties

Sergejs Gaidukovs, sergejs.gaidukovs@rtu.lv, Anda Barkane, Oskars Platnieks, Inese Filipova, Vijay Thakur.

(1) Faculty of materials science and applied chemistry, Riga Technical university, Riga, Latvia (2) Institute of Polymer Materials, Riga Technical University, Riga, Latvia (3) LS Institute of wood chemistry, Riga, Latvia (4) Cranfield university, Cranfield, United Kingdom

We report herein a wood-like sustainable composites with bio-based and biodegradable components e.g. polybutylene succinate and nanocellulose. Polybutylene succinate, as a biodegradable aliphatic polyester derived from renewable resources, has potential being completely bio-based and biodegradable. While nanocellulose, as a relatively cheap novel filler material, has great advantage due to its availability from various waste products and sources. The challenges to discover more efficient processes and technologies to utilize nanocellulose in WPC processing and inventing novel composite materials with improved properties are still there. These composites mimic some properties of wood. Appropriate solution and melt blending composite preparation strategies were used to process these materials through adjustment of composition formulation, functionalization of nanocellulose component, compatibilization of polymer and control the properties at the nanoscale in the interface. The above stated ability to control the features in the interface of the biocomponents and evaluation of their influence on the micro and macroscopic properties provides a new aspect to the development of the bio-nanocomposites. Thermal, tensile, viscoelastic, rheological and biodegradation properties of prepared bio-based composites are presented.

CELL 449

Mechanics of cellulose nanomaterials using a bottom-up scalable modeling scheme
The quest for alternative biodegradable materials such as cellulose to replace plastics is attracting tremendous attention among the materials science community in addition to being directly aligned with the public interest. Most cellulose nanomaterials comprises of a combination of small (~nm) but strong nanofibers and long (~ μm) but weak microfibers. We investigate the role of interactions of such fibers, spanning across different length-scales, in improving the mechanical properties of the nanocomposite. To qualitatively understand the interface mechanics in the composite material, we devise a bottom-up multi-scale coarse-grained (CG) modeling scheme. The levels of the CG scheme are as described: (a) Cellulose molecular chain level (~ Å); (b) Elementary fibril level (~ nm); and (c) fiber level (μm). We characterize the length and diameter of the fibers using Atomic Force Microscopy and thereby choose the 2nd and the 3rd level of the CG scheme to model the nano and the microfibers respectively to reproduce analogous experimental conditions. We construct hybrid models by mixing the nano and micro fiber models. Changing the mass % of the separate nano fibers help explore the fundamental reason behind why the hybrid show greater strength and toughness than the material separately fabricated using only nano or microfibers. From the quantitative aspect, we obtain that the fracture resistance enhance efficiently by around 57 times when the nanofiber content is about 85.7%. Independent molecular simulations of inter-fiber sliding in the nano-, micro- and hybrid fibers elucidate the formation and breaking of hydrogen bonds and clearly explain the role of hydrogen bonding across their interfaces which directly imparts the superior mechanistic properties in the hybrids. Implementing the above CG scheme, we also study the interaction between two neighboring fibers (nano & micro) shedding fundamental insight on the mechanical response of cellulose nanomaterials under various representative loads. Such multi-scale modeling investigations, in addition to being very timely, can also be extended to other fundamental building blocks and directly influence the material design of novel hybrid materials having tunable interfacial properties.

**CELL 450**

**Wood-mimic bio-based resin for additive manufacturing**

*Anda Barkane², Sergejs Gaidukovs², Oskars Platnieks², Nejib Kasmi⁷, Youssef Habibi⁷, Youssef.Habibi@list.lu.* (1) Materials Research and Technology Departement, Luxembourg Institute of Science and Technology (LIST), Esch-sur-Alzette, Luxembourg (2) Institute of Polymer Materials , Riga Technical University, Riga, Latvia

Fossil-based products future is condemned and the development of alternative products derived mainly from renewable resources for more sustainability has grown enormously. Many industrial sectors already have made tremendous advancement to replace petroleum-based polymers, but there are many sectors were renewable raw materials are for high need. Among these sectors, additive manufacturing also known as 3D printing is fast growing and has evolved in more that 10 different types for 3D printing
processes and each of them requires materials with specific characteristics. UV-assisted additive manufacturing technologies like stereolithography (SLA) and digital light processing (DLP) has a promising future in biomedicine and other fields that need complex structures and high resolution. Nevertheless, conversion to bio-materials has been slower than for more common 3D printing technologies with extruder type systems and thermoplastic polymers as feeding materials. This is due to the fact that raw material for UV-assisted technologies has more requirements like high photosensitivity, low shrinkage after polymerization among others.

In the present work we developed an UV-curable bio-based resin filled with wood-derived fillers for SLA 3D printing exhibiting wood-mimic textural aspects along with good mechanical properties. This presentation will highlight some of our findings.

CELL 451

Bioinspired lignocellulose matrices for tunable sorption and release: From sustainable agriculture to environment remediation

Tahira Pirzada¹, tpirzad@ncsu.edu, Jacob John¹, Charles Opperman², Saad A. Khan¹.
(1) Chemical & Biomolecular Engineering, NCSU, Raleigh, North Carolina, United States (2) Entomology & Plant Pathology, NCSU, Raleigh, North Carolina, United States

Being major components of woody and non-woody plants, lignocellulosic materials have recently found enormous applications in a variety of fields ranging from biofuels and filtration to battery materials. Owing to the characteristic nature of lignin and cellulose for sorption and release of various types of substances, we present an innovative approach to fabricate various physical forms and compositions of lignocellulosic materials to fine tune their sorption and release profiles. We have prepared lignin-cellulose hybrid nanofibers and particles via respectively electrospinning and anti-solvent precipitation of mixtures containing biodegradable cellulose and alkali lignin. We find an interesting correlation between the precursor mixture composition and the fiber/particle physical properties. When sorption and release profile of these matrices is investigated, the composition of the matrix seems to monitor its capacity and kinetics to sorb and release various types of molecules. In particular, we have examined the scope of these matrices as sorbents for industrial contaminants using model dyes, while efficacy of the matrices as sustained release media for agrochemicals is analyzed by using model pesticides. We have also determined bioavailability of model pesticides from various matrices using in-vitro bioassays. We believe that by manipulating the composition of the matrices, we can fine tune their sorption and release profiles, while flexibility in fabricating the matrices in different physical forms further enhance the scope of our approach to be applied in diverse applications.

CELL 452

Wood-derived materials and structures for multiple applications
Hongli Zhu, h.zhu@neu.edu. Northeastern University, Arlington, Massachusetts, United States

Plastics impregnate all aspects of our daily lives. Now white pollution plagues the planet. Creating a solid platform for growth of sustainable alternatives to fossil-based products is important. Wood, as the largest biomaterial on the earth, is abundant, sustainable, and versatile. Cellulose, hemicellulose, and lignin are three primary earth abundant biomaterials derived from wood; however, cellulose is mainly used for paper fabrication, and most lignin and hemicellulose are under-utilized. In this talk, we will introduce our studies on broadening the application of biodegradable materials from wood with small environmental footprint, such as nanocellulose for bio/electronic/energy, tannin from bark for pseudocapacitor, lignin from wood as anolyte in flow batteries, galactomannan from seeds for transient biosensor, indigo carmine from flowers as anolyte in flow system, compressible carbon aerogel made from bacterial cellulose as anode of K ion batteries and so on. More interesting, because of the metabolism, wood tracheids are perfectly aligned for the transportation of water and ions. In this talk, we will also introduce our works on using the well-aligned structure for mass and charge transport in both energy storage and energy generation.

CELL 453

Chitosan-graft-vinyl acetate dispersions for greener wood adhesives

Linda Fogelstrom1,2, lindafo@kth.se, Xiuting Zhang1, Tijana Todorovic1, Emelie Norström1, Farideh Khabbaz1, Eva E. Malmstrom3,2. (1) Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden (2) Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden

Wood adhesives are important in many large-scale applications such as load-bearing constructions, flooring, furniture, windows, and doors, and in 2015 the wood adhesives market size was estimated to nearly 2 million tons. Historically, wood adhesives were produced from various natural polymers such as starch and proteins from blood or milk. During the 1960’s, however, the natural polymers were replaced by fossil-derived polymers due to their superior properties regarding bonding performance, easy handling, and favorable cost development. Today, poly(vinyl acetate), PVAc, is a commonly used polymer as a binder in wood adhesives. Advantages of PVAc-based adhesives include being easy to use and do not contain the harmful component formaldehyde, which is very common in commercial adhesives. However, PVAc adhesives are fossil-based and they are also limited to indoor applications due to their poor water resistance. The aim of this study is to combine PVAc and the biobased polysaccharide chitosan (CS) into a wood adhesive with improved properties and increased biobased content. Apart from being biobased, chitosan itself shows very good bonding performance, but the high viscosity of chitosan dispersions limits its applicability. In this study, vinyl acetate was grafted from chitosan by emulsion polymerization in an effort to combine the promising bonding properties of chitosan with the applicability of PVAc. The monomer conversion was as high as 97 %. Apart from
being an efficient yield, this also means that there will be a minimal amount of residual monomer in the adhesive, which is beneficial from health aspects. The Tg of the produced CS-g-PVAc was increased from 28 °C to 42 °C, compared with commercial PVAc. The obtained latexes had similar appearance and applicability as a commercial PVAc-based adhesive. The bonding performance was investigated by bonding thin wood veneers, and measuring the tensile shear strength after conditioning. The resulting bonding performance of the CS-graft-PVAc adhesive was very good, especially regarding the wet strength of the bond line, which is superior to that of the commercial benchmark PVAc-based wood adhesive. The improved properties and maintained applicability of the CS-graft-PVAc adhesive, together with the possibility of replacing ca 20 % of the fossil-based content with biobased material, are promising features for the competitiveness of this type of wood adhesive.

CELL 454

**Swelling and softening mechanisms of natural fibres under hygro- and hydrothermal conditions**

*William Garat*¹, *Nicolas Le Moigne*¹, nicolas.le-moigne@mines-ales.fr, *Stéphane Corn*¹, *Johnny Beaugrand*², *Anne Bergeret*¹. (1) C2MA, IMT Mines Alès, Alès, France (2) BIA, INRA, Nantes, France

Measuring and understanding the swelling and softening behaviour of plant fibres under controlled humidity in relation with their moisture content are critical for their valorization in composites applications. Indeed, they directly influence the processing and in-service behaviour of biocomposites. The aim of this work is to characterize, under controlled hygro- and hydrothermal conditions (from 20% to 73% RH and immersion), the moisture content, dimensional variations and mechanical behaviour of natural fibre bundles from various botanical origins with contrasting biochemical and structural characteristics. Automated laser scanning cross-sectional measurements and micro-tensile tests conducted either in a climate chamber or in an immersion cell allowed measuring cross-dimensional variations and tensile properties of the fibre bundles in relation with their moisture content determined by DVS and WRV. These analyses lead to determine the surface hygro- and hydroexpansion coefficients of the different natural fibre bundles in relation with the structural characteristics of the cell walls. The softening effect of water on the cell walls and loss of stiffness of fibre bundles is also discussed in relation with swelling and water sorption. These results open interesting perspectives for the predictive modelling of “in-service” mechanical behaviour of biocomposites that would better take into account the swelling of natural fibres in relation with their structural features.
Biorefining technology determines the macromolecular characteristics and interfacial properties of spruce galactoglucomannans

Mamata Bhattarai², mamata.bhattarai@helsinki.fi, Inkeri Kontro, Irina Sulaeva¹, Fabio Valoppi², Antje Potthast¹, Kirsi S. Mikkonen². (1) Department of Chemistry, University of Natural Resources and Life Sciences, Tulln, Austria (2) Department of Food and Nutrition, University of Helsinki, Helsinki, Finland

A large range of products in food, cosmetics, pharmaceuticals, and chemical industries are emulsion-based. In emulsion, the interface formation is aided, and the system is stabilized by emulsifiers and/or stabilizers that modify the interfacial and bulk properties of the system. Wood hemicelluloses, specifically spruce galactoglucomannans (GGM), have shown very promising features as emulsifiers and stabilizers. Currently, several biorefinery approaches exist to obtain GGM from forest resources, such as sawdust or process water of pulp mills. Each approach and subsequent purification technique to remove non-polysaccharide compounds yields GGM samples with different macromolecular and chemical characteristics. However, their effect on the interfacial and bulk properties of GGM-stabilized emulsions has not been understood.

In the present study, we studied the emulsification and stabilization potential of GGM obtained from three promising biorefinery procedures—pressurized-hot water extraction (PHWE), thermo-mechanical pulping process (TMP) and BLN, which is a modified hot water extraction method operating at near-vacuum conditions. First, to understand the bulk properties in emulsions, a detailed characterization of the solution properties of GGM was performed by asymmetric field-flow field fractionation coupled with multi-angle light scattering and small-angle X-ray scattering (SAXS). Second, emulsions were prepared from GGM and characterized for their physical stability during storage. The
droplet size distribution was monitored, and the droplets’ morphology was visualized by optical microscopy. The morphology of GGM at the oil/water interface in emulsions was characterized by SAXS. The results show that the isolation and subsequent purification procedure of GGM has a significant effect on their macromolecular characteristics. They determine the interfacial morphology, bulk properties, and stability of GGM emulsions. The current results provide insight 1) for the evaluation of biorefinery technique 2) for the optimization of extraction and purification procedure of each technique to produce functional emulsifiers from wood biomass, and 3) to design complex multiphasic systems from GGM.

CELL 456

Centrifugal fractionation of pressurized hot water softwood extracts leads to improved functional emulsifier

Fabio Valoppi\textsuperscript{1,2}, fabio.valoppi@helsinki.fi, Maarit H. Lahtinen\textsuperscript{1}, Mamata Bhattarai\textsuperscript{1}, Satu J. Kirjoranta\textsuperscript{1}, Venla Juntti\textsuperscript{1}, Leena J. Peltonen\textsuperscript{3}, Petri O. Kilpelainen\textsuperscript{4}, Kirsi S. Mikkonen\textsuperscript{1,2}. (1) Department of Food and Nutrition, University of Helsinki, Helsinki, Finland (2) Helsinki Institute of Sustainability Science, University of Helsinki, Helsinki, Finland (3) Division of Pharmaceutical Chemistry and Technology, University of Helsinki, Helsinki, Finland (4) Natural Resources Institute Finland (Luke), Espoo, Finland

The fractionation of complex biomass is essential to obtain value added functional molecules for energy, chemical, and material production. During cellulose refinement, hemicelluloses and lignin which make up 40-70% of wood mass end up in the pulping liquor that is burnt to regenerate the pulping chemicals and produce electricity. Lignin and hemicelluloses are low-value by-products remaining outside the circular economy concept. Recently, new and alternative routes have been explored to use hemicelluloses and lignin in high-value products, contributing to the reuse of industrial waste. Softwood extracts (SE) obtained from wood industry by-products through the environmentally friendly pressurized hot water extraction are heterogeneous mixtures rich in hemicelluloses such as galactoglucomannans (GGM), free and GGM-bound phenolics, and residual lignin. SE have been recently identified as novel emulsifying agents able to physically stabilize oil-in-water emulsions and protect the oil phase against oxidation. These unique characteristics make SE very attractive in food, pharmaceutical, cosmetic, and chemical industries.

Although SE have remarkable stabilizing ability, there is a lack in understanding the role of SE fractions in emulsion formation and stabilization. This information is fundamental in optimizing the extraction method. To tackle this issue, we developed a centrifugal fractionation method to separate SE in different lignin- and hemicelluloses-rich fractions. These fractions were obtained at different relative centrifugal force and time, and were studied by phenolic content, recovery yield, FTIR, molar mass, monosaccharide composition, particle size distribution, zeta-potential, surface tension, and NMR. Then, we used selected fractions to evaluate their ability to form and stabilize oil-in-water
emulsions. The physical stability of the emulsions was studied following the evolution of droplets’ size and distribution during storage at 40 °C. Results highlighted that using centrifugal fraction it is possible to modulate the composition and characteristics of lignin- and hemicelluloses-rich fractions by simultaneously improving the production process. This method also shed light on the complex mechanism underlying interfacial stabilization of SE which comprises the anchoring of GGM-bound phenolics and lignin-rich micro- and nanoparticles at the droplet interface, followed by a spatial reorganization of the molecules and particles at the interface.

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Valorization of agro-food residues to obtain multifunctional biopolymers for building and automotive parts processed through additive manufacturing, BARBARA project

Alfonso Jimenez¹, alfjimenez@ua.es, Francisco Vilaplana², Debora Puglia³, Lidia García⁴, María del Carmen Garrigós⁵. (1) Analytical Chemistry, University of Alicante, San Vicente del Raspeig, Alicante, Spain (2) KTH Royal Institute of Technology, Stockholm, Sweden (3) University of Perugia, Terni, Italy (4) Tecnopackaging, Zaragoza, Spain

The BARBARA project aims at the valorization of side-stream fractions and residues from agro-food production into two different pathways: (i) polysaccharides using by-products obtained from Kernel corn processing to be incorporated in engineering matrices; and (ii) functional additives with high value properties extracted from lemon, pomegranate, broccoli and almond residues. Different advanced extraction techniques were followed to valorize these side-streams: microwave assisted extraction (MAE), supercritical fluid extraction (SFE) and pressurized subcritical water extraction (SWE). All they were selected by their sustainable approach by reducing extraction times and avoiding the use of potentially hazardous solvents. Bio-based matrices were reinforced with extracted and functionalized additives to obtain customized formulations showing high mechanical and thermal performance, antibacterial properties, customized fragrance release and new optical and texture properties for aesthetical improvement. Selected formulations were processed by Fused Filament Fabrication (FFF) additive manufacturing to get prototypes with enhanced processability and targeted functionalities. These multifunctional biocomposites were validated in two key industrial sectors, such as automotive and construction. Extraction protocols were designed, developed and optimized by following response surface methodologies. Simple enrichment and purification processes, based on the use of adsorption resins, were studied and optimized. The optimized and validated processes were developed and the produced final pure fractions were characterized in terms of pigment concentration and molecular structure. The enrichment processes were then scaled up.

CONCLUSIONS
New biocomposites based on the addition of bioadditives extracted from several agricultural residues with different functionalities to commercial bio-based matrices have shown as successful to get multifunctional tailor-made materials with applications in automotive and building sectors. In addition, these formulations have shown potential for use in other key sectors, such as cosmetics and food packaging. The solution proposed in the BARBARA project gives rise to many possibilities for valorization of agricultural residues contributing to close the loop of the lemon, pomegranate, broccoli and almond residues and the circular economy concept.

**CELL 458**

**High internal phase oil-in-water Pickering emulsions stabilized with nanochitin and potential applications**

Ya Zhu¹, Long Bai¹, long.bai@aalto.fi, Siqi Huan¹, Xuetong Shi², Xiao Zhang¹, Orlando Rojas¹,². (1) Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland (2) Department of Chemical & Biological Engineering, Chemistry, and Wood Science, The University of British Columbia, Vancouver, British Columbia, Canada

Chitin is nontoxic, biocompatible and biodegradable, making it a promising candidate to produce biobased materials, especially for foodstuff. Among the various applications of chitin, colloidal chitin nanofibers (nanochitin, NCh), which are produced by deacetylation and mechanical treatment, have been used as Pickering stabilizers. Here, we introduce bio-colloidal NCh as a stabilizer of high-internal-phase Pickering emulsions (HIPPEs). Oil-in-water HIPPEs comprising a volume fraction of the dispersed phase (edible oil) as high as 88% are produced, the highest value achieved so far for edible oil in food-grade systems. The mechanism of stabilization with nanochitin involves: 1) structuring the continuous phase to form a highly interconnected fibrous network surrounding the oil droplets, which prevents flocculation and, 2) irreversible adsorption of nanochitin at the oil/water interfaces, inhibiting coarsening and breakage of oil droplets. The processability of HIPPEs for multiple applications is demonstrated for their moldability, and to facilitate changes in the composition of the internal phase. A substitute for food products such as margarine and a 3D-printed, edible foodstuff are achieved with HIPPEs containing 88 vol% edible oil. Highly porous, light-weight, solid foams bearing tunable internal structures are obtained by formulating HIPPEs using a sacrificial oil with a high vapor pressure. Overall, an alternative green HIPPE synthesis is proposed as a route to engineer functional materials.

**CELL 459**

**Preparation of slow-release encapsulated insecticide and fertilizer based on superabsorbent polysaccharide microbeads**

Prutha Joshi¹, ppj0001@auburn.edu, Ashleigh Stokes², David W. Held³, Julie Howe⁴, María L. Auad¹. (1) Chemical Engineering/CPAC, Auburn University, Auburn, Alabama, United States (2) Crop, Soil and Environmental Sciences, Auburn University, Auburn,
ABSTRACT
The use of encapsulated fertilizers and pesticides is a key approach for slowing the release of agrochemicals for long-term feeding and growing of plants, while simultaneously reducing economic costs and environmental problems. The use of hybrid systems (fertilizers and pesticides) for encapsulation in organic-based agriculture, which enables the slow-release forms of agrochemicals in a single application, has been a growing field of interest. In this approach, a formulation of *Bacillus thuringiensis* (*Bt*) as bio-pesticide and nitrogen, phosphorus, and potassium fertilizer materials (e.g., fish emulsion, KNO₃, and K₂HPO₄) were formulated using superabsorbent polymers (SAPs) microbeads based on alginate (ALG) then evaluated for release. Different formulations were prepared using 15% by wt. of *Bt*, fish emulsion, nitrogen, and phosphorus. The encapsulated microbeads were prepared by a wet-extrusion processing technique using ALG as the SAP and calcium chloride (CaCl₂) as the gelling agent. The resulting beads were characterized in terms of size, morphology, water uptake, and biodegradability. The results showed that the prepared microbeads have narrow size distributions ranging from 1.2 to 2.1mm and increased water uptake (1200% to 3200%). Moreover, loaded microbeads were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and Elementar CHNS analyzer to obtain the fertilizer grades as (6.2-0.8-1.05), (0-6.3-6.4), and (0.62-0-2.4) for the one loaded with fish emulsion, for K₂HPO₄ loaded beads, and for KNO₃ loaded beads respectively.
Amphoteric and amphiphilic soy protein microfibrils and their functional applications

You-Lo Hsieh, ylhsieh@ucdavis.edu, Xingchen Liu. Biological & Agricultural Engineering, University of California, Davis, Davis, California, United States

Homogeneous and highly stable aqueous soy protein (SP) colloids have been facilely prepared at up to 9 % to exhibit amphoteric (4.5 isoelectric point), amphiphilic (41.2 mN/m surface tension), and polyelectrolyte behaviors (+32.4 mV to -39.1 mV ζ-potentials). The colloidal nanoparticulates (6.0 nm thick, 16.4 nm wide) associate into pH-dependent 157 and 233 nm hydrodynamic dimension aggregates at pH 2.2 and 7.1. SP colloidal particulates have been ice-templated to self-assemble into concentration-dependent ultrafine fibrils (230-680 nm at up to 0.1 %) to laminated fibrous structures (1-1.5 mm at 1-9 %) that subsequently selectively disassembled into semi-crystalline 1.2 µm wide and 45-70 µm long microfibrils. These protein microfibrils are excellent amphiphiles, capable of stabilizing both high-internal-phase o/w and w1/o/w2 double emulsions as well as retaining amphiphilicity even with bound hydrophobic and hydrophilic compounds as demonstrated by lipophilic and water-soluble dyes. This approach of processing globular proteins is scalable and offers a facile way to convert the abundant, but highly under-utilized byproducts of food and biofuel into novel and versatile microfibrils for many potential applications.

Linear (IR & Raman) versus non-linear (SFG) vibrational spectroscopy for plant cell wall study: Pros and cons

Seong H. Kim, shkim@engr.psu.edu, Mohamadamin Makarem. Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania, United States

This talk will briefly review principles and data interpretations of infrared, Raman, and sum frequency generation (SFG) vibrational spectroscopy for analysis of cellulose in the isolated and purified form as well as in the native form inside plant cell walls. It will cover the vibrational modes of crystalline celluloses, how the chain orientation in crystalline domain is analyzed in each method, and how the concentration and spatial distribution of crystalline cellulose domains interspersed in amorphous matrices are manifested or analyzed differently in these three methods. Lastly, a few examples of IR, Raman, and SFG including spectroscopic imaging will be presented for analysis of crystalline cellulose in plant cell walls or lignocellulose biomass.

Raman spectroscopy and imaging in organization, processing and functionalization of polysaccharide materials
The Raman spectra of polysaccharide materials provide plenty of information on the local organization of polysaccharides in biological materials, their structural variations during processing and surface composition upon functionalization. Each of these aspects is covered by three case studies in our laboratory. First, the organization of polysaccharides in a chitin-protein matrix of crustacean exoskeleton is monitored to reveal differences in microstructure and composition throughout the cuticle cross-section of different skeletal segments with mineral and polysaccharide regions. A Raman study on organized layers provides better insight into the structure of biological materials and consequent possibilities for their extraction. Second, the processing of cellulosic nanofibers from pulp fibers by swelling in ionic liquids is a favorable pretreatment to facilitate fiber fibrillation. Therefore, the selection of an appropriate swelling medium and conditions should be based on monitoring the influence of ionic liquid composition on swelling efficiency and resulting cellulose properties after different processing time. The local structural variations in crystallinity and internal stress distributions are monitored by in-situ micro-Raman mapping at single fiber-level as a function of time, indicating variations between mild and severe pre-treatment with possible increase in crystallinity, while extreme degradation upon complete dissolution is noticed. Third, the functionalization of micro- to nanofibrillated cellulose by deposition of oil-filled organic nanoparticles provides an active system for tuning of the surface hydrophobicity, which is quantified and visualized as a controlled thermal release of oil from the fiber surface by Raman mapping. After melt-processing of the functionalized fibers with a biopolymer, the different crystallization kinetics within the polymer matrix can be followed from specific spectral bands. All observations from Raman analysis are further supported by complementary analytical techniques and/or theoretical calculations.

CELL 463

Dissolution kinetics of cellulose in ionic liquids: Raman spectral mapping

Tyler Cosby\textsuperscript{1}, cosby@usna.edu, Ashlee Aiello\textsuperscript{1}, David P. Durkin\textsuperscript{1}, Paul C. Trulove\textsuperscript{2}. (1) Chemistry, US Naval Academy, Annapolis, Maryland, United States (2) Chemistry, U.S. Naval Academy, Annapolis, Maryland, United States

Ionic liquids (ILs) are promising solvents for the treatment and processing of cellulose as well as many other biopolymers. Despite the discovery of numerous ILs capable of dissolving varying amounts of cellulose, a detailed understanding of the dissolution process in ILs is still lacking. In this study, a new approach, Raman spectral mapping, is employed to investigate the kinetics of cellulose (cotton yarn) dissolution in ILs. To elucidate the interplay of kinetic (viscosity) and thermodynamic (solvation) factors in the dissolution process, the treatment temperature, IL chemical structure, and IL
composition are systematically varied. The results are discussed within the framework of the current understanding of polymer dissolution.

CELL 464

Raman imaging with multivariate analysis: New insights in topochemistry of plant cell walls

Feng Xu, xfx315@bjfu.edu.cn, Xun Zhang. Beijing Forestry University, Beijing, China

Raman imaging is finding ever-increasing applications in understanding topochemistry of components in plant cell walls. However, the imaging dataset often contains thousands of spectra measured at hundreds or even thousands of individual frequencies, which raises difficulties when extracting hidden information, especially for components with similar chemical structures (e.g. cellulose and hemicelluloses). To address this issue, we combined Raman imaging with multivariate analysis for visualizing lignin, cellulose and hemicelluloses in plant cell walls. The method consists of three steps: 1) noise reduction for removing contaminants in imaging dataset; 2) principal component analysis (PCA) for identifying spectra in different cell wall layers; 3) self-modeling curve resolution (SMCR) analysis for obtaining pure spectra of cellulose and hemicelluloses. The results indicated that the several thousand spectra could be classified into groups in accordance with different morphological regions, including cell corner (CC), compound middle lamella (CML), secondary wall (SW), gelatinous layer (G-layer) and cell lumen. It was found that the Raman peak at 1331 cm\(^{-1}\) is more related to lignin rather than cellulose. The semi-quantitative concentrations of hemicelluloses and cellulose are identified based on SMCR of Raman images. Cellulose is mostly concentrated in the secondary wall, whilst the distribution of hemicelluloses is almost uniform throughout the cell wall of fibers except for a higher concentration found in the S1 and the outer S2 layer. The xylem ray and the vessel have relatively high concentrations of hemicelluloses that are comparable to the outer S2 layer of fibres, but the cellulose concentrations are relatively low in these two cell types. With the help of this method, a typical spectral analysis can be performed by a non-specialist user to obtain useful information from a Raman imaging dataset.

CELL 465

Insight into plant cell morphological and molecular structure by combination of Raman scattering with multimodal micro-spectroscopy at different scales

Janina Kneipp\(^1\), janina.kneipp@chemie.hu-berlin.de, Rivka Elbaum\(^2,3\), Victor R. Zancajo\(^1,2,3\), Zsuzsanna Heiner\(^1\), Ingrid Liedtke\(^1\), Sabrina Diehn\(^1\). (1) Department of Chemistry, Humboldt-Universität zu Berlin, Berlin, Germany (2) School of Analytical Sciences Adlershof (SALSA), Humboldt-Universität zu Berlin, Berlin, Germany (3) The Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Jerusalem, Israel
In order to obtain a complete picture of the structure and composition of plant cells, vibrational spectra obtained by Raman spectroscopy are extremely helpful, though in some cases additional information would be very useful. Here we discuss the role of different kinds of vibrational information obtained in experiments on cell walls using Raman scattering as well as infrared microspectroscopy at the microscopic and nanoscopic length scales. The spontaneous Raman scattering spectra can be ideally combined in one microscopic setup with non-linear coherent and incoherent multiphoton-excited effects, in particular second harmonic generation (SHG) and two-photon excited fluorescence (2PF). We will illustrate how these different types of optical information are used in combination to characterize the morphology together with the chemical composition of the cell wall in native plant tissues.

For the analysis of the data, a combination of hyperspectral analysis and image reconstruction on the non-resonant and pre-/resonant Raman data reveals details about the distribution and composition of the major cell wall constituents. Information on the orientation of cellulose microfibrils is obtained from polarization-resolved SHG signals. Furthermore, two-photon autofluorescence images can be used to image lignification. At the nanoscopic scale, both organic and inorganic components in the tissue can be imaged using infrared spectral information obtained in a near-field set-up. The combined microscopic approach covers several scales from the micron to the nanometer range, and represents an extension of existing Raman imaging and multiphoton microscopic approaches not only for plant tissues.

**CELL 466**

**Label-free visualization of fungal cell and spore wall architecture by confocal Raman microscopy**

**Hemanth Noothalapati**¹,², **nvhnag@life.shimane-u.ac.jp**, **Tatsuyuki Yamamoto**³,¹. (1) Raman Center for Medical and Biological Applications, Shimane University, Matsue, Japan (2) Research Administration Office, Shimane University, Matsue, Shimane (島根県), Japan (3) Faculty of Life and Environmental Science, Shimane University, Matsue, Shimane (島根県), Japan

Fungal cell wall is a dynamic organelle that plays a vital role, particularly in cellular growth, elongation and division. Any modification or disruption of the wall leads to lysis and cell death, hence serving an excellent target for anti-fungal drugs. Fungal cell walls are unique in that it differs greatly from well studied cellulose based plant cell walls. Chemically, the cell wall architecture in fungi is complex comprising mainly polysaccharides (glucan, mannan and chitin) and a small proportion of glycoproteins. Traditionally, electron microscopy and biochemical extraction methods were employed while recently immunocytochemical analysis is used to understand its structure. The former lacks chemical specificity requiring genetically modified cells to study different structures in detail while the later involves development of fluorescent monoclonal antibodies specific to glycosidic linkages among cell wall polysaccharides. Hence we aim to develop a label-free method based on confocal Raman microscopy, which is both simple and robust, to visualize distribution of various polysaccharide components of
fungal cell and spore wall. Fission yeast *Schizosaccharomyces pombe* is used as a model to demonstrate our method. First, space-resolved Raman spectra from lipid droplets, cytoplasm and cell wall were obtained to identify marker bands for individual components (Figure 1A) followed by imaging. We distinguished α- and β-glucans using anomeric vibrational bands in a straightforward manner. Then, by employing multivariate curve resolution (MCR) analysis, we successfully separated Raman spectra of several pure bio-macromolecular components whose detailed chemical images are shown in Figure 1B. We believe that our method will help in understanding the structure and dynamic re-organisation of fungal cell/spore wall architecture and eventually lead to advancements in drug discovery and development in the future. Our method can be directly adopted for plant cells to solve some of the challenges in understanding plant cell wall structure and its development.

**Figure 1.** (A) Raman spectra from lipid droplet, cytoplasm and cell wall. (B) MCR Chemical images of protein, glucan, mannan, polyphosphate and lipid.

**CELL 467**

**Characterization of functionalized cellulose fibers with Raman spectroscopy and atomic force microscopy**

*Julia Auernhammer¹, Alena Bell¹, Marcus Schulze¹, Tobias Meckel², Markus A. Biesalski², Robert W. Stark¹, stark@pos.tu-darmstadt.de. (1) Institute of Materials Science, TU Darmstadt, Darmstadt, Germany (2) Department of Chemistry, Technische Universität Darmstadt, Darmstadt, Germany*

The properties of paper sheets can be tuned by adjusting the surface or bulk chemistry with functional polymers. Functionalization can be applied during (online) or after (offline) papermaking processes. In particular, polymers are widely used to enhance the
mechanical strength of the wet state of paper sheets. However, the mechanical strength
depends not only on the chemical nature of the polymeric additives but also on the
distribution of the polymer on and in the lignocellulosic paper. Thus, we analyzed the
polymer distribution in the paper fleece and on single cellulose fibers. To better
understand the effect of coating on the network we also investigated the mechanics of
single cellulose fibres and the response to varying relative humidity.
The photochemical attachment and distribution of hydrophilic poly dimethyl acrylamide-
co-methacrylate-benzophenone P(DMAA-co-MABP) copolymers with defined amounts
of photoreactive benzophenone moieties in model paper sheets was investigated by
means of Raman microscopy. P(DMAA-co-MABP) could be separated unambiguously
from cellulose specific bands and thus the copolymer distribution within the cellulose
matrix could be identified. Two-dimensional Raman spectral maps at the intersections of
overlapping cellulose fibers document that the macromolecules only partially surround
the cellulose fibers, favor to attach to the fiber surface, and connect the cellulose fibers
at crossings. The copolymer appears to accumulate preferentially in holes, vacancies,
and dips on the cellulose fiber surface. Correlative brightfield, Raman, and confocal
laser scanning microscopy finally reveal a reticular three-dimensional distribution of the
polymer and show that the polymer is predominately deposited in regions of high
capillarity. Investigations on the single fiber level revealed that the coating was
considerably inhomogeneous along the fiber. Mechanical testing experiments by means
of an atomic force microscope (AFM) validated this observation.
These data provide deeper insights into the effects of paper functionalization with a
copolymer and aid in understanding how these agents ultimately influence the local and
overall properties of paper.

CELL 468

Mapping targeted acetylation of Norway spruce wood by use of Raman
microscopy

Ramunas Digaitis, Maria Fredriksson, Emil Thybring, Lisbeth G. G. Thygesen

Wood is susceptible to fungal degradation, but the susceptibility may be reduced by a
range of non-toxic wood modification methods. The exact mechanisms responsible for
the protective effect are not entirely clear, but are for some methods known to have to
do with a reduced moisture content in the wood cell walls. To explore how different
wood modification systems function is interesting per se, and it is also helpful when
designing novel wood modification systems aimed at for example simplifying process
set-ups or reducing modification costs.

Acetylation is one of the most well-known non-toxic wood modification methods.
Acetylation implies that wood is impregnated with acetic anhydride and thereafter cured.
This causes part of the hydroxyl groups within the wood cell wall biopolymers to be
replaced by acetyl groups. By tuning the acetylation protocol, samples with different
acetylation profiles can be designed and their interactions with water and fungi studied. This is helpful when trying to understand how and where modification is needed to prevent fungal decay, and which role the content and location of moisture plays in this. Such studies can also help clarify the interactions between fungal decay mechanisms and the presence of moisture within the xylem tissue. Spatially resolved chemical information at the scale needed for this endeavor is offered by Raman microscopy. In the present study Raman microscopy data analyzed with MCR-ALS (Multiplicative Curve Resolution - Alternating Least Squares) were used to document that Norway spruce wood specimens with different acetylation profiles could be produced by varying the acetylation conditions. The conditions were varied by omitting or allowing the xylem tissue to swell in pyridine during the acetylation, and by regulating the time and temperature of the impregnation step. In this way, documented acetylation was achieved of either the whole cell wall, part of the cell wall or of cell wall lumen surface.

The amount and location of water within the differently acetylated wood specimens was studied using the Raman microscopy data as well as by use of other experimental methods, including Low-Field Nuclear Magnetic Resonance and sorption balance techniques.

**CELL 469**

**Raman spectroscopy for analyzing cellulosics and cellulose materials**

*Umesh P. Agarwal, uagarwal@fs.fed.us.* Forest Products Lab, Madison, Wisconsin, United States

When applied to investigate cellulosics and cellulose materials, Raman spectroscopy has generated important information. For instance, while investigating the aggregated state of cellulose information on cellulose crystallinity and cellulose supramolecular structure has been obtained. Other advances in this arena include improved interpretation of various spectral changes, studies of nanocellulosics in their never-dried state, detection and quantitation of cellulose polymorphs, investigation of the supramolecular state of wood-cellulose in its native state, and mapping of cellulose in nanocellulose-polymer composites. Results of investigations on some of these topics will be presented.