



European Polysaccharide
Network Of Excellence

N°18 - JULY 2011



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

editorial

Dear Reader,

In the previous Newsletter, I was writing that this issue will bear a description of the new project called EPNOE CSA sponsored by the European Commission. Unfortunately, the negotiation on its final content is not yet finished, despite the project is supposed to start in November 2011. The objectives are to add to the present activities of EPNOE a specific action aimed at developing interactions between industry and EPNOE members in all sectors and to expand EPNOE activities towards health and food related topics. This new project has four Work Packages (WP) that are reflecting these objectives: WP1 (Management), WP2 (Expanding EPNOE activities towards health-related materials and products), WP3 (Expanding EPNOE activities towards food-related materials and products) and WP4 (Increasing industrial participation and innovation).

Another activity of the last months was the preparation of an agreement with the American Chemical Society, and more specifically with its Cellulose and Renewable Materials division (<http://cell.sites.acs.org/>), in order to jointly co-organise at least two technical symposia or meetings per year, one in the USA, one in Europe. The planning for 2012 includes a common ACS-CELL/EPNOE symposium during the next ACS national meeting in San Diego (March 25-29) and the participation of ACS-CELL to Narotech-EPNOE industrial meeting in Erfurt (5-6 September). The program for 2013 includes common technical symposia in the ACS National Meeting, New Orleans, April 7 – 11 and the co-organisation of EPNOE 2013, which location will be announced during the banquet of EPNOE 2011 in Wageningen, end of this month (sorry, you have to wait a bit to know the name of the winner!!).

Looking forward to meeting you in person during the EPNOE 2011 conference in Wageningen, I send you all my best wishes.



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

news

Members' info



New diploma student

Kristin Ganske, topic "Investigations on cellulose carbonates", supervised by Prof. Heinze, University of Jena.

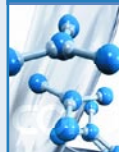
Phd Defense

Innocent Boudimbou defended his PhD on June 23rd 2011, at Cemef MINES Paristech (Sophia-Antipolis, France). Topic: Elementary mechanisms of dispersion of precipitated silica micropearls in an elastomer matrix.

New patent

Verfahren zur Verformung von Cellulosecarbammat und Produkte, die nach diesem Verfahren hergestellt worden (Process for shaping cellulose carbamates and the related products); *L.T.T. Vo, B. Široká, A.P. Manian, T. Bechtold* - Austria Patent Application A 163/2011, Priority Date 08.02.2011.

Forthcoming articles



Morphology of Polysaccharide Blend Fibers Shaped from NaOH, N-Methylmorpholine-N-oxide and 1-Ethyl-3-methylimidazolium acetate; *F. Wendler, Z. Persin, K. Stana-Kleinschek, M. Reischl, V. Ribitsch, A. Bohn, H.P. Fink, F. Meister* - Cellulose, DOI no. 10.1007/s10570-011-9559-2.

Properties of spruce sulfite pulp and birch kraft pulp after sorption of cationic birch xylan; *K. Schwikal, T. Heinze, B. Saake, J. Puls, A. Kaya, A.R. Esker* - Cellulose, Vol. 18, 727-737

What can cellobiohydrolase I+II mixture and endoglucanase of *Trichoderma reesei* strain change on lyocell fibres?; *H.B. Öztürk, A. Ehrhardt, H. Vu-Manh, T. Oksanen, B. Široká, A. Suurnakki, T. Bechtold* - Fibers and Textiles in Eastern Europe, No.5.

Surface activation of dyed fabric for cellulase treatment; *C.B. Schimper, C. Ibanescu, T. Bechtold* - Biotechnology Journal, DOI 10.1002/biot.201100002



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Special focus on Innovation

High β -glucan and protein fractions from oats using VTT's lipid removal and dry fractionation technology

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Oats are a good raw-material for healthy and functional food products due to the high content of soluble dietary fibre, mainly β -glucan, which has beneficial effects on serum cholesterol as well as on blood glucose and insulin levels. Production of high-fibre oat fractions is, however, technologically challenging due to the high lipid concentration of oats.

VTT Technological Research Centre of Finland has developed a novel dry fractionation technology to enrich the valuable compounds of oats. By defatting non-heat treated grains with supercritical CO₂, we obtained a porous matrix which was easy to mill into very fine particles and then fractionate by air classification. The main components of oats – lipids, starch, protein and cell walls – were separated into specific fractions (Fig. 1). The highest β -glucan concentration of the cell wall-enriched fraction was 34 % (Fig. 2). An oat protein concentrate with a protein concentration of 73 % was also separated. A trial with 2300 kg of whole grain oats showed that the process was industrially applicable.

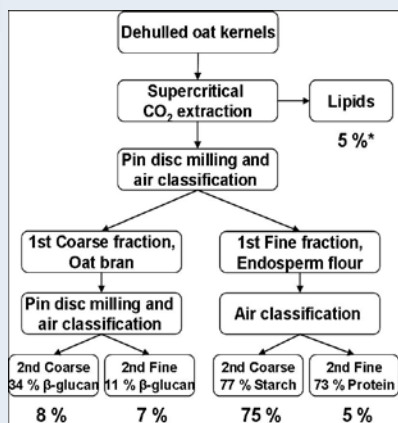


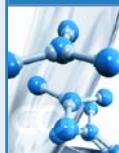
Figure 1. Process flow chart of oat dry fractionation. *Percentages show the mass yields of each fraction.

J. Sibakov, O. Myllymäki, U. Holopainen, A. Kaukovirta-Norja, V. Hietaniemi, J.-M. Pihlava, K. Poutanen, P. Lehtinen

Lipid removal enhances separation of oat grain cell wall material from starch and protein, *J. Cereal Sci.* 54 (2011) 104-109. <http://dx.doi.org/10.1016/j.jcs.2011.04.003>.

news (continued)

► Forthcoming articles



Application of ATR-FT-IR Single-Fiber Analysis for the Identification of a Foreign Polymer in Textile Matrix; *B. Široká, J. Široký, T. Bechtold* - *International Journal of Polymer Analysis and Characterization*, 16 (4), 259-268

Alkali treatment of cellulose II fibres and effect on dye sorption; *J. Široký, R.S. Blackburn, T. Bechtold, J. Taylor, P. White* - *Carbohydrate Research*, 84 (1), 292-298

Attenuated total reflectance Fourier-transform Infrared spectroscopy analysis of crystallinity changes in lyocell following continuous treatment with sodium hydroxide; *J. Široký, R. S. Blackburn, T. Bechtold, J. Taylor, P. White* - *Cellulose*, 17 (1), 103-115

The Influence of Alkali Pretreatments in Lyocell Resin Finishing - Changes in Fiber Accessibility to Crosslinker and Catalyst; *A. Jaturapiree, A.P. Manian, M. Lenninger, T. Bechtold* - *Carbohydrate Polymers*

Temperature, relative humidity, and water absorption in ski boots; *P. Hofer, M. Hasler, G. Fauland, T. Bechtold, W. Nachbauer* - *Procedia Engineering*

Synthesis and characterization of novel amino cellulose esters; *C. S. P. Zarth, A. Koschella, A. Pfeifer, S. Dorn, Th. Heinze* - *Cellulose*, DOI 10.1007/s10570-011-9557-4

Tailoring the Degree of Polymerization of Low Molecular Weight Cellulose; *M. Meiland, T. Liebert, Th. Heinze* - *Macromolecular Materials and Engineering* 2011, DOI: 10.1002/mame.201000424

Thermal studies of plant carbohydrate polymer hydrogels; *M.S. Iqbal, J. Akbar, S. Saghir, A. Karim, A. Koschella, Th. Heinze, M. Sher* - *Carbohydrate Polymers*, CARBPOL-D-11-00903R2

Investigation of the spinnability of cellulose/alkaline ferric tartrate solutions; *H. Vu-Manh, F. Wendler, H. Bahar Öztürk, T. Bechtold* - *Carbohydrate Polymers*, DOI: 10.1016/j.carbpol.2011.07.038.

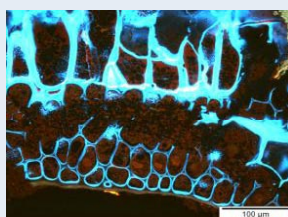


Figure 2. Microscopic picture of β -glucan enriched oat bran fraction. Acid Fuchsin / Calcofluor White staining, showing protein as red and β -glucan rich cell walls as light blue.



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Special focus on Innovation

Cellulosic fibers with a depot-function for insecticide substances

Permethrin – an insecticidal agent recommended by the WHO for textile treatments – is used to protect humans from malaria or tick-borne encephalitis, which is a serious acute central nervous system infection mostly transmitted in Europe by *Ixodes ricinus*. Impregnation of textiles with permethrin has been performed so far by dipping or spraying as well as by coating methods whereas the agent is adsorbed on the surface of the fabric. Broad usage of impregnated textiles is limited because of the high concentrations required for a sufficient biological effect and the poor laundering resistance.

Therefore, a new concept of in-situ incorporation of lipophilic substances into cellulosic fibers via the Lyocell process was developed. A stable spinning-process is a challenge when hydrophobic additives are pre-mixed with cellulose and N-methylmorpholine-N-oxide. Beside of compounds bearing insecticidal activity, also paraffin, primrose oil or panthenol can be inserted successfully. To stabilize thermodynamically incompatible phases, a mediator is used: highly dispersed nano-scaled silicic acid combined with organically modified layered silicate. Its incorporation into a cellulose skeleton overcomes the mentioned drawbacks of existing fabrics.

Fibers produced with this novel technique exhibit a sponge-like matrix of cellulose. During the spinning process, tube-like structure of lipophilic storage depots are formed. Fig. 1 shows REM images of the lipophilic, drop-shaped regions surrounded by cellulose matrix. Fiber structure and the lipophilic carrier determine the depot-effect of permethrin. The lower the melting point of the carrier is, the higher the velocity of permethrin diffusion is. This special feature ensures a high and constant release rate even after 100 washing cycles (Fig. 2).

The authors want to thank the Federal Ministry of Education and Research for their financial support (Project „NanoCell“ FKZ 13N9758).

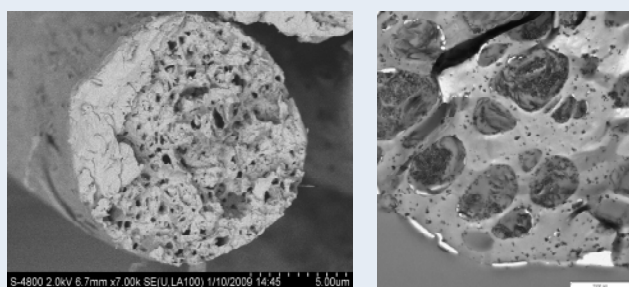


Figure 1. REM images of a Lyocell fiber (cryo-cut). Bright: cellulose, dark: lipophilic region.

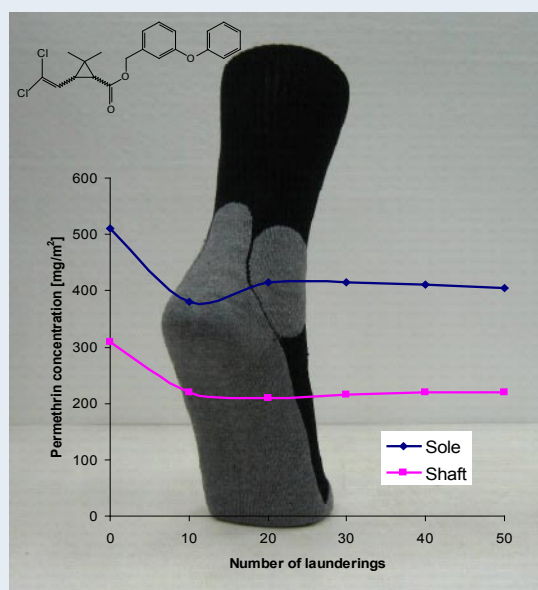


Fig. 2: Washing resistance of gym socks made with the new permethrin containing fibers

Marcus Krieg, Frank Wendler, Frank Meister
Thuringian Institute of Textile and Plastics Research, Rudolstadt, Germany



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TROMBOGUARD® - FIRST AID WOUND DRESSING

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Recently, the market of medical devices shows serious need for wound dressings for first aid and temporary traumatic wounds. Such a wound dressing should show primarily the hemostatic effect and antibacterial activity allowing protection against infection.

Tromboguard® topical wound dressing is a three-layer dressing with active layer. The active layer contains chitosan – a natural polysaccharide, sodium alginate/calcium alginate with addition of silver salt to enhance the antimicrobial effect. The dressing provides protective performance as well as is characterized by the ability to immediately stop bleeding and antibacterial activity allowing protection against infection and occurrence of secondary infection without the need for or with limited participation of antibiotics. Tromboguard® topical wound dressing is a first aid dressing

designed for the uniform services (military and homeland) and rescue.

The aim of this study was to confirm the safety and performance (in scope of multifunctionality) of Tromboguard® wound dressing in the wide range of preclinical and clinical studies.

Preclinical studies of Tromboguard® wound dressing confirmed its: high chemical and microbiological purity; absence of cytotoxicity; absence of the irritation and allergenicity; reduction in time of wound healing; and haemostatic and antibacterial mode of action.

Clinical studies of Tromboguard® wound dressing confirmed its: high hemostatic effectiveness in scope of the clinical repeatability (100% patients) and quick hemostasis (till 3 min.); high antibacterial effectiveness. Tromboguard® wound dressing protects wounds against infection till 5 days; clinical universality: mode of action of Tromboguard® wound dressing is independent on hematopexis and synergistic with blood clotting pathway; safety: Tromboguard® wound dressing indicates absence of allergenicity, adverse effects connecting with the hematology, biochemistry, urine analysis, microbiology.

The work was realized due to cooperation of Institute of Biopolymers and Chemical Fibres, TRICOMED S.A., and Institute of Security Technology “MORATEX”.

M. Kucharska 1), M. H. Struszczyk 2), A. Niekraszewicz 1), D. Ciechańska 1), E. Witczak 2), S. Tarkowska2), K. Fortuniak2), A. Gulbas-Diaz3), A. Rogaczewska3), I. Płoszaj3), A. Pluta3), T. Gąsiorowski3)

1) Institute of Biopolymer and Chemical Fibres, 2) Institute of Security Technologies “MORATEX”, 3)TRICOMED SA

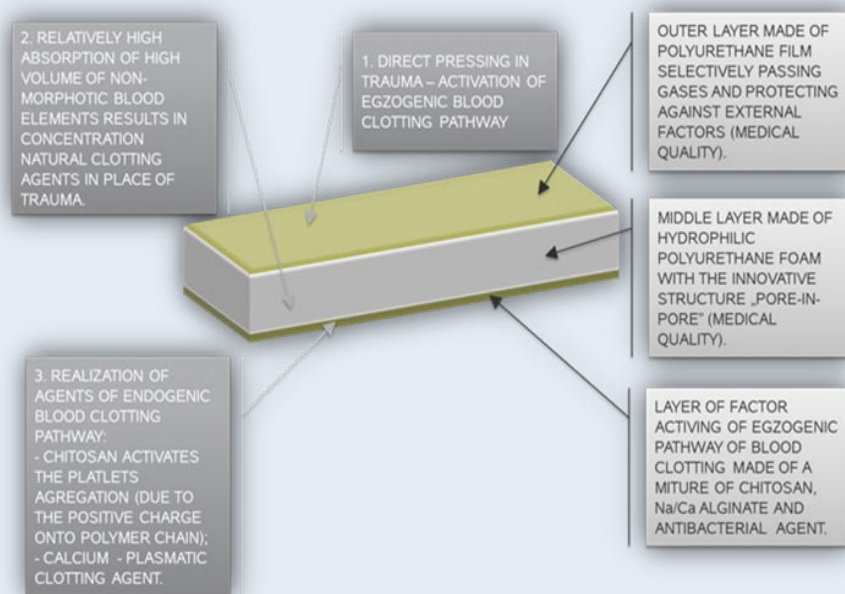


Fig. 1. Schema of Tromboguard® wound dressing design and its mode of action



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Special focus on Innovation

Novel Hemicellulose Materials Based on Wood pulps: Hydrogels

Until 1980's water hold up in personal disposable hygiene products was made with cellulose derivatives after which was developed super absorbing polymers SAP. In future biodegradable cellulose is real a choice due waste problem. Natural based hydrogels are of interest also because of nontoxic nature and biocompatibility advantageous in tissue engineering, controlled drug release, agriculture and hygiene products. E.g. forest industry sidestream xylan have hydroxyl groups in each repeating unit which can be chemically derivatized to new reactive groups. Polysaccharides have been derivatized with allyl groups for hydrogel preparation, e.g. Huijbrechts et al. (1) have modified starch with allyl glycidyl ether and Shen et al. (2) have modified carboxymethyl cellulose to obtain an allyl functionalized derivative, N-allylcarbamoymethyl cellulose.

Now we report novel xylan based hydrogels prepared in water solution by cross-linking derivatized xylans with or without N, N'-diallyldardiamides (DA). Xylan was first modified to derivatives with crosslinking allylic functionalities and different degrees of substitution. We chose bio-based aldaric acid based cross-linkers – N,N'-diallyldardiamides (DA). The hydrogels were prepared in water solution by UV induced cross-linking polymerization of derivatized xylan polymers without and with 1 or 5 wt-% of DA cross-linker. The hydrogels were examined with FT-IR showing that the DA derivatives worked successfully and conversions of DSs were 30-80 %.

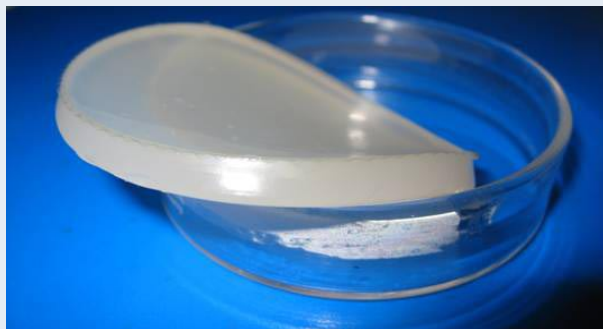


Figure 1. Hydrogel prepared from xylan derivative with 5 mass-% crosslinker.

Degree of swelling varied from 70 to 1000 % depending on the degree and type of substituents of xylan derivatives and on the amount and type of N,N'-diallyldardiamide crosslinker. SAP may absorb only 50 times its weight in a 0.9% saline solution. In the respect the novel cellulose derivatives are closer the real performance of the oil-based and non-bio-degradable counterparts.

(1) Huijbrechts, A. M. L.; Desse, M.; Budtova, T.; Franssen, M. C. R.; Visser, G. M.; Boeriu, C. G.; Sudhölter, E. J. R. *Carbohydr. Polym.* 2008, 74, 170-184.

(2) Shen, X.; Kitajyo, Y.; Duan, Q.; Narumi, A.; Kaga, H.; Kaneko, N.; Satoh, T.; Kakuchi, T. *Polym. Bull.* 2006, 56, 137-143.

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