N°17 - MAY 2011

European Polysaccharide Network Of Excellence



"Nature makes polysaccharides, EPNOE turns them into products"

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editorial

The European Commission which helped the European polysaccharide community to establish EPNOE in 2005 launched a second call for proposals in July 2010 targeted to existing networks, with the objective of helping them to develop in a durable manner, ensuring a financial viability in the long term.

The EPNOE community submitted a proposal in February 2011, called **EPNOE CSA**. It has three main objectives, expanding from the initial focus on Materials to (1) Food and (2) Health and (3) establishing an innovation strategy, increasing industrial participation and organizing knowledge transfer to SME's.

We are very happy to be selected among the happy five networks that will be funded, among thirteen proposals. We are now in the process of negotiating the contract with the European Commission. The next EPNOE newsletter will describe in details the various actions that will be engaged to expand the scope of EPNOE and bring EPNOE closer to industry.

The present Newsletter is focused on **innovation**, source of competitiveness of industry. You will find inside several innovations that were born in EPNOE member's laboratories, both academic and industrial. The sixteen academic and research members of EPNOE are all engaged in collaborative research with industry where the aims are to increase the understanding of phenomena and invent new concepts or products. In addition, they are all involved in education actions that promote inter-disciplinarity.

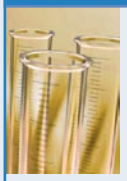
I wish to remind all our readers that the **Second EPNOE Conference will take place in Wageningen**, the Netherlands from 29 August to 2 September 2011. All information is available at http://www.vlaggraduateschool.nl/epnoe2011/.

Please note the organisation of two other events:
- **Pre-conference course «Tools in Polysaccharide Engineering»** for young researchers and professionals from industry on Sunday August 28 in Wageningen.
- **Satellite meeting «Stability and Degradation of Complex Carbohydrate Structures: Mechanisms and Measurement»,** organised by the Royal Society of Chemistry, September 5th, 2011, London, UK (http://www.nottingham.ac.uk/ncmh/RSC-London-2011/index.html).

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

news

Past events



Intensive Course

Åbo Akademi provided an intensive course «Cellulose Technology» on May 11th-13th 2011, on the topics of basic chemistry of cellulose, various analytical tools for solid cellulose and cellulose solutions as well as on the technology for innovative products and industrial applications. Next course will be provided on spring 2012.

Forthcoming events

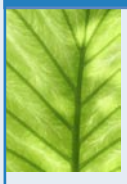
International Advanced Course

From 31 October to 3 November 2011 will be held the 4th edition of the International Advanced Course "Food and Biorefinery Enzymology" in Wageningen, The Netherlands.
Target group: University graduates in food science and bioprocess engineering (PhD students, participants from industry and research centres).
More info: http://www.vlaggraduateschool.nl/courses/food-enzym.htm
Contact: chantal.doeswijk@wur.nl

STEP Meeting on Polysaccharide

The third end-year meeting of the Marie Curie Initial Training Network (STEP) will be held on September 20-23, 2011, at the University of Maribor, Slovenia. The meeting will include research presentations, and lectures from eminent scientists on fundamental topics. You are invited to present your research in lectures or posters. There is no participation fee. More information on the website:
http://www.stepitn.eu/?page_id=1841

Members' info



PhD Defense

Li Shen from Utrecht University successfully defended her PhD on 16 March 2011. Title of her PhD: "Bio-based and recycled polymers for cleaner production - An assessment of plastics and fibres". The supervisors were: Prof. Ernst Worrell and Dr. Martin Patel. The thesis can be downloaded from: http://nws.chem.uu.nl/nws.html

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Zoom on EPNOE partner's research

Extracting biopolymers with new biotechnological methods

In the LIGNOS joint research project, three partners from Potsdam - the University of Potsdam, the Fraunhofer Institute for Applied Polymer Research IAP and aevotis GmbH – are focusing on the sustainable processing of crops and wood renewable materials. Together, they want to find ways of recovering the biopolymers contained in plants and waste materials from agriculture and forestry and in biomass-containing waste materials from established production processes in food production, the chemicals industry and fuel production. The partners want to put into practice new concepts for innovations in biochemical process technology. The biopolymers are to be used in three areas in particular:

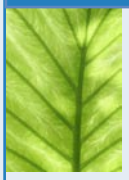
1. The development of new materials such as bio-based plastics and composite materials, films, fibres, non-wovens
2. Life-science products in pharmaceutics, cosmetics and health care
3. Special products for a wide variety of non-food applications, including additives in the areas of building materials, paper production and detergent manufacturing.

As part of a kick-off event on 17 March 2011, the three research partners, supported by the pearls Potsdam Research Network, presented the content and aims of their project. The molecular biology working group of the University of Potsdam will develop new enzyme systems that enable the digestion of lignocelluloses. These enzymes will then be optimised so that the constituents can be separated out of various lignocellulosis resources. In order to provide sufficient quantities of enzymes, the biotechnological processes for producing them will be upscaled to small-scale production. At Fraunhofer IAP, these enzymes will be used to extract cellulose, hemicellulose and lignin. These will be the basic materials for new bio-based products.

LIGNOS Team: Dr. V. Landschütze (aevotis GmbH), Dr. J. Krebs (pearls), Dr. W. Vorwerg (Fraunhofer IAP), Prof. B. Müller-Röber (UP Potsdam)

news (continued)

Members' info



New staff and students

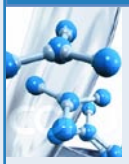
- Jasmina Obradovic, new researcher in Åbo Akademi is working on the topic of cellulose bioplastics and is supervised by Pedro Fardim.

- Haolin Lu, new MSc student in Åbo Akademi, supervised by Prof. Stefan Willför and Ms Ann-Sofie Leppänen, tentative title «Sorption of hemicelluloses to cellulosic surfaces».

- Martin Gericke, new post-doc in Åbo Akademi, is working on the topic of Functional cellulosic beads.

- Dr. Ludmila C. Fidale joined the group of Thomas Heinze at the university of Jena as postdoctoral fellow in the Marie Curie Initial Training Network «Shaping and Transformation in the Engineering of Polysaccharides» (STEP).

Forthcoming articles



Surface chemistry of vessel elements by FE-SEM, µ-XPS and ToF-SIMS; *E. Orblin, V. Eta and P. Fardim* - Holzforschung, published online 14/03/2011.

Interactions between cationic polyelectrolyte and pulp fines; *E. Orblin and P. Fardim* - BioResources 6(3), 2340-2355.

Enhancement of cellulose dissolution in water-based solvent via ethanol-hydrochloric acid pretreatment; *J. Trygg and P. Fardim* - Cellulose. DOI: 10.1007/s10570-011-9550-y.

A «Click-Chemistry» Approach to Cellulose-based Hydrogels; *A. Koschella, M. Hartlieb, Th. Heinze* - Carbohydrate Polymers 2011,DOI: 10.1016/j.carbpol.2011.04.031

Expedient, accurate methods for the determination of the degree of substitution of cellulose carboxylic esters: Application of Uv-vis spectroscopy (dye solvatochromism) and FTIR; *R. Casarano, L. C. Fidale, C. M. Lucheti, Th. Heinze, O. A. El Seoud* - Carbohydrate Polymers 2011 DOI: 0.1016/j.carbpol.2010.09.035

Homogeneous Sulfation of Xylan from Different Sources; *S. Daus, K. Petzold-Welcke, M. Kötteritzsch, A. Baumgaertel, U. S. Schubert, Th. Heinze* - Macromolecular Materials and Engineering 2011, DOI: 10.1002/mame.201000390

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Zoom on EPNOE Partner's research

Payen Award for Professor Thomas Heinze

During the 241th National Meeting of the American Chemical Society in Anaheim, CA, which was held from March 27-31, Thomas Heinze from the Friedrich Schiller University in Jena was honoured with the Anselme Payen Award.

The Anselme Payen Award is an annual prize presented by the American Chemical Society's Cellulose and Renewable Materials Division to honour «outstanding professional contributions to the science and chemical technology of cellulose and its allied products».

Thomas got this price because of his work towards the chemical modification of polysaccharides especially cellulose and the development of analytical tools for cellulose derivatives. The award ceremony included a formal dinner and a two and a half day symposium during which most of the leading scientists of cellulose research gave talks (some of the talks were recorded and can be found on the ACS homepage).

EPNOE 2011 Conference

The 2nd International Polysaccharide Conference "Polysaccharides as Source of Advanced and Sustainable Materials" EPNOE 2011, to be held in Wageningen, the Netherlands, between 29 August – 2 September 2011, has attracted many contributions from the carbohydrate community all over the world. Over 200 abstracts from 32 countries have been submitted. With renowned plenary and keynote speakers and many outstanding contributions from academia and industry, the conference will offer the latest developments in the science and the application of polysaccharides. Special emphasis is on innovation, with a dedicated session "Knowledge for Innovation" and a panel discussion.

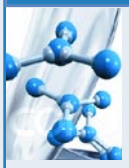
More information: www.vlaggraduateschool.nl/EPNOE2011

Contact: Mrs. Eva Oudshoorn (eva.oudshoorn@wur.nl)

Deadline early registration: June 30, 2011

news (continued)

Forthcoming articles



The dissolution of cellulose in NaOH-based aqueous system by two-step process; *H. Qi, Q. Yang, L. Zhang, T. Liebert, Th. Heinze* - Cellulose 2011, DOI: 10.1007/s10570-010-9477-8

Tailored Media for Homogeneous Cellulose Chemistry: Ionic Liquid/Co-Solvent Mixtures; *T. Heinze, M. Gericke, O. A. El Seoud, T. Liebert* - Macromolecular Materials and Engineering 2010, DOI: 10.1002/mame.201000330.

Synthesis of rare sugars by hydrolysis of hemicelluloses; *P. Mäki-Arvela, T. Salmi, S. Willför, B. Holmbom, D.Y. Murzin* – A review. Chem. Rev.

Carboxymethylated spruce galactoglucomannans: preparation, characterization, dispersion stability, water/oil emulsion stability, and sorption on cellulose surfaces; *C. Xu, C.Eckerman, A. Smeds, M. Reunanen, P.C. Eklund, R. Sjöholm, S. Willför* - Nord. Pulp Pap. J.

Aerocellulose from cellulose-ionic liquid solutions: preparation, properties and comparison with cellulose-NaOH and cellulose-NMMO routes; *R.Sescousse, R.Gavillon, T.Budtova* - Carbohydrate Polymers, 83, 1766–1774.

Wet and dry highly porous cellulose beads from cellulose-NaOH-water solutions: influence of the preparation conditions on beads shape and encapsulation of inorganic particles; *R. Sescousse, R.Gavillon, T. Budtova* - Journal of Materials Science, 46, 759-765.

Synthesis and properties of platinum nanocatalyst supported on cellulose-based carbon aerogel for applications in PEMFCs; *J. Rooke, C. De Matos Passos, M. Chatenet, R. Sescousse, T. Budtova, S. Berthon-Fabry, R. Mosdale, F. Maillard* - Journal of The Electrochemical Society.

Influence of ZnO on the properties of dilute and semi-dilute cellulose-NaOH-water solutions; *W. Liu, T. Budtova, P. Navard* - Cellulose.

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Special focus on Innovation

Photo-switchable laminated glass composites based on starch

A new method for a very efficient and by-product free esterification of starch was developed at the University of Jena in the group of Prof. Th. Heinze. Long chain starch esters can be prepared by a new patented method using molten imidazole as solvent for the biopolymer. The advantage is the simplicity of the reaction mixture. Imidazole is acting not only as solvent, but also as reagent and base. The reaction succeeds via the imidazolide, which is formed in situ with an acid chloride.

The high quality of the products prepared is responsible for the defined melting. Colorless and completely transparent melts of the starch esters are obtained without any additives in the range of 40 to 255°C. The melting properties can be adjusted by the type of ester moiety and the amount of ester functions introduced. Upon cooling the melts form homogeneous, stable and transparent films on different supports including glass, metal and synthetic polymers. Due to this behavior these esters are the material of choice as bio-based hot melt adhesives in a variety of applications, e.g. in laminated glass.

Besides its role as adhesive the starch ester can also be the matrix for the incorporation of other functional materials. In the frame of a cooperative project the use of such starch esters for the manufacture of photo-switchable laminated glass was investigated (BMBF/AiF project KF 2258001AK9). Among the partners in the project are two Thuringian institutions (Innovent e.V. Jena, OMPG Rudolstadt) and two companies. The first prototype of such a responsive laminated glass is now available. Upon irradiation with UV- or sun light the glass composite turns from colorless to dark blue within seconds and back to colorless when the irradiation stops.

Tim Liebert, Thomas Heinze
University of Jena, Germany

Zoom on EPNOE Partner's research

Nanostructured biomass-based materials for thermal insulation

A new project on the development of nanostructured biomass-based materials for thermal insulation started a year ago in France. The goal of the project is to propose aerogel-like materials – alternatives to silica aerogels that are presently the best thermal insulating materials but have bad mechanical performance. New mesoporous aerogel-like materials will be based on cellulose and cellulose esters as well as their various hybrids with silica.

The materials are developed in two laboratories belonging to MINES ParisTech: Centre for Energy and Processing (CEP, coordinator) and Centre for Materials Forming (CEMEF). The consortium consists of Montpellier university (morphology and structure characterisation), CEA (supercritical solvent extraction), INSA Lyon (thermal modelling), CSTB (thermo-physical properties), NEOTIM (thermal conductivity measurements) and EDF (hydro-thermo analysis).

The work is supported by French National Research Agency (ANR), project « Nanocel » ANR-09-HABISOL-010 and labelled by the competitiveness clusters «Capenergies", "Tennerdis" and "Derbi».

Tatiana Budtova
Center for Material Forming (CEMEF), MINES ParisTech / CNRS, Sophia Antipolis

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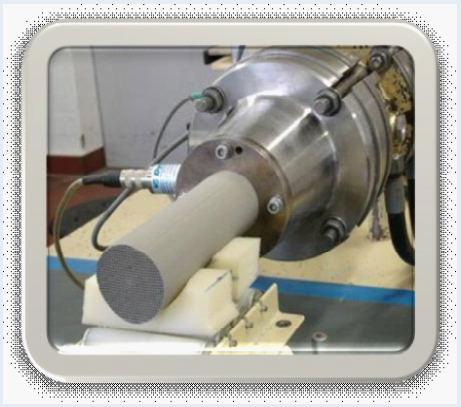
Special focus on Innovation

A New Class of Methylcellulose for Ceramic Extrusion at Elevated Temperatures with Improved Shape Retention

Ceramic powders are commonly mixed with cellulose ethers, water, and other ingredients to form extrudable pastes. In ceramic paste formulations, cellulose ethers act as important sacrificial binders which strongly affect extrusion and extrudate properties. Commonly used cellulose ethers are methylcellulose (MC), hydroxypropyl methylcellulose (HPMC), and hydroxyethyl methylcellulose (HEMC). Using methylcellulose like METHOCELTM A4M in the extrusion of ceramic profiles like autohoneycombs yields extrudates with excellent shape retention properties immediately after emerging from the extruder die. This is due to the high wet green modulus and wet green strength of the ceramic paste.



On the other hand, currently used methylcelluloses only allow a very narrow temperature window for the extrusion process due to the low gelation temperature of this component in the paste formulation. The gelation point of the paste depends on the binder dosage and can be at or near room temperature. An extrusion that is performed close to the gelation temperature leads to decreased extrudability and higher extrusion pressures reducing throughput.

The incorporation of binary cellulose ethers, such as HPMC or HEMC, allows extrusion at much higher temperatures, but results in weaker shape retention than MC based formulations. Dow Wolff Cellulosics has a new class of methylcellulose which allows higher temperature extrusion and improved shape retention. The significant improvement of these properties was obtained by adjusting the amount of methyl group substituents on the cellulose chain to a value which has not been commercially available until now. Currently marketed methylcelluloses typically have a degree of substitution (DS) ranging from 1.6 - 1.9 while the DS of the newly developed products is in the range of 1.3 - 1.6. Table 1 illustrates the observed gelation temperatures in a ceramic paste containing 2 parts MC and 100 parts cordierite. The combination of lower extrusion pressure, increased shape retention, and higher operating temperatures enables increased production rates.

Table 1.

Sample	D.S. (Me)	Gelation Temp. (°C)
METHOCEL™ A4M	1.8	43
MC Sample 1	1.5	47
MC Sample 2	1.4	61

Roland Bayer*, Jason Folkenroth**, Grit Grote*

* Dow Wolff Cellulosics GmbH, August-Wolff-Str. 13, 29699 Bomlitz
** Dow Wolff Cellulosics, 1691 N. Swede Rd., Larkin Lab, Midland, MI 48674

Special focus on Innovation

Development of a Manufacturing Method for Surgical Meshes Modified by Chitosan

Hernias are a very serious social problem, statistically appearing in 2% of the human population. They can be healed by surgical methods, and special surgical meshes are used in the so-called non-tension method applied in 50%-70% of hernia cases. These meshes are mostly manufactured of non-resorbable synthetic fibres. An essential disadvantage of surgical procedures, which use non-resorbable implants, is the patients' discomfort which appears after longer time-periods from the implantation, connected with the stiffening of the implant; this latter is caused by streaking the implant with fibrous tissue. This phenomenon can even lead to problems with an inadequate blood supply to the organs lying in the implant's surroundings, as well as to complications of the stoma or adhesion type in the case of an implant's direct contact with inner organs. Applying surgical meshes, which would be partially resorbable, would allow us to eliminate the majority of the disadvantages caused by meshes manufactured of non-resorbable polymers.

The aim of the research work was to develop a method for manufacturing modern, partially resorbable surgical meshes or partially resorbable surgical implants dedicated to protecting hernias. The investigations were conducted within the two following variants:

- Variant I consisted in the use of a knitting technique. Two kinds of yarns were used: a resorbable multifilament chitosan thread and a non-resorbable biocompatible monofilament polypropylene thread.
- Variant II consisted in the use of a complex technique. The surface of the non-resorbable OPTOMESH^{TM} Macropore surgical mesh was covered by a microporous resorbable chitosan coating. Various useful forms of chitosan prepared at the Institute of Biopolymers and Chemical Fibres were applied for the purpose.

The modified surgical meshes were tested, after sterilisation by ethylene oxide (EO), in order to determine their physico-mechanical features and their chemical & biological purity. Further steps of the research examined the biocompatibility in respect of the cytotoxicity of the chitosan coating and the susceptibility to enzymatic degradation as well as irritating and allergenic action.

On the basis of estimating the physico-mechanical properties, and evaluating the chemical properties, as well as the chemical and biological purity, we stated that the implants of variant II with a surface weight of about 100 g/m2 are potentially optimal products for further modification, considering their better strength parameters. It was documented that the chitosan coating underwent biodegradation under the action of lysozyme, and that the biodegradation products were water-soluble. The chemical and biological purity of the prepared modified surgical meshes was tested in accredited laboratories and adequate departments of medical academies.Tests made on animals showed that the modified implants did not exert any irritating or allergenic action. The modified surgical meshes show a slight cytotoxic effect upon mouse fibroblasts caused by the chitosan in the coating itself or the used plasticizer. This is a disadvantage of the new materials, though it does not limit its application in the implants. The prepared composite surgical meshes, modified by chitosan, are candidates for commercialization. Chitosan preparations can be manufactured according to IBWCh proprietary technology and the depositing of the coating is to be made by known, simple techniques.

The work was realized due to cooperation of Institute of Biopolymers and Chemical Fibres, TRICOMED S.A., and Technical University of Lodz.

A. Niekraszewicz, M. Kucharska, D. Wawro, *M. H. Struszczyk, **K. Kopias, *A. Rogaczewska

Institute of Biopolymers and Chemical Fibres, *TRICOMED S.A., **Department of Knitting Technology and the Structure of Knitted Products Technical University of Łódź

Special focus on Innovation

Cold Soluble Bio-Polymer for Sustainable Coating

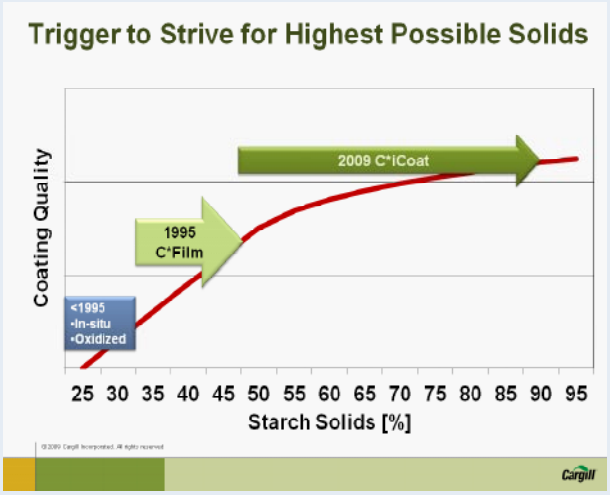
The high water content of 70-80% of starch pastes traditionally used as co-binders in paper coatings leads inevitably to a significant dilution of the solids content of coating colours when higher proportions of starch binders shall be used. A lot of negative effects of using starch as co-binder like mottling and low binding power can be attributed to this dilution effect.

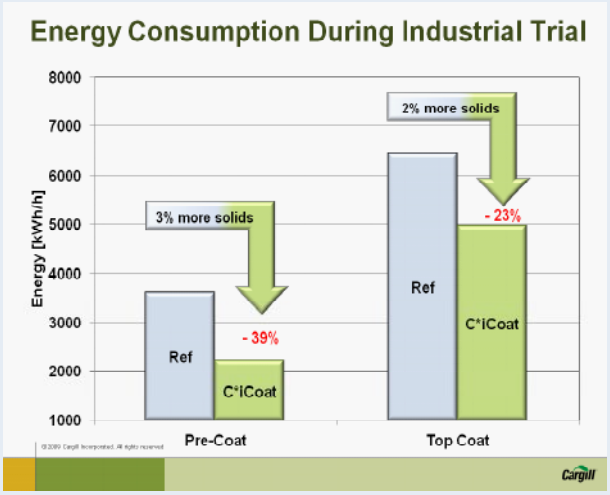
As there is consensus that higher solids of coating colours have a positive effect on the quality of coated papers we developed a range of cook-up starch that could be prepared at higher solids levels so that their pastes had a reduced water content of only 55-65%. Already with the help of these products we were able to disprove some of the old prejudices against starch binders.

However, it was obvious that in order to replace even more significant amounts of latex by a more sustainable bio-binder, this should have an even lower water content than the 50% a latex has. The recently developed C*iCoat Bio-Polymer adds only ~8% water as it can be added as a dry powder directly to the pigment slurry or coating colour. Now we thus can formulate coating colours with even higher solids contents than when using only latex.

Due to the excellent pseudoplasticity and water retention of C*iCoat coatings with solids above 70% are not theory but can indeed be applied on high speed coaters under industrial conditions. Various industrial applications have been realized in woodfree paper, LWC and coated board. Higher coating solids allow a 1:1 replacement of latex and improved paper properties at the same time. The new sustainable binder thus allows replacing more latex than before and also a part of the thickeners and FWA-carriers used. This improves the economy of a variety of pre- and top-coating formulations significantly. In addition to that the new bio-polymer also allows significant savings of drying energy that are higher than calculated based on the solids increase.

All in all C*iCoat thus allows a more sustainable coating process.





Detlev Glittenberg
Technical Director Cargill Industrial Starches

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