



European Polysaccharide
Network Of Excellence

N°14 - MARCH 2010



***“Nature makes polysaccharides,
EPNOE turns them into products”***

editorial

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Through the window of my office, I can see the polysaccharide world at work to offer us Spring. The same is occurring with EPNOE with the flowering of new collaborative projects between academic/research members and companies.

Recently, seven European projects involving EPNOE academic/research members were submitted. Three projects are networks in materials science. The other four are application-oriented in the areas of materials, food and health, showing the wide scope of interest of EPNOE scientists. These seven projects involve twelve out of the sixteen academic/research EPNOE members and many companies.

The EPNOE Business and Industry Club is also flourishing with the arrival of three new companies for the year 2010: Kiram AB from Sweden, Novamont S.p.A from Italy and Biobasic Environnement from France.

The next EPNOE Business and Industry Club meeting will take place by the end of March at Unilever R&D in the Netherlands. It will be the occasion to review the activity plan of EPNOE for 2010 (a public version is available at www.epnoe.eu). As usual, these meetings are wonderful occasions to discuss, interact and build projects, without forgetting a nice banquet!

I wish all of you living in the Northern hemisphere to enjoy Nature revival, and those living in the Southern hemisphere to profit from the wonderful colours of the start of Autumn.



Dr. Patrick Navard
Coordinator of EPNOE
Centre for Material Forming
Sophia-Antipolis
(France)

news

▶ Forthcoming events



EPNOE-BIC and STEP meetings

The second mid-year meeting of STEP-ITN will be held on 29-31 March 2010 at Unilever R&D Vlaardingen, Netherlands, followed by the next EPNOE Business and Industry Club (BIC) meeting that will take place on 31 March-01 April 2010 at the same location.

11th EWLP in Hamburg

The 11th European Workshop on Lignocelluloses and Pulp (EWLP) will take place in Hamburg, Germany, on August 16-19, 2010. EWLP is a conference series which takes place every second year and which was originally started 1990 in Hamburg, Germany. The 10th EWLP, recently organised in Stockholm, attracted 230 participants from 26 countries. More information: <http://www.ewlp-2010.org>. Contact of the conference secretariat: info@ewlp-2010.org.

Next COST meeting

The next meeting of COST FP0901 (Analytical Methods for Biorefineries) will be organised in Hamburg, Germany, 19-21 August 2010, right after the 11th EWLP. The topic of the meeting will be "Analytical methods for non-wood raw materials and their products and processes". More information on the submission of abstracts and on the application for Short Term Scientific Missions for younger researchers: www.abo.fi/costfp0901.

▶ Members' info



Biobased Performance Materials

The new Biobased Performance Materials research program, headed by Wageningen UR Food & Biobased Research, will invest € 11 million into projects to make biomaterials that are at

least as good and as affordable as crude oil-based products, both improving existing biomaterials and developing new biopolymers. In the program thirty-four companies and four knowledge institutions are working together.

New NMR spectrometer in BOKU university

A new 600 MHz NMR spectrometer will be installed in April 2010 at the Department of Chemistry of BOKU university in Vienna, Austria. The instrument will serve as analytical core facility in structural work related to complex oligo- and polysaccharides, peptides, lipids and plant-derived natural products.



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Appointment

Bodo Saake, former Professor at the Federal Research Institute for Rural Areas, Forestry and Fisheries in Hamburg (Germany), received his appointment as Chair of Chemical Wood Technology (Hamburg University) on February 25, 2010.

New position

Martin Zenker disputed his PhD on February 18, 2010, on the topic of "By-products in dissolving pulps and changes in their composition within the production process of cellulose acetate and filter tow". He is now working as a process engineer at the company Zellstoff Stendal GmbH in Arnedberg, Germany.

Visiting scientist

Prof. Stephen Harding (University of Nottingham, UK) joined the Friedrich Schiller University of Jena as visiting scientist in the frame of the Marie Curie Initial Training Network "Shaping and Transformation in the Engineering of Polysaccharides" (STEP-ITN).

Appointment

Dr Roger Ibbett has been appointed to the Division of Food Sciences University of Nottingham to work on processing of lingo cellulose wastes for biofuels. Roger has had over 20 years experience in polysaccharides, which has included recent fundamental studies on the properties, chemistry and characterisation of regenerated cellulosic fibres.

Research Fellowship

Prof. Carlos Martin Medina from the University of Mantanzas/Cuba will start to work from April 1st at the vTI Institute of Wood Technology and Wood Biology, Hamburg. He received the prestigious 3 years Georg Forster Research Fellowship for Postdoctoral Researchers from the Alexander von Humboldt Foundation. He will work on a biorefinery concept for sugar cane bagasse.

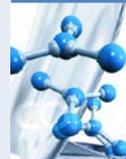
New Diploma student

Thomas Elschner, "Polysaccharide nanoparticles based on dextran carbonates", supervised by Prof. Thomas Heinze, at the University of Jena, Germany.

New PhD students

- Torstan Jordan, "Hotmelt-type adhesives as matrix for photo-switchable dyes", supervised by Prof. Thomas Heinze, at the University of Jena, Germany.
- Yvonne Jüttke, "Conversion of agriculture waste products into cellulose products of industrial significance", supervised by Prof. Thomas Heinze, University of Jena, Germany.
- Ionela Oanea, "Hydrogels with biomedical applications", supervised by Dr Valeria Harabagiu, Petru Poni Institute, Romania.
- M. Phil. Uttam Chandra Paul, "Modification of physical performance of regenerated cellulose substrates by chemical and physical processes", joined the group of Prof. Bechtold in the frame of the STEP Initial Training Network, at the University of Innsbruck.
- M. Sc. Hossam El Sayed Emam, "Chemical modification and characterization of polysaccharide based material", joined the group of prof. Bechtold in the frame of the STEP Initial Training Network, at the University of Innsbruck.

Forthcoming articles



Polysaccharide blend fibres shaped from NaOH, N-methylmorpholine-N-oxide and 1-Ethyl-3-methylimidazolium acetate ; *F. Wendler, F. Meister, D. Wawro, E. Wesolowska, D. Ciechanska, B. Saake, J. Puls, N. Le Moigne, P. Navard* - *Fibres&Textiles in Eastern Europe*

Biosynthesis of Modified Bacterial Cellulose in Tubular Form ; *D. Ciechanska, J. Wietecha, J. Kazimierzczak, D. Kazmierczak* - *Fibres&Textiles in Eastern Europe*

Biological studies and implementation of modified polyester vascular prosthesis ; *A. Niekraszewicz, M. Kucharska, I. Kardas, D. Ciechanska* - *Fibres&Textiles in Eastern Europe*

Solution states of cellulose in selected direct dissolution agents; *B. Kosan, K. Schwikal, F. Meister* - *Cellulose*

Determination of heavy metals in activated charcoals and carbon black using inductively coupled plasma optical emission spectrometry and direct solid sampling high-resolution continuum source graphite furnace; *F.G. Lepri, D.L.G. Borges, R.G.O. Araujo, B. Welz, F. Wendler, M. Krieg, H. Becker* - *AAS. Talanta*

Trace element status of activated charcoals and carbon black: Influence on thermal stability of modified Lyocell solution; *F. Wendler, F.G. Lepri, D.L.G. Borges, R.G.O. Araujo, B. Welz, F. Meister* - *J. Appl. Polym. Sci.*

Aspects of the Interaction of Native and Synthetic Polymers with Direct Dissolving Liquids; *B. Kosan, K. Schwikal, S. Hesse-Ertelt, A. Nechwal, F. Hermanutz, F. Meister* - *ACS Symposium Series*

Study on Synthesis and NMR Characterization of 2,3-O-hydroxyethyl Cellulose Depending on Synthesis Conditions; *K. Petzold-Welcke, M. Kötteritzsch, D. Fenn, A. Koschella, Th. Heinze* - *Macromolecular Symposia*

Cellulose Solvents: For Analysis, Shaping and Chemical Modification; Editor(s): *T.F. Liebert, T.J. Heinze, and K.J. Edgar*, Volume 1033; Publication Date (Web): February 23, 2010

Individual swollen starch granules under mechanical stress: evidence of deformation and volume loss; *M. Desse, D. Fraiseau, J. Mitchell, T. Budtova* - *Soft Matter*

On the specific behaviour of native cellulose fibers upon dissolution; *N. Le Moigne, P. Navard* - *ACS series*



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Zoom on EPNOE Partner's research

New biorefinery concept can meliorate all wood components

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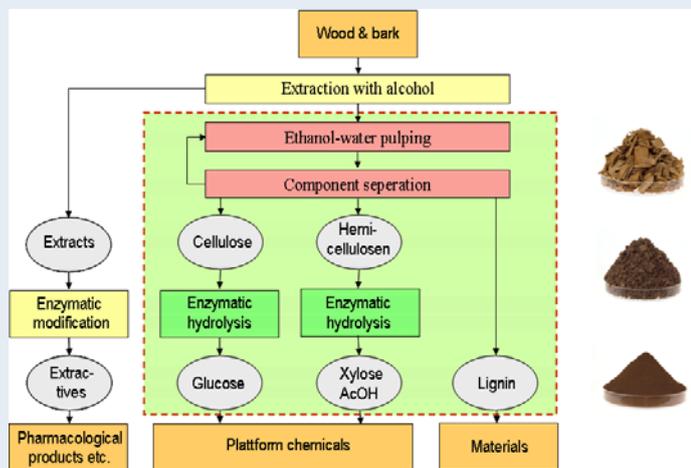
Since 2007 vTI - Institute of Wood Technology and Wood Biology in Hamburg together with partners from academia and industry successfully developed and evaluated a lignocellulose biorefinery in the laboratory scale.

Hardwoods like beech and poplar can be processed in such a way that cellulose, hemicelluloses and lignin are separated from each other.

This procedure opens new possibilities for the use of hemicelluloses and lignin besides of cellulose. Chemical intermediates as well as adhesives for derived timber products, polyurethane and carbon fibres can be obtained from the recovered fractions.

A first estimation for upscaling the process came to the conclusion that the proven and tested concept of a lignocellulose biorefinery could be economically realized with an annual capacity of 400.000 t hardwood, provided that the lignin fraction can be used for the manufacture of products which have been conventionally based on crude oil.

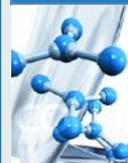
As an intermediate step a pilot plant has been planned in the frame of a follow-up project for processing of around 1.5 t wood chips per week. The new project as well as the completed one is supported by the German National Agency for Renewable Resources.



Dr Juergen Puls, vTI-Institute for Wood Technology and Wood Biology, Germany.

news (continued)

► Forthcoming articles



Delivery of fullerene-containing complexes via microgel swelling and shear-induced release
E. Tarabukina, Z. Zoolshoev, E. Melenevskaya, T. Budtova - International Journal of Pharmaceutics

Comparison of solution-state properties of cellulose dissolved in NaOH/water and in ionic liquid (EMIMAc); *T. Budtova, M. Egal, R. Gavillon, M. Gericke, T. Heinze, T. Liebert, C. Roy, K. Schluffer, P. Navard* - ACS book series, volume 1033 «Cellulose Solvents: For Analysis, Shaping and Chemical Modification», Chapter 10, 2010

Swelling and dissolution mechanism of lyocell fiber in aqueous alkaline solution containing ferric tartaric acid complex; *H. Vu-Manh, H.B. Öztürk, T. Bechtold* - Cellulose

Attenuated total reflectance Fourier-transform Infrared spectroscopy analysis of crystallinity changes in lyocell following continuous treatment with sodium hydroxide; *J. Siroky, R.S. Blackburn, T. Bechtold, J. Taylor, P. White* - Cellulose

Non persistent nitroxyl radicals as potential mediators for oxidation of regenerated cellulose fibers; *G. Biliuta, L. Fras, S. Strnad, S. Coseri* - Cellulose

Protonation behavior of 6-deoxy-6-(aminoethyl)amino cellulose: A potentiometric titration study; *L. Fras Zemljič, D. Čakara, N. Michaelis, T. Heinze, K. Stana Kleinschek* - Cellulose

Structural changes and alkaline solubility of wood cellulose fibers after enzymatic peeling treatment; *N. Le Moigne, K. Jardeby et P. Navard* - Carbohydrate Polymers

Dissolution mechanisms of wood cellulose fibers in NaOH-water; *N. Le Moigne et P. Navard* - Cellulose

Restricted dissolution and derivatization capacities of cellulose fibres under uniaxial elongational stress; *N. Le Moigne, M. Spinu, T. Heinze et P. Navard* - Polymer

Contraction and rotation and contraction of native and regenerated cellulose fibres upon swelling and dissolution: the role of stress unbalance; *N. Le Moigne, J. Bikard et P. Navard* - Cellulose



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EPNOE partners' research Polysaccharides from microalgae

It has become increasingly clear that continued reliance on fossil fuel energy resources is unsustainable, owing to both depleting world reserves and the greenhouse gas emissions associated with their use. Therefore, there is intensive research initiatives aimed at developing alternative renewable and potentially carbon neutral feedstocks for the chemical, material and energy-related industries.

The challenge is not only to substitute limited fossil resources with undepletable renewable resources but also to do this with feedstocks having a very high productivity and requiring a minimum of arable land to avoid competition with food production and destruction of biodiversity.

Based on current knowledge and technology projections, advanced chemicals and biofuels specifically derived from microalgae are considered to be a technically viable alternative energy resource that is devoid of the major drawbacks associated with terrestrial feedstock sources.

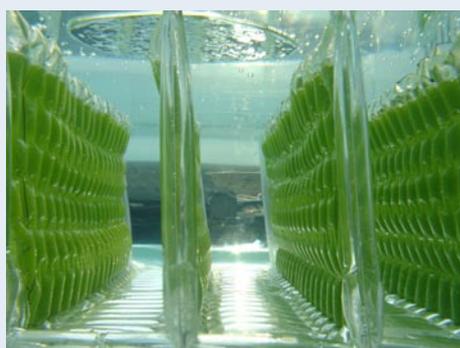


Fig 1. Proviron Reactor (ProviAPT)

Despite its inherent potential as a resource for bio-fuels and bulk chemicals many challenges remain; the cost price for production needs to be a factor ten reduced, the scale of production needs to be increased significantly and a suitable biorefinery concept for microalgae will be needed in order to optimize profit.

The introduction of this new technology in the fuel market, which is its present main driver, will imply a large production of the remaining cellular components, such as polysaccharides (PS) that need to be valorized.

The research on PS from microalgae and its applications in the chemical, material and energy industries is still weakly explored.

Two main PS complexes can be found in microalgae; extracellular PS that can either dissolve in the medium (facilitating extraction) or remain bound to the cell-wall and the intracellular PS.

To the present, most of the research has been focused on the characterization of extracellular PS dissolved in the medium of only a few microalgae strains (e.g. *Porphyridium* and *Botryococcus*).



Fig 2. Chlamydomonas

Research on the application of the PS as well as the characterization of the PS composition of more microalgae strains, with potential to be used as a feedstock for biofuels, is mandatory to establish a biorefinery approach for microalgae biomass and therefore facilitate the implementation of this technology in the near future.

Dr Maria Barbosa, Wageningen University, The Netherlands



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EPNOE partners' projects

Industrial Chair in Bioplastics

The Industrial Chair in Bioplastics was inaugurated in Cemef/MINES ParisTech laboratories in Sophia-Antipolis, France, on the 12th of February 2010. A work-shop entitled «Bioplastics : scientific advances and industrial perspectives » was organised at this occasion.

The Industrial Chair in Bioplastics started at the end of 2008. It is supported by five French companies: Arkema, L'Oreal, Nestle, PSA and Schenider Electric. All partners are strongly involved in the sustainable development: reduction in environmental impact, replacement of petrol-based polymers by bioplastics and use of recycled materials. The overall goal of the Chair is to develop and study biomass-based materials with long life time.

All partners are strongly involved in the sustainable development: reduction in environmental impact, replacement of petrol-based polymers by bioplastics and use of recycled materials. The overall goal of the Chair is to develop and study biomass-based materials with long life time.

During the work-shop three examples were given to illustrate the work of CEMEF in the area of new biomass-based materials and their processing : preparation of new highly porous and light cellulose material, Aerocellulose (Tatiana Budtova); advances in cellulose dissolution (Patrick Navard) and some specific aspects in the processing of starches (Bruno Vergnes).



Fig 2. Some of the students working for the Chair

Four PhD topics started since 2008: two on composites (with natural fibers and lignin-based) and two on mixtures (PLA/PHA and polyolefin/cellulose derivatives). Two more topics are open to start in October 2010. PhD students are accompanied by trainees.

For more information please see: <http://www.chaire-bioplastiques.cemef.mines-paritech.fr>

Dr. Tatiana Budtova, Cemef - MINES Paristech - CNRS



Fig 1. Tatiana Budtova and Yvan Chastel, director of Cemef

The industrial partners explained their expectations towards bioplastics, in correlation with the targeted applications.

The work-shop was followed by the official inauguration with the representatives from Mines ParisTech administration, partners' companies and local officials.



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BIC Members' research

Lubrication Fundamentals of METHOCEL™ Cellulose Ethers for Ceramic Extrusion

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Dow Wolff Cellulosics (DWC) is actively researching lubrication fundamentals of cellulose ethers in extruded ceramic honeycombs. The partitioning of methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) between the liquid and solid phases of ceramic pastes affects lubricity and subsequently extrusion pressure and wet green strength. This paper illustrates the first findings using cordierite precursor and commercially available METHOCEL™ Cellulose Ethers.



Methylcellulose clearly shows higher extrusion pressure which was accompanied by excellent wet green strength. Wet green strength was measured by 4-point bend testing of freshly extruded bars. Although the wet part has a very small elastic range, it is sufficient to calculate the modulus.

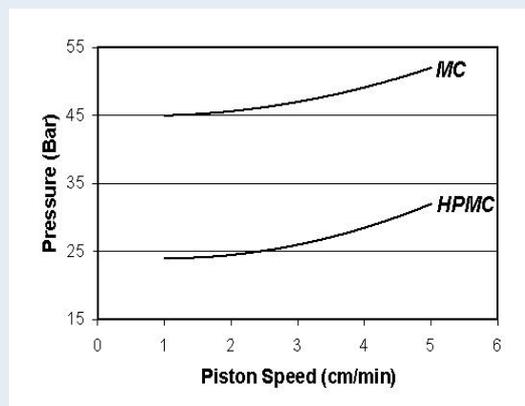
The average modulus of methylcellulose pastes was 230% of that for HPMC pastes. Solutions of methylcellulose also show higher surface tension due to the polymers lack of surface activity. Methylcellulose gave a higher extraction recovery at 90% while HPMC gave a much lower recovery at 69%.

The adsorption of METHOCEL™ polymers onto cordierite is primarily physical but there is an additional chemical adsorption component with the introduction of the hydroxypropyl functionality. Contact angle measurements of dilute METHOCEL™ solutions on cordierite precursor demonstrate the relationship between surface tension, surface activity, and substrate wetting.

Cordierite precursor has a strong affinity for water as demonstrated through low contact angles and excellent surface wetting. Higher contact angles were seen in the HPMC polymer which strongly disrupts the water-cordierite interaction. Through these studies we are deciphering the behavior of various cellulose ether chemistries to develop new products with excellent wet green strength at lower extrusion pressures.

Jason Folkenroth, Michael Baumann, Roland Bayer, Dow Wolff Cellulosics, TS&D
Grit Grote, Dow Wolff Cellulosics, R&D
Steve Lakso, Robert Sammler, Dow Chemical, Core R&D
Yongfu Li, Dow Chemical, Analytical Sciences

Cordierite pastes of methylcellulose and comparable hydroxypropyl methylcellulose were prepared, extruded, and the wet green strength measured. To better understand the dramatic performance differences, the polymer interaction with the inorganic particles was explored through contact angle (surface wetting) and surface tension measurements. The polymer dissolution-adsorption partitioning in the pastes were determined by extracting the polymer with cold aqueous solutions and analyzing the supernatant by size-exclusion chromatography. As a surrogate for lubrication, pressure drop (figure below) was monitored during extrusion at various speeds.



Plot of pressure drop vs. piston speed of the ram extruder. Note the dramatically higher pressure for the paste prepared from methylcellulose.