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*"Nature makes polysaccharides, EPNOE turns them into products"* 

## editorial

ear Readers of the EPNOE Newsletter,

We are now within a few weeks from the EPNOE 2013 Conference "Polysaccharides and polysaccharide-derived products, from basic science to applications" that will take place in Nice, France, on 21-24 October 2013. EPNOE 2013 is organised by the Materials Forming Center (CEMEF/Armines) in partnership with EPNOE and the American Chemical Society.

More than 400 participants will discuss, learn, exchange knowledge and, of course, enjoy the French Riviera and Nice city beauties. There will be 236 oral presentations in four parallel sessions plus 29 plenary, key-note and invited lectures. 200 posters will be presented during the whole duration of the meeting. Such a wide participation is the clear sign of the importance and dynamism of our field, so rich in innovative science and potential applications.

More than 70 people registered to the pre-conference course on "Challenges and perspectives in making materials from polysaccharides", which will take place on Sunday 20 October 2013.

You are welcome to look at the conference website to see the program: http://epnoe2013.sciencesconf.org.

The academic, research and industrial members of EPNOE will take the opportunity of the conference to spend one day and a half on Thursday 24 and Friday 25 to brainstorm and organize R&D projects.

#### Best wishes,



**Dr. Patrick Navard** Coordinator of EPNOE Armines/Mines ParisTech/CNRS CEMEF - Centre for Material Forming Sophia-Antipolis (France)

## news

#### Member's info

New staff:



At the Friedrich Schiller University
 of Jena, Germany:

- Dr Andreas Stammwitz joined the group as coordinator of the project "Thuringian application platform for homogeneous polysaccharide chemistry";

- Denny Renner joined the group as technical assistant in the frame of a project dealing with floor tile adhesives from bipolymer mixtures;

• At the University of Natural Resources and Life Sciences, Austria:

- Vera Malinina (Mendeleyev University of Chemical Technology, Moscow), Mitsuharu Koide (Kyoto Institute of Technology, Japan), Slavica Koprivica (University of Belgrade, Serbia), Gottfried Eilenberger (TU Vienna, Austria), Josua Oberlerchner, Nora Odabas and Philipp Vejdovszky (all BOKU, Austria) joined the group recently for PhD projects;

- Dr. Ivan Sumerskiy (Saint-Petersburg State Forest Technical University, Russia) and Prof. Hassan Amer (National Research Center Cairo, Egypt) joined the group as staff members for a three-year project on Future Lignin and Pulp Processing Research (FLIPPR).

#### New organisation:

• University of Natural Resources and Life Sciences, Austria:

During summer break the former Wood, Pulp and Fibre Research Group at the Division of Organic Chemistry has been transformed into the new Division of Chemistry of Renewables complementing the divisions of biochemistry, organic chemistry, and analytical chemistry at the Department of Chemistry.



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# EPNOE Member's research

## Fraunhofer IAP establishes new processing pilot plant for biopolymers in Schwarzheide

n April 24th, 2013, the Fraunhofer Institute for Applied Polymer Research IAP Potsdam-Golm inaugurated its new processing pilot plant for biopolymers in Schwarzheide on the third largest production site of BASF in Europe. "The pilot plant is the first element of the Innovation Center Bioplastics Lausitz and is strengthening significantly the biopolymer competence of the Fraunhofer IAP" said the institute head, Prof. Hans-Peter Fink in the opening ceremony. The innovation center in its final structure has the potential to possibly become also a European Demonstration Center for bioplastic R&D. Dr. Mathias Hahn as the current head of the IAP processing pilot plant explained the new possibilities for biopolymer development to a large audience of invited guests

With the integration of the pilot plant in local and national networks, the new IAP unit shall support the mainly small and medium-sized plastic manufacturing industry in the introduction of biobased plastics in production processes. For this, necessary processing equipment (extruders, nozzles for the production of flat and blown films, injection molding equipment, etc.) has been installed. The approach fits well into the current bio-economy initiatives of the German Federal Government and the European Commission.

The project group is supported by the Ministry of Science, Research and Culture (MWFK) of Brandenburg, the BASF Schwarzheide GmbH and the Fraunhofer-Gesellschaft. From the beginning, the project group will be working together with the Competence

Network

ed by the Agency

Resources (FNR) of

the Federal Ministry

of Agriculture. Close

ties to EPNOE are also envisioned.

fund-

Renewable

Bioplastics

for



Prof. Dr. Hans-Peter Fink, and Dr. Mathias Hahn explain flat film processing equipment to guests of honor. © Picture BASF Schwarzheide

This article was proposed by Dieter Hofmann, Fraunhofer Institute for Applied Polymer Research, Germany.

## **news** (continued)

#### Member's info



New innovation and research platform:

 University of Maribor, Slovenia:

The University of Maribor has established its CORE@UM (www. core.um.si), a common innovation and research platform in Podravje in the field of je Active Healthy Aging. The priority research fields are "Advanced Materials and Technologies", "Advanced Computing", and "Applied Studies of Complex Systems". More info at: https://docs.google. com/file/d/0BxCJ2bOP0jJ1UWZubjlsN0tZV28/edit.

#### New position:

• University of Utrecht, the Netherlands:

In September 2013, Martin Patel moved from Utrecht University (Netherlands) to the University of Geneva (Switzerland) where he has been nominated for a new chair on Energy Efficiency (within the Institute for Environmental Sciences, Energy Group).

The objective of the chair is to bridge the gap between technical, economic, environmental and policy aspects. In view of Switzerland's phase-out of nuclear energy there is large interest in this type of interdisciplinary research.

Martin's research will include energy efficiency in buildings and in industry and he will closely collaborate with the local energy supplier. In parallel, he will continue working on bio-based products (esp. LCA and economic assessment).

While, in general, most attention (e.g., in university research and national energy and climate policy) is paid to energy supply, this chair aims to close important knowledge gaps related to the more efficient use of energy (demand side) and the production and use of less energy intensive and more sustainable materials.



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## **EPNOE Member's research**

## NewS – Network washable Sensor Textiles

ne of the biggest societal challenges of the next decades is the progressive ageing of the society. As an estimate the Austrian population will grow by 2030 to approximately 9.0 Mio people. The share of people with an age over 60 will increase from 24 % at 2030 to 31 % in 2030, which corresponds to an absolute value of 2.8 Mio. people. In the same period the number of people 80+ will increase from 405.000 to 635.000 (+57%) in 2030.

Sensor textiles, which support patient monitoring and care givers work, will take a significant role in the required increase in efficiency of care providing organisations.

An immediate detection of wetness in bedding is of high relevance for hospital and care application. The project NewS (FFG 841054) concentrates on research for new technologies to produce cellulose based composite textiles, which function as washable sensors. New embroidery techniques will be used to integrate sensor functions in bed textiles. In a care home for elderly the washable sensor-textiles will be tested for usability and lifetime.

The development of washable textile based sensors is an interdisciplinary activity. In the research project NewS all relevant production stages including application in care home are represented by partners.

The research activities include textile production (Fussenegger Textilveredlung, Grabher Günter Textilveredlung), technical embroidery (Brodissima, Globe-Tex), electronic data acquisition and transfer (Identec Solutions), application tests (Care homes Dornbirn) and life-time analysis in laundry (Berendsen).

Detection of wetness in bedding forms the representative case for the application testing. A phase of clinical testing in a care home for elderly will be executed, to assess the functionality under practical

conditions. The life-time of a sensor bedsheet will be the cost determining factor, thus a series of ageing tests under practical conditions will be performed.

In the project NewS the fundamentals for production of embroidered sensors in textile/soft material will be laid. The new production technology will enable the partners to develop sensors for a high number of further applications.

Robust washable sensors are of interest in textiles for hospital and care (e.g. sensors for moisture, temperature, position), in seats and interior (movement sensors, switches), in protective clothing (safety functions, detection of liquid and contamination), as technical sensors (filter, textiles in construction, detection of condensate).



Fig. 1: Embroidered stainless steel sensor fabric, responding to moisture

This article was proposed by Barnaby Caven, University of Innsbruck, Austria.



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## EPNOE Member's research Electrospinning – an attractive and promising technology for academia and industry

lectrospinning is the most promising method used for forming micro or nano sized fibres using electrostatic forces. During the electrospinning process, the polymer solution is exposed to high-electric voltage causing the formation of charged polymeric jet in the form of fine and thin fibres deposited on the base material. Fibres can be formed using synthetic or natural polymers dissolved in organic solutions or water. Nanofibres with specific properties can be obtained by adding different additives, e.g. nanoparticles (metal, ceramic), nanocapsules and other nanostructures, as well as drugs, essential oils, proteins, etc. Morphology, diameter, volume/ surface ratio and porosity of formed fibres depend on various parameters, i.e. i) polymer solution (viscosity, surface tension,



Fig. 1: SEM image of formed polyvinyl alcohol nanofibres

conductivity), ii) technology process (voltage, current, flow, electrode distance), and iii) environment (temperature, humidity). Formed nanofibres can be oriented or randomly interweaved into a net (Figure 1). Nanofibres mats possess excellent properties, i.e. large accessible surface compared to

volume (103–times bigger surface-to-volume ratio compared to microfibers), flexibility, surface functionality, mechanical strength and elasticity.

Electrospun nanomaterials can be applied in a broad range of fields including energy and electronics (batteries/cells and capacitors, sensors, etc.), filtration (air, oil, fuel, liquid filters, etc.), insulation (thermal, sound), clothing and smart textiles (protective cloths, health monitoring, sportswear, military, etc.), biomedical applications such as drug delivery, tissue engineering, wound dressings, hygienic products (diapers, napkins, etc.), and cosmetics (pigments).

Although, some of these applications are still remaining on a laboratory scale, plenty of successful examples have proved that electrospun nanofibres have a bright future in a variety of industries. The future of nanotechnology-based materials depends on the ability to scale-up the production, which is a huge problem of most of the known technologies. In our institute we possess ElMarco – Nanospider NS500 pilot-scale apparatus (Figure 2), designed for effective transfer from lab-scale into industrial-scale

nanofibres production. Research on electrospinning technology, performed at our institute in cooperation with

Centre of Excellence Polimat, involves formation of nanofibres used for filtration, nanofibres with different finesses and porosity applicable for scaffolds, nanofibres with incorporated NSAID drugs with controlled release, and natural antioxidant and antimicrobial additives (Figure 5 and 6) showing beneficial potential in human health. Our research area is disseminating also in other application field, since we are the member of COST Action MP1206: Electrospun Nano-fibres for Bio Inspired Composite Materials and Innovative Industrial Applications.

Pilot-scale

#### More information could be found:

4

2.

Electrospinning apparatus

ElMarco - Nanospider NS500

Fig.

http://www.tekstilec.si/wp-content/uploads/2013/01/ Elektropredenje-Postopek-izdelave-nanovlaken.pdf



Fig. 3: The course of natural antimicrobial substance release from electrospuned nanofibres

This article was proposed byZdenka Peršin and Manja Kurečič, University of Maribor, Slovenia.



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## EPNOE Member's research Quaternary Ammonium Chloride based Cellulose Solvents

#### Background

Results

A state-of-the-art strategy to obtain new high-tech cellulosic products with controlled structural features is the homogeneous chemical modification. At present, most widely

used cellulose solvents are N,N-dimethylacetamide (DMA)/LiCl and ionic liquids (ILs). Nevertheless, DMA/LiCl dissolves cellulose slow and energy intensive while typical problems of IL/cellulose solutions are their high viscosities, decomposition, side reactions and insolubility of various reagents. Hence, novel cellulose solvents are still of high interest. We have found new systems for cellulose dissolution that consists of quaternary ammonium electrolyte alone or mixed with organic liquids.

The electrolytes have been prepared in high yields and purity by Menshutkin quaternization, an inexpensive and

easy synthesis route. The pure molten triethyloctylammoni-

um chloride (N2228 CI) dissolves up to 15 wt% of cellulose

upon heating and mechanical stirring. The cellulose solution

is miscible with various cosolvents such as pyridine, N,N-



Fig. 1: Cellulose dissolved in N,Ndimethylacetamide (DMA)/triethyloctylammonium chloride (N2228 Cl).

dimethylformamide (DMF), dimethylsulfoxide (DMSO) and 1,3-dimethyl-2-imidazolidinone (DMI). In particular, DMA could be added in large excess leading to a system of decreased viscosity



(Figure 1). Contrary to the well-established solvent DMA/ LiCl, cellulose could also be dissolved directly in the DMA/ N2228 Cl/DMA mixture (Figure 2) without any pretreatment. Thus, the use of the new solvent avoids disadvantages of DMA/LiCl and ILs.

References: M. Kostag, T. Liebert, O.A. El Seoud, Th. Heinze, Efficient Cellulose Solvent: Quaternary Ammonium Chlorides, Macromol. Rapid Commun., in press, DOI 10.1002/ marc201300497; Patent "Cellulose- und Cellulosederivat-Lösungen und deren Verwendung, 10 2012 727.3, Ass.: SE Tylose GmbH & Co. KG, FSU Jena, Inv.: M. Kleinert, Th. Heinze, T. Liebert, M. Kostag.

Fig. 2: Viscosity curves of 2.4 wt% cellulose solutions at 20 °C in 1-ethyl-3-methylimidazolium acetate (EMIM Ac), N,N-dimethylacetamide (DMA)/BMIM Cl, 1,3-dimethylimidazolidin-2-one (DMI)/triethyloctylammonium chloride (N2228 Cl), DMA/lithium chloride (LiCl) and DMA/N2228 Cl.

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## **Scientific papers**

## Selection of articles published by EPNOE partners in 2012 and 2013

#### Center of Materials Forming, Mines-ParisTech-CNRS (France)

• T. Domenech, E. Peuvrel-Disdier, B. Vergnes (2013) The importance of specific mechanical energy during twin screw extrusion of 3, organoclay based polypropylene nanocomposites, Compos. Sci. Technol., 75, pp7-14

• A. Durin, P. de Micheli, J. Ville, F. Inceoglu, R. Valette, B. Vergnes (2013)A matricial approach of fibre breakage in twin-screw extrusion of glass fibres reinforced thermoplastics, \_Compos. Part A\_., 48, pp47-56

• J. Ville, F. Inceoglu, N. Ghamri, J.L. Pradel, A. Durin, R. Valette, B. Vergnes (2013) Influence of extrusion conditions on fiber breakage along the screw profile during twin screw compounding of glass fiber-reinforced PA/, \_Intern. Polym. Proc\_., 28, pp49-57

• W. Liu, T. Budtova (2013) Dissolution of unmodified waxy starch in ionic liquid and solution rheological properties, Carbohydrate Polymers, 93, pp199-206

• N.Le Moigne, M. van den Oever, T. Budtova (2013) Dynamic and capillary shear rheology of natural fibre-reinforced composites", Polymer Engineering and Science, published on-line march 2013, 10.1002/pen.23521

#### University of Natural Resources and Life Sciences (Austria)

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• T. Hosoya, A. D. French, T. Rosenau (2013) Chemistry of 2,5-dihydroxy-[1,4]-benzoquinone, a key chromophore in aged cellulosics. Mini-Rev. Org. Chem., 10, pp309-315.

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• L. Bamonti, T. Hosoya, K.F. Pirker, S. Böhmdorfer, F. Mazzini, F. Galli, T. Netscher, T. Rosenau, L. Gille (2013) Tocopheramines and tocotrienamines as antioxidants: ESR spectroscopy, rapid kinetics and DFT calculations, Bioorganic and Medicinal Chemistry, 21 (17), 5039-5046

#### Friedrich Schiller University of Jena (Germany)

• R. B. Gillis, G. G. Adams, Th. Heinze, M. Nikolajski, S. E. Harding, A. J. Rowe (2013) MultiSig: a new high-precision approach to the analysis of complex biomolecular systems, European Biophysics Journal, DOI: 10.1007/s00249-013-0924-y

• Th. Elschner, M. Kötteritzsch, Th. Heinze (2013) Synthesis of cellulose tricarbonates in 1-butyl-3-methylimidazolium chloride/pyridine, Macromolecular Bioscience, DOI: 10.1002/ mabi.201300345

• S. Genest, S. Schwarz, K. Petzold-Welcke, Th. Heinze, B. Voit (2013) Characterization of highly substituted, cationic amphiphilic starch derivatives: Dynamic surface tension and intrinsic viscosity, Starch/Stärke 65, DOI: 10.1002/star.201200295

• H. Wondraczek, A. Kotiaho, M. Niemi, P. Fardim, Th. Heinze (2013) Studies on the structure of coumarin-modified dextran nanoparticles by fluorescence spectroscopy, Carbohydrate Polymers 97, pp45-51

• J. Cuers, A. Koschella, Y. Wang, Th. Heinze, P. Mischnick (2013) Comprehensive analysis of the substituent distribution in 3-O-ethyl/propyl cellulose derivatives, Carbohydrate Polymers 96, pp246-252



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## Selection of articles published by EPNOE partners in 2012 and 2013 (continued)

#### Fraunhofer Institute for Applied Research (Germany)

• H-P. Fink, A. Lehmann, J. Ganster (2013) Bio-based carbonfibers - efforts and prospects, Chemical Fibers International 1, pp29-30

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• H. Petersen, S. Radosta, W. Vorwerg, B. Kießler (2013) Cationic starch adsorption onto cellulosic pulp in the presence of other cationic synthetic additives, Colloids and Surfaces A: Physicochemical and Engineering Aspects 433, pp1-8

• M. Horbens, A. Pfriem, J. Ganster, A. Wagenführ (2012) Holzfasern als Verstärkungsfasern in Holz-Polypropylen-Verbundwerkstoffen, Holztechnologie 53, pp21-25

• J. Erdmann, J. Ganster, H.-P. Fink (2012) PLA meets Rayon – Tough PLA compounds reinforced with cellulose rayon for injection moulding, Bioplastics MAGAZINE 7, pp22-25

#### VTT Technical Research Centre of Finland (Finland)

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• R. Coda, I. Karki, E.Nordlund, R.-L. Heinio, K. Poutanen, K.Katina (2013) Influence of particle size on bioprocess induced changes on technological functionality of wheat bran, Food Microbiology, in press

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#### Abo Akademi University (Finland)

• J. Krogell, E. Korotkova, K. Eränen, A. Pranovich, T. Salmi, D. Murzin, S. Willför, (2013) Intensification of hemicellulose hot-water extraction from spruce wood in a batch extractor - effects of wood particle size, Bioresource Technology 143, pp212-220 (Elsevier Ltd., ISSN: 0960-8524)

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• H. Lindqvist, J. Holmback, A. Rosling, K. Salminen, B. Holmbom, A. Sundberg (2013) Galactoglucomannan derivates and their application in papermaking, BioResources 8(1), pp994-1010

• H. Wondraczek, A. Kotiaho, M. Niemi, P. Fardim, T. Heinze (2013) Studies on the structure of coumarin-modified dextran nanoparticles by fluorescence spectroscopy, Carbohydrate Polymers 97, pp45–51

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## Selection of articles published by EPNOE partners in 2012 and 2013 (continued)

#### "Petru Poni" Institute of Macromolecular Chemistry (Romania)

• S. Coseri, A. Doliska, K. Stana-Kleinschek (2013) Immobilization of Water-Soluble 6-Carboxylcellulose on Poly(ethylene terephthalate) Films Monitored by a Quartz Crystal Microbalance with Dissipation, Industrial and Engineering Chemistry Research, 52(22), pp7439-7444.

• S. Coseri, G. Biliuta, B. C. Simionescu, K. Stana-Kleinschek, V. Ribitsch, V. Harabagiu (2013) Oxidized cellulose—Survey of the most recent achievements, Carbohydrate Polymers, 93(1), pp207-215

• G. Biliuta, L. Fras, M. Drobota, Z.Persin, T. Kreze, K. Stana-Kleinschek, V. Ribitsch, V. Harabagiu, S. Coseri (2013) Comparison study of TEMPO and phthalimide-N-oxyl (PINO) radicals on oxidation efficiency toward cellulose, Carbohydrate Polymers, 91(2), pp502-507.

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#### University of Maribor (Slovenia)

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• A. Doliška, V. Ribitsch, K. Stana-Kleinschek, S. Strnad, (2013) Viscoelastic properties of fibrinogen adsorbed onto poly (ethylene terephthalate) surfaces by QCM-D, Carbohydrate Polymers [Print ed.], pp246-255, doi: 10.1016/j.carbpol.2012.02.075

#### University of Wageningen (the Netherlands)

• S. van Kempen, C. G. Boeriu, H. A. Schols, P. de Waard, E. van der Linden, L. M. C. Sagis (2013) Novel surface-active oligofructose fatty acid mono-esters by enzymatic esterification, Food Chemistry, 138(2-3), pp1884-1891

• L. A. M. van den Broek, C. G. Boeriu (2013) Enzymatic synthesis of oligo- and polysaccharide fatty acid esters. Carbohydrate Polymers, 93(1), pp65-72

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• R. Croitoru, F. Fitigau, , L. A. M. van den Broek, C. M. Davidescu, C. G. Boeriu, F. Peter (2013) Biocatalytic acylation of sugar alcohols by 3-(4-hydroxyphenyl)propionic acid, Process Biochemistry, 47, pp1894-2012

• A. A. E. Chavaroche, L. A. M. van den Broek, C. Boeriu, G. Eggink (2012) Synthesis of heparosan oligosaccharides by Pasteurella multocida PmHS2 single-action transferases, Appl. Microbiol. Biotechnol. 95, pp1199-1210



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## Selection of articles published by EPNOE partners in 2012 and 2013 (continued)

#### IBWCh Institute of Biopolymers and Chemical Fibres (Poland)

• D. Wawro, W. Stęplewski, A. Komisarczyk, I. Krucińska (2013) Formation and Properties of Highly Porous Dibutyrylchitin Fibres Containing Nanoparticles, Fibres & Textiles in Eastern Europe; 21, 4(100), pp31-37

#### University of Nottingham (United Kingdom)

F. M. Almutairi, G. G. Adams, M. S. Kok, C. J. Lawson, R. Gahler, S. Wood, T. J. Foster, A. J. Rowe, S. E. Harding (2013) An analytical ultracentrifugation based study on the conformation of lambda carrageenan in aqueous solution, Carbohydrate Polymers, vol. 97, pp203-209
M. Lad, T. Todd, G. A. Morris, W. MacNaughtan, G. Sworn, T. J. Foster (2013) On the origin of sharp peaks in the X-ray diffraction patterns of xanthan powders, Food Chemistry, vol. 139, no. 1-4, pp1146-1151

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