

1st International EPNOE Junior Scientists Meeting

»FUTURE PERSPECTIVES IN POLYSACCHARIDE RESEARCH«

BOOK OF ABSTRACTS

19-20th January 2015, Wageningen, The Netherlands

Wageningen UR Food & Biobased Research

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1. Gericke, Martin 2. Cemef

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FOREWORD

Dear Students, Colleagues, and Friends,

The possibilities to advertise a conference devoted to polysaccharides are as plentiful as the approaches to assess the unique features of this interesting class of natural products. Polysaccharides are ubiquitous in nature and as such bioresources of untold potential. Polysaccharides are highly complex macromolecules with unique physical, chemical, and biological properties that are highly desired yet seldom achieved by synthetic polymer chemists. The areas in which polysaccharides are employed reach from every-days-products, such as food-ingredients and construction materials, to high value added applications in medicine and biotechnology. Polysaccharides can be utilized as produced by nature, brought into various types of shapes, or modified by specific mechanic, chemical, and/or enzymatic treatments.

Following the versatility of polysaccharides, the term '*polysaccharide research*' spans a broad spectrum of scientific disciplines largely differing from the background and motivation of individual researches (e.g., industry vs. academia, chemistry vs. biology vs. material sciences). Yet, two common aspects remain: (i) Despite any differences, '*polysaccharide researcher*' share a set of basic understanding and terminology. They can easily work together on a multi-disciplinary level, bridging fundamental and applied aspects from polysaccharide biosynthesis to the final application. (ii) As is the nature of scientific progress, research in the field of polysaccharides is constantly evolving with new topics emerging in the context of current socio-political discussions such as '*green chemistry*', '*bio-refinery*', and '*bio-based plastics*'. This results in a constant need for innovative perspectives and creative impulses from different sites.

The '*European Polysaccharide Network Of Excellence*' (EPNOE) is a research and education network connecting 16 European laboratories from 9 countries. Its main objective is to focus and promote polysaccharide science by bringing together leading scientists from different polysaccharide related topics. It is unquestioned that polysaccharide research can benefit a lot from the creative input of young scientist, the '*leading scientist of tomorrow*'. The '*1st EPNOE Junior Scientist Meeting*' was hosted in this spirit from January 19-20 in Wageningen/The Netherlands. Aim of this meeting was to provide junior scientists' a platform for discussing their personal visions of what might be the future perspectives in polysaccharide research along with an opportunity to present results of their work in close discussion with fellow young researchers and senior scientists. Thus, the call for abstracts was explicitly addressed to PhD students, Post-Doctoral scientists and junior Assistant Professors at the very beginning of their scientific career without placing particular restriction regarding the scientific topic.

As a last personal remark I would like to thank all participants for sharing both, their work and their unique personal views on the question '*In which direction(s) will polysaccharide research evolve in the near future?*' The large positive response on such a short notice was surprising in the first place yet likewise reassuring because it demonstrated the need of young scientist for a closer scientific discourse.

Martin Gericke

Jena, 02.02.15



Topics and Scientific Program:

All polysaccharide related topics with a high degree of novelty and innovation are within the focus of the meeting including but not limited to:

- **Isolation and production of polysaccharides**: exploration of novel bioresources (e.g., algae, fungi, bacteria, new crops and plants, waste products), improved techniques for obtaining polysaccharides of superior quality, biotechnological processes for polysaccharide production

- **Chemical and enzymatic functionalization of polysaccharides**: novel techniques (polysaccharide solvents, derivatization reactions, greener processes) for homogeneous/heterogeneous derivatization of polysaccharides, novel types of polysaccharide derivatives, enzymatic catalysis and advanced chemical modification of polysaccharide based materials

- **Preparation of polysaccharide based materials**: innovative processes for shaping of polysaccharides (e.g., into fibers, films, membranes), "non-classical" polysaccharide shapes (e.g., nm-/ μ m-sized particles, hydrogels, aerogels), composites of polysaccharides blended with other organic/inorganic materials, polysaccharides with functional surface modifications

- **Polysaccharides in advanced applications**: innovative applications of polysaccharides, polysaccharide derivatives, or polysaccharide based materials, e.g., in health, food, biotechnology, materials engineering, consumer products, agriculture, environment, and other areas in which they can demonstrate beneficial effects over non-polysaccharide based materials

- **Biorefinery of polysaccharide biomass**: degradation of polysaccharides into sugar monomers and platform chemicals, conversion of polysaccharides into energy or fuel.



Schedule of the meeting:

Monday, January 19 2015			
Time	Speaker	Title	Chair
09:00-09:20	Welcome		
09:20-09:40	P. Gašparič	Ink-jet printing for fabrication of paper-based sensing devices	M. Gericke
09:40-10:00	N. Castro	Elaboration of bio-based materials by twin-screw extrusion	
10:00-10:20	M. Nagalakshmaiah	Surface modified cellulose nanocrystals in aqueous medium with quaternary salt and reinforced in polypropylene by melt extrusion	
10:20-10:40	M. Mariano	Influence of coated cellulose nanocrystals in thermal and mechanical properties of extruded thermoplastic materials	
10:40-11:10	Break		
11:10-11:30	M. Gericke	Innovative materials through chemical modification of polysaccharides - Homogeneous tosylation of agarose	R. Kargel
11:30-11:50	N. Rosa-Sibakov	Birch pulp xylan as dietary fibre ingredient and hydrocolloid for dairy applications	
11:50-12:10	M. Bulota	Algae and its waste as bio-based filler in thermoplastic composites	
12:10-14:00	Lunch + Poster		
14:00-14:20	Z. Jamsazzadeh Kermani	Mechanical and enzymatic functionalization of pectin in situ in mango derived products	S. Botelho da Silva
14:20-14:40	A. G. Sousa	The impact of rhamnogalacturonan-I side chain monosaccharides on the rheological properties of citrus pectin	
14:40-15:00	N. Le Moigne	From cells to materials: challenges and future trends	
15:00-15:20	J. Mougel	Multifunctional architectures based on cellulose nanocrystals and carbon nanotubes hybrids	
15:20-15:40	Break		
15:40-16:00	S. Antunes	Production of extracellular polysaccharide by Enterobacter A47 using cheese whey as the sole carbon source	J. Girones
16:00-16:20	L. Sobhana	Layered double hydroxides, Micro-crystalline cellulose, Template/structure directed synthesis, Co-precipitation synthesis, Microwave-hydrothermal treatment (MWHT)	
16:20-16:40	S. Spirk	Photopatterning of Cellulose Thin films - from Transistors to 3-D Microfabrication	
16:40-17:00	L. Vo	Biomass for cementitious building materials	
18:30	Dinner at the Hof van Wageningen Hotel		



Tuesday, January 20 2015			
Time	Speaker	Title	Chair
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09:20-09:40	L. Jowkarderis	Viscoelastic properties of cellulose nanofibril (CNF) hydrogels	
09:40-10:00	L. Chupin	Extraction of maritime pine bark tannins for bio-based adhesives	
10:00-10:20	M. Króllicka	Chitin as a resource for production of chemicals	
10:20-10:40	Break		
10:40-11:00	S. Weigl	Cellulose nanocrystals used for the immobilization of polymer antioxidants	R. Kargel
11:00-11:20	A. Galais	Access to amphiphilic 4-(alkyloxy)aniline-linked chitooligosaccharide-2,5-anhydro-D-mannofuranoses from chitosan	
11:20-11:40	S. Boulos	Oxidized Cereal Beta-Glucan and Iron – Reducing Capacity and Complexation Behavior	
11:40-13:00	Lunch + Poster		
13:00-13:20	I. Farinha	Characterization of the chitin-glucan complex extracted from Komagataella pastoris cell wall	S. Botelho da Silva
13:20-13:40	S. Safari Mohsenabad	Mechanism of copper adsorption on electrosterically stabilized nanocrystalline cellulose: From star-like bridging to raft-like aggregation	
13:40-14:00	K. Kalinov	Novel antitumor nanofibrous implants Containing quaternized chitosan and gossypol with antitumor activity against graffi myeloid tumor	
14:00-14:20	Break		
14:40-15:00	S. Botelho da Silva	TEMPO oxidation of polysaccharides as a strategy to modify and enhance functional properties: comparison between chemical and chemoenzymatic approaches	J. Girones
15:00-15:20	A. Shpigelman	The effect of high pressure homogenization on pectin – Novel information regarding the importance of source dependent variation of pectin structure on the outcomes of processing	
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¹University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers, Maribor, Slovenia

²Mondi Uncoated Fine & Kraft Paper GmbH, Marxergasse 4A, 1030 Wien, Austria

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¹Université de Toulouse, INP-ENSIACET, LCA (Laboratoire de Chimie Agro-industrielle), F-31030 Toulouse, France

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¹Laboratoire Rhéologie et Procédés, 63 rue de la Chimie- Bâtiment B - Domaine Universitaire – BP 53 - 38041 Grenoble cedex 9

²Univ. Grenoble Alpes, LGP2, F-38000 Grenoble, France

³CNRS, LGP2, LRP, F-38000 Grenoble, France

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¹Grenoble Institute of Technology (Grenoble INP) - The International School of Paper, Print Media and Biomaterials (Pagora), CS10065, 38402 Saint Martin d'Hères Cedex, France



²Laboratoire Rhéologie et Procédés, Grenoble INP-CNRS-UJF, UMR 5520, BP 53, 38041 Grenoble Cedex 9, France

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2 Rue de la Houssinière BP32229 44322 Nantes, France

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¹REQUIMTE/COFB, Chemistry Department, FCT/Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

²CEER - Biosystems Engineering, ISA/Technical University of Lisbon, Tapada da Ajuda, 1349-017 Lisboa, Portugal

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¹Chair of Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, 8700 Leoben, Austria

²Materials-Institute for Surface Technologies and Photonics, Joanneum Research Forschungsgesellschaft mbH,

Franz-Pichler-Straße 30, 8160 Weiz, Austria

³University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers, Smetanova 17, 2000 Maribor, Slovenia

⁴Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

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²Mines ParisTech, CEMEF – Centre de Mise en Forme des Matériaux, CNRS UMR 7635, BP 207, 1 rue Claude Daunesse, 06904 Sophia Antipolis Cedex, France

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¹REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

²CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa and CEMOP-UNINOVA, Campus de Caparica, 2829-516 Caparica, Portugal

³Interfaculty Research Centre of Biomaterials (CEIB), University of Liège, B-4000, Liège, Belgium

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¹McGill University, Department of Chemical Engineering, Montreal, Quebec H3A 0C5, Canada

²McGill University, Department of Chemistry, H3A 2A7 Montreal, Quebec, Canada

²McGill University, Department of Chemistry, Pulp and Paper Research Centre, H3A 2A7 Montreal, Quebec,
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³McGill University, Centre for Self-Assembled Chemical Structures, H3A 2A7 Montreal, Quebec, Canada

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¹Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 103A, BG-1113 Sofia, Bulgaria,

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¹ University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers, Smetanova 17, 2000 Maribor, Slovenia

²University Graz, Institute of Chemistry, Heinrichstraße 28/III, AT-8010 Graz, Austria

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¹Jan Dlugosz University in Czestochowa, Faculty of Mathematics and Natural Sciences, Institute of Chemistry, Environmental Protection and Biotechnology, 13/15 Armii Krajowej Ave., 42-200 Czestochowa, Poland

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²Center of Excellency PoliMaT, Tehnoloski park 24, 1000 Ljubljana, Slovenia

³University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory of Separation Processes and Product Design, Smetanova 17, 2000 Maribor, Slovenia

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¹Jan Długosz University in Częstochowa, Faculty of Mathematics and Natural Sciences,
Institute of Chemistry, Environmental Protection and Biotechnology, Ave. Armii Krajowej 13/15,
42-200 Częstochowa, Poland

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¹Division Technologies et Développement -DTD (ex CRD), Direction Géologie SONATRACH,
Avenue du 1er Novembre, Boumerdès, 35000, Algérie

^{2,3}Laboratoire de Physico-Chimie des polymères, IPREM UMR CNRS/UPPA 5254, Pau,

⁴Directeur de Laboratoire traitement et mise en forme de polymères, Université M'HAMED
BOUGUERRA Boumerdès 35000, Algérie

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Ink-jet printing for fabrication of paper-based sensing devices

Petra Gašparič¹, Andreas Kornherr², Silvo Hribernik¹, Karin Stana Kleinschek¹

karin.stana@um.si

¹ University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers,
Smetanova 17, 2000 Maribor, Slovenia #

² Mondi Uncoated Fine & Kraft Paper GmbH, Marxergasse 4A, 1030 Wien, Austria
Member of the European Polysaccharide Network of Excellence

General topic: Polysaccharides in advanced applications

Keywords: ink-jet printing, paper-based, sensor, hydrophobic pattern

Abstract:

Drinking water quality varies throughout the world. Due to global environmental issues water quality is increasingly compromised, especially in the third world countries. Hence a need for inexpensive disposable colorimetric sensors has emerged. Paper as an inexpensive and abundant material from natural resources is, owing to its unique properties, an ideal substrate for creating such sensing devices.

Piezoelectric ink-jet printing is a simple and effective way to prepare paper-based materials for advanced applications. With this method we were able to create hydrophobic patterns on a paper surface in order to prepare a novel sensing device for environmental analytics. In our work hydrophobic patterns and colorimetric indicators were printed using ink-jet technology, while the capillary action of the paper allows aqueous samples to move within the hydrophobic pattern in order to reach the indication sites. The advantage of such system is that it requires a small sample volume only.

Different types of commercially available and widely used sizing agents were used to create a variety of hydrophobic patterns, i.e. ASA (alkyl succinic anhydride) and AKD (alkyl ketene dimer). The wettability of these patterns was studied by means of static water contact angle measurements. In addition, a study of the interaction between the hydrophobic agents and model cellulosic surface was performed using quartz crystal microbalance with dissipation (QCM-D). The topography of the printed patterns was visualized with scanning electron microscopy (SEM).

Ink-jet technology has proven itself as a reliable and reproducible technique for fabrication of such devices; with it we were able to overcome the main challenge of our work and create precise patterns with high resolutions on a structurally heterogeneous substrate such as paper.

Acknowledgement: This work was funded by the Slovenian Research Agency (ARRS) and supported by Mondi Uncoated Fine & Kraft Paper GmbH.

Future perspective in PS research: My future perspective in PS research lies in the implementation of polysaccharide materials for advanced applications since PS materials, such as paper, are renewable, environmentally friendly and, with their unique properties, they are the perfect substrate for creating novel and functional materials.



Elaboration of bio-based materials by twin-screw extrusion

Natalia Castro^{1, 2}, Vanessa Durrieu^{1, 2}, Christine Raynaud^{1, 2}, Antoine Rouilly^{1, 2}

nathalia.castro@ensiacet.fr

¹ Université de Toulouse, INP-ENSIACET, LCA (Laboratoire de Chimie Agro-industrielle), F-31030 Toulouse, France

² INRA, UMR-1010-CAI, F-31030 Toulouse, France

General topic: Preparation of polysaccharide based materials; Polysaccharides in advanced applications

Keywords: twin-screw extrusion, maltodextrins, microencapsulation, thermal relaxation,

Abstract:

Seeking for new bio-based materials to replace the petrochemical ones has been and, still is, a major challenge for the scientific community.

Inspired by the technology employed in the food industry, twin-screw extrusion appears as a versatile process to elaborate bio-based materials. Twin-screw extrusion combines mechanical, thermal and chemical processes all in one-pot reaction, allowing the transformation of the biomass into bio-based materials.

Nowadays, twin-screw extrusion has been extensively used to create new bio-based materials from starch and starch derivatives (Averous, 2004). However maltodextrins have not yet been deeply explored.

Maltodextrins are oligo-polysaccharides mostly used for encapsulation of active principles, mainly by spray-drying, due to their good film forming properties. Nonetheless, all their physicochemical properties (e.g., thermal relaxation and viscosity) remain difficult to measure because of their macromolecular structure.

Under this context, twin screw extrusion was chosen as the encapsulation technology, using maltodextrins as the main encapsulating agent to create new bio-based materials. To conduct the experiments, maltodextrin-I12 was blended with two different additives i.e. pea proteins and modified potato starch as encapsulating material. The selected active principle was Miglyol, a model hydrophobic compound used to optimize and validate the extrusion and encapsulation process. The initial encapsulation rate of Miglyol varied from 8 to 15% (w/w).

All extrusion operating conditions were recorded and compared and the physicochemical characteristics of the extruded bio-based materials were determined. These include thermal transitions, measured through dynamic mechanical analysis (DMA), and their hydration rate. Interesting results were obtained, showing that Miglyol act as a plasticizer. This behaviour was observed for the four formulations tested. Moreover, the incorporation efficiency was determined by accelerated solvent extraction (ASE). For all formulations, the resulting incorporation efficiency was higher than 65%. Therefore, these maltodextrin-based materials can be considered as a performant delivery system for encapsulation of hydrophobic compounds (i.e. pigments, vitamins and essential oils). Additional analyses were also carried in order to determine the properties of the raw materials and, to better understand their behaviour in order to adjust the process parameters.

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Acknowledgement: The laboratory kindly acknowledges Givaudan France SAS for funding the PhD thesis of Natalia Castro.

Future perspective in PS research: Could short chains polymers, i.e maltodextrins be considered as thermoplastic polymers? In other words, could maltodextrins be molded, as to obtain maltodextrin based-materials?

Surface modified cellulose nanocrystals in aqueous medium with quaternary salt and reinforced in polypropylene by melt extrusion

Malladi Nagalakshmaiah^{1, 2, 3}, Nadia Elkissi^{1, 3}, Alain Dufresne^{2, 3}

nagalakshmaiah.malladi@ujf-grenoble.fr, nadia.el-kissi@ujf-grenoble.fr, alain.dufresne@pagora.grenoble-inp.fr

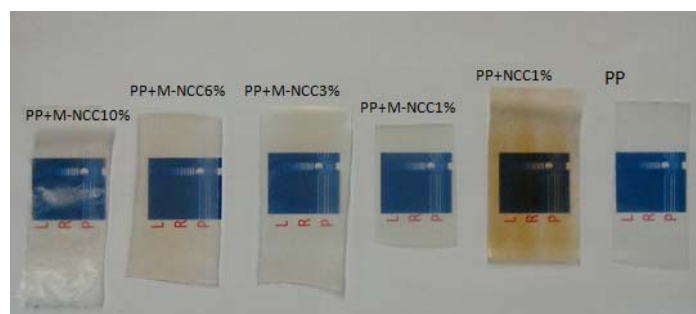
1. Laboratoire Rhéologie et Procédés, 63 rue de la Chimie- Bâtiment B - Domaine Universitaire - BP 53 - 38041 Grenoble cedex 9.
2. Univ. Grenoble Alpes, LGP2, F-38000 Grenoble, France.
3. CNRS, LGP2, LRP, F-38000 Grenoble, France.

General topic: Preparation of polysaccharide based materials (composites)

Keywords: cellulose nanocrystals, scanning electron microscopy, dynamic mechanical analyzer and thermo gravimetric analysis

Abstract:

Due to their enormous mechanical properties along with high reinforcing capacity, cellulose nanocrystals (CNC) could be the ultimate choice for polymer composites as filler. In this study the recently announced commercial grade CNC prepared by sulfuric acid hydrolysis from university of Maine were used and characterized by using atomic force microscopy (AFM) and X-ray diffraction (X-RD). From last few years most of the researchers are showing interest on nanocomposites processing by extrusion method since it is a solvent free process and also this system is most viable for commercial industrialization. However, sulfuric acid-prepared CNC limits the processing due to the sulfate groups degradation on surface because most polymers are processed at high temperatures. In this study CNC have been adsorbed with quaternary ammonium salts by simple aqueous method and their surface adsorption was proved by FT-IR and thermo gravimetric analysis (TGA). The modified CNC were used in extrusion with polypropylene at 190°C and the composites were characterized to understand the thermal, mechanical and morphological properties by DMA, TGA and scanning electron microscopy (SEM) and their results have been reported.



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Future perspective in PS research: According to my knowledge NANOCELLULOSE are ideal for health care as a **drug delivery** system.



Influence of coated cellulose nanocrystals in thermal and mechanical properties of extruded thermoplastic materials

Marcos Mariano^{1,2}, Nadia El Kissi², Alain Dufresne¹

marcos.mariano@lgp2.grenoble-inp.fr

¹ Grenoble Institute of Technology (Grenoble INP) - The International School of Paper, Print Media and Biomaterials (Pagora),
CS10065, 38402 Saint Martin d'Hères Cedex, France

² Laboratoire Rhéologie et Procédés, Grenoble INP-CNRS-UJF, UMR 5520, BP 53, 38041 Grenoble Cedex 9, France

General topic: Polysaccharides in advanced applications

Keywords: *cellulose nanocrystals, extrusion, composites*

Abstract:

As the most abundant polymer on earth, cellulose is the focus of many scientific researches. In the polymer field, the nanocellulose is used to prepare new light, strong and functionalized materials. The use of cellulose nanocrystals (CNC) in process as extrusion, hot molding and injection is, still, a challenge due its lower thermal stability. The degradation of this material during processing is dependent of its source, sulfate charges and, of course, temperature.

In this work, CNC was coated by polycarbonate (PC) trough its addition into the polymer solution, followed by precipitation into a non-solvent. The resultant capsules are composed by a white-porous material, which suggest the presence of crystalline PC. This coating stage seems to provide good dispersion of CNC. Also, its facilitates the extrusion process due to its easy addition into the equipment and increase in CNC thermal stability.

Thermogravimetric analyses shows that in high temperature processing, as polycarbonate extrusion, the degradation of CNC can anticipate the matrix degradation by the reduction of its Activation Energy. The processing of PC below its T_m (needed condition to keep the CNC integrity) seems to keep the coated material organization. The XRD analysis shows an increase in the crystallinity content for the final material, in comparison to virgin extruded pellet.

By itself, the presence of CNC seems to not affect the final composites crystallinity. Its well reported in the literature that a presence of CNC can improve mechanical properties of polymeric materials, acting as reinforcement agent, specially above the T_g. The coating technique can be used to increase the thermal stability of the CNC, avoiding an earlier degradation of the matrix. However, at the same time, the coating polymer can influence the final crystalline content of the composite and modify its properties.

Acknowledgement: The authors gratefully acknowledge "Ciência sem Fronteiras". Brazilian program for the financial support.

Future perspective in PS research: The collective effort made by researchers is fundamental to the building of new technologies and materials adequate to the real needs of the society. Each year, biomaterials came closer of overcome its biggest barrier: competitiveness. If, in many ways, these materials still fail due to commercial factors, is know that they have advantages due to the progressive environmental conscientization. The growing in the number of researches about this subject in comparison to the conventional materials, derived from petrol, can reflect the industrial reality in some years. I don't believe in a future without lighter, strongest and less aggressive materials that came from abundant sources.



Birch pulp xylan as dietary fibre ingredient and hydrocolloid for dairy applications

Natalia Rosa-Sibakov, Terhi Hakala, Nesli Sozer, Kaisa Poutanen, Anna-Marja Aura

natalia.rosa-sibakov@vtt.fi

VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland

Member of the European Polysaccharide Network of Excellence

General topic: Polysaccharides in advanced applications

Keywords: wood xylan, soluble dietary fibres, acid milk gel, colonic fermentation, short-chain fatty acid

Abstract:

There has been an increased interest in the utilization of plant biomass for conversion into sugars, chemicals and fuel, as well as for food applications. Pulp and paper industry wishes to valorise fractions from pulp in order to secure renewal and added value from forest resources. Food ingredients are valuable products and present a potential end-use for fractions isolated from wood. The aim of this work was to evaluate the potential of wood derived xylan to be used as a dietary fibre in food applications. A pure white xylan was isolated from bleached birch kraft pulp. To improve the technological properties, the isolated xylan was enzymatically hydrolysed to a shorter chain-length dietary fibre. Predicted physiological functionality of both xylan samples (isolated and hydrolysed) as dietary fibre was evaluated. The applicability of xylans as food hydrocolloids was also studied, i.e. xylans were added in low-fat acid milk gels (yoghurt model) and their effects on structural properties (texture and water retention) were also studied. Physiological and technological properties of xylans were compared to other reference dietary fibre (inulin, fructooligosaccharide and xylooligosaccharide). Both isolated and hydrolysed xylan showed slow fermentation in the *in vitro* colon model measured as slow rates of gas pressure evolution and formation of short-chain fatty acids. Acid milk gels enriched with xylans had improved water retention properties (higher water holding capacity and lower spontaneous syneresis) when compared to control or reference dietary fibres. The firmness and elasticity of milk gels were reduced by the addition of both xylan samples. In conclusion, birch xylans had suitable properties for acid milk gel applications and the slow fermentation rate predicted that birch xylans would cause less intestinal discomfort due to delayed colon fermentation.

Acknowledgement:

Future perspective in PS research:

- Better use of biomass derived polysaccharides to produce new healthy foods (low calorie/high in dietary fibre).
- Understanding of the stability of polysaccharides in food matrices (solid, semi-solid and liquid).

Algae and its waste as bio-based filler in thermoplastic composites

Mindaugas Bulota, Tatiana Budtova

mindaugas.bulota@mines-paristech.fr

Mines ParisTech, Centre de Mise en Forme des Matériaux (CEMEF), UMR CNRS 7635, Sophia Antipolis, France

Member of the European Polysaccharide Network of Excellence

General topic: Preparation of polysaccharide based materials

Keywords: (seaweed, thermoplastic composites, melt-mixing, tensile properties)

Abstract:

Marine biomass, in particular, macro-algae is widely used in food and beauty industries and thus procurement is already available. Extraction of water soluble polysaccharides from algae results in a huge amount of non-soluble waste. The exploitation of macro-algae and their waste would thus result in societal and environmental benefits.

Herein, a study on macro-algae filled poly(lactic) acid PLA composites is presented. Algae "as is" and its waste after the extraction of alginate were used. Composites were prepared using a melt mixing process followed by injection moulding to produce test bars. Three different types of seaweeds (red, brown and green) or dry algae waste have been mixed with PLA matrix at different weight fractions. Analysis has shown that filler-matrix interactions are affected, due to the presence of various salts on the surface of macro-algae flakes. Furthermore, thermal decomposition of composites starts at temperatures below melting temperature of polymer which effectively influences the structure of final composite material and thermal stability. Chemical and heat treatment have been carried out in order to alter algae surface and composition prior melt mixing. The results show that composites can be filled even up to 40 wt%, with minor changes in the Young's modulus of composites. Strain at break, however, significantly decreases upon the addition of macro-algae. Overall, the results show that both macro-algae and its waste can be used as filler in polymer composites.

Acknowledgement: The work is performed within the frame of the Industrial Chair in Bioplastics, organised by CEMEF/Mines ParisTech and supported by Arkema, L'Oreal, Nestlé, PSA and Schneider Electric. We thank Agrimer, Cargill and Prof. Deslandes (Université de Bretagne Occidentale, Brest) for providing algae and their waste.

Future perspective in PS research: In order to produce value added sustainable materials, future of PS research shall be focused on their modification and better control of properties as well as detailed understanding of the interactions with other materials. Man-made cellulose fibre shall attract more attention in order to alter and control their properties hence broadening the range of applications.



Mechanical and enzymatic functionalization of pectin *in situ* in mango derived products

Zahra Jamsazzadeh Kermani, Avi Shpigelman, Tom M.M. Bernaerts, Ann M. Van Loey, Marc E. Hendrickx

marc.hendrickx@biw.kuleuven.be

Laboratory of Food Technology, Leuven Food Science and Nutrition Research Centre (LFoRCe), Department of Microbial and Molecular Systems (M²S), Katholieke Universiteit Leuven, Kasteelpark Arenberg 22, Box 2457, 3001 Leuven, Belgium

General topic: Chemical and enzymatic functionalization of polysaccharides

Keywords: High pressure homogenization, Enzymatic treatment, Pectin, Mango purée.

Abstract:

Mango purée, a food suspension obtained after disintegration of ripe mango, has an extremely high consistency limiting its further processing and utilization. A common practice in industry to handle this problem is by diluting purée with water for which flavor reconstitution and sugar addition are required. It has been suggested that the high consistency is related to two common polysaccharides: pectin and starch. Recent studies showed that the functional (flow) properties of food suspensions are governed both by the plant-based particles and the serum properties, and by the ratio between these two phases. Our study aimed at better understanding and controlling the flow properties of mango purée by both physical (high pressure homogenization, HPH) and enzymatic manipulation. Fungal and bacterial commercial enzymes such as pectin methylesterase (PME), endo-polygalacturonase (PG), endo-cellulase (endo- β -glucanase), and α -amylase without/with HPH (20 MPa) were used to understand the contribution of specific accessible (cell wall) polysaccharides to consistency changes. HPH only, although largely changing the particle size, did not change purée consistency, however when combined with enzymatic treatments a substantial decrease in consistency was observed. Enzymes, while having minimal effect on particle sizes, induced a type-dependent modification of particles' morphology, showing the accessibility of particle polymers (in addition to the expected serum polymers) to enzymes. The enzymatic treatments resulted in clear pectin structural changes (such as degree of methoxylation) in both phases. Polymer conformation and weight average molecular weight were also affected. Our results clearly show that polymers of both phases are accessible to enzymatic treatments and that the main contributing factor to the high consistency is the relative weight of the serum phase.

Acknowledgement:

We acknowledge the financial support of the KU Leuven Research Council through the long term structural funding – Methusalem funding by the Flemisch Government.

Future perspective in polysaccharide research:

In my point of view polysaccharides functionalization *in situ* can be expected to be a hot topic in the next few years, as it exploits natural polysaccharide functionality in complex food systems rather than model systems. Such functionalization could be an alternative to commonly used additives in food systems for controlling the sensorial properties (such as taste and texture).



The impact of rhamnogalacturonan-I side chain monosaccharides on the rheological properties of citrus pectin

António G. Sousa^{1,2}, Heidi L. Nielsen¹, Ibrahim Armagan¹, Jan Larsen¹, Susanne O. Sørensen¹

susanne.o.soerensen@cpkelco.com

¹ CP Kelco ApS., Ved Banen 16, DK-4623 Lille Skensved, Denmark

² University of Copenhagen, Faculty of Science, Department of Plant and Environmental Sciences, DK-1871 Frederiksberg, Denmark

General topic: Polysaccharides in advanced applications

Keywords: Rhamnogalacturonan-I, rheology, pectin, branching, entanglements.

Abstract:

Citrus peel is the preferred raw material for pectin production, mainly due to its high pectin content but also due to its gelling capabilities. Especially the high galacturonic acid content and the high degree of methyl esterification make it an attractive starting material for further modification. Until now the presence of rhamnogalacturonan I (RG-I) in commercial pectin has received less attention due to its relatively low abundance. Using a gentle industrial extraction process we discovered a slightly higher composition in neutral sugars of RG-I. In particular, the arabinose concentration in mildly extracted pectin was higher compared to conventionally extracted pectin. The use of enzymes specific for either arabinan or galactan allowed assessing the implications of varying neutral sugar composition on the gelling capabilities of pectin. A comparison between untreated and debranched pectin revealed a significant decrease in both gelling temperature (up to 20 °C) and gel strength (up to 38 %), following the specific reduction in neutral sugars concentration. Coil-overlap and entanglement effects were analysed to further understand the impact of RG-I side chains on polymer rheology.

Acknowledgement:

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Future perspective in PS research:

Synthetic Biology is an interdisciplinary science which combines biotechnology, molecular biology, systems biology and biophysics for the creation of »biological devices« for useful purposes. The aim of this research area is to form the scientific basis for developing the sustainable production of plant-based bioenergies, biomaterials aimed at medicine applications, functional foods and molecular bioelectronics.



From cells to materials: challenges and future trends

Nicolas Le Moigne¹

nicolas.le-moigne@mines-ales.fr

¹ Centre des Matériaux des Mines d'Alès (C2MA), Ecole des Mines d'Alès, 6 avenue de Clavières, F-30319 Alès, France

Member of the European Polysaccharide Network of Excellence

General topic: Preparation of polysaccharide based materials

Keywords: Plant cells, micro-algae, processing, polymer solutions, biocomposites

Abstract:

Plant cells and micro-organisms such as micro-algae are already used in many industrial applications for food, materials and energy, and are intended to be extensively used in the next years as a potential answer to environmental concerns. These cells present complex and heterogeneous structures made of biopolymers such as polysaccharides, proteins, lignins... generally organized in several concentric layers. These specific structures are of great interest to build up new polymer blends and biocomposites materials. However, they exhibit complex behaviour during processing such as differential dissolution capacity in solvents or dispersion ability in polymer melts, interfaces between the components being a key issue. In this sense, physical, chemical as well as enzymatic selective treatments can be used to better control the processing and the final properties of polymer blends and biocomposites materials, although being often degrading. New trends consist in acting directly on the cells origin by the use of specific species or genotypes more suitable for processing so as to limit treatment steps, and hence preserve as much as possible the original properties of the cells. This presentation will be illustrated by several examples of plant cells and microalgae processing to make polymer solutions and biocomposites. The role of their structural features as well as those of selective treatments in the development of structured materials will be discussed. Finally, perspectives in the selection of particular cells to make new materials will be raised.

Acknowledgement:

NLM thanks the Carnot Institute, LabEx CheMISyst and industrial partners for their support.

Future perspective in PS research:

In the next years, strengthening interdisciplinary research involving biologists and materials scientists should provide new insights in the development and the selection of raw materials (plant cells, micro-algae) for a better control of processing and properties of polysaccharide based materials.



Multifunctional architectures based on cellulose nanocrystals and carbon nanotubes hybrids

Jean-bruno Mougel^{1,2}, Christophe Olivier¹, Patricia Bertoncini¹, Céline Moreau², Isabelle Capron², Bernard Cathala², Olivier Chauvet¹
jean-bruno.mougel@cnrs-imn.fr

¹ Institut des Matériaux Jean Rouxel (IMN), Université de Nantes-CNRS, UMR 6502, 2 Rue de la Houssinière BP32229 44322 Nantes, France

² Institut National de la Recherche Agronomique (INRA), UR 1268, Rue de la Géraudière BP 71627 44316 Nantes, France

General topic: Preparation of polysaccharide based materials

Keywords: Cellulose, whiskers, carbon nanotubes.

Abstract:

The cellulose nanocrystals (CNCs) are obtained after acid hydrolysis of cotton's linter. It results in negatively charged rod-like particles with individual dimensions about 200 nm long and 13 nm wide. Moreover, the CNCs show amphiphilic properties which offer the possibility to stabilize oil-in-water Pickering emulsions [1]. In a previous work [2], we have shown that it is possible to associate carbon nanotubes (SNWTs) and CNCs in aqueous media after sonication. The dispersions of these hybrids are obtained with a long term stability and the noncovalent approach allows to preserve the SWNTs' properties. We have also shown that it is possible to use these dispersions to build multilayered thin films by the layer-by-layer method. Those films demonstrated combined properties such as semi-reflective, conductive and luminescent properties. The aim of the present work is to explore more in details the properties of the CNCs/SWNTs dispersions, the conditions of the association of both components and to investigate the possibility to built 3D structures like emulsions.

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Future perspective in PS research:

The possibilities of nanocelluloses to build complexes 2D/3D structures offer a high specific surface available. Their association with different materials offering different functionality should be interesting for sensing applications.

Production of extracellular polysaccharide by *Enterobacter A47* using cheese whey as the sole carbon source

Sílvia Antunes^{1,*}, Vítor D. Alves², Christian Grandfils³, Filomena Freitas¹, Maria A.M. Reis¹

¹REQUIMTE/CQFB, Chemistry Department, FCT/Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

²CEER - Biosystems Engineering, ISA/Technical University of Lisbon, Tapada da Ajuda, 1349-017 Lisboa, Portugal

³Interfaculty Research Centre of Biomaterials (CEIB), University of Liège, B-4000, Liège, Belgium

saa19281@campus.fct.unl.pt

General topic: Isolation and production of polysaccharides

Keywords: *Enterobacter A47*; Cheese whey; Extracellular polysaccharide (EPS); Glucuronic acid; Fucose

Abstract:

Cheese whey, a lactose-rich by-product of the dairy industry, can be used as a biotechnological resource for the generation of energy and several value-added products, including microbial polymers. *Enterobacter A47* is well-known to produce a high molecular weight fucose-rich exopolysaccharide (EPS), named FucoPol, using as substrate glycerol by-product from the biodiesel industry. As an alternative, this work aimed to evaluate the ability of this strain to produce EPS adopting cheese whey as substrate. The culture grew on cheese whey with a specific growth rate of 0.15 h^{-1} and, under fed-batch conditions, achieving an EPS production of 6.70 g L^{-1} , corresponding to a volumetric productivity of $1.51 \text{ g L}^{-1} \text{ d}^{-1}$. The sugar analysis has highlighted that the resulting EPS had an original composition differing totally from FucoPol. With a high content in glucuronic acid (29 %mol) and fucose (28 %mol), this unique composition of EPS made it attractive in terms of bioactive polymer (detoxification, anti-aging). Glucose and galactose were minor sugar monomers of this EPS which disclosed also an high acyl group content of 32 wt.%. The polymer's molecular weight was $1.8 \times 10^6 \text{ Da}$ and characterized by a low polydispersity index (1.2).

This novel polymer possesses interesting rheological properties in aqueous media. The intrinsic viscosity obtained in 0.01 M NaCl at pH 8 was 8.0 dL g^{-1} and a Huggins constant of 0.36. Furthermore, the EPS produces viscous aqueous solutions with a shear thinning behaviour, with a zero shear viscosity (η_0) approaching 0.1 Pa s at a concentration of 1 wt.%.

The results obtained show that cheese whey can be used as the sole carbon source for the production of an exopolysaccharide, composed of bioactive monomers, by the *Enterobacter A47* strain. According to its known properties, it is envisaged a high potential for the biopolymer to be applied in several areas, including cosmetic, food, pharmaceutical and biomedical products.

Acknowledgement:

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Future perspective in PS research:

Use of agro-industrial byproducts/wastes to decrease EPS production costs. Polysaccharides as sources of rare sugar monomers as an alternative to chemical synthesis.



Cellulose as biotemplates for layered double hydroxides

Liji Sobhana S S¹, Pedro Fardim^{1*}

liji.sobhanadhas@abo.fi, pfardim@abo.fi

¹ Åbo Akademi University, Department of Chemical Engineering, Laboratory of Fibre and Cellulose Technology, Porthansgatan 3, Åbo 20500, Finland

Member of the European Polysaccharide Network of Excellence

General topic: Preparation of polysaccharide based materials

Keywords: Layered double hydroxides, Micro-crystalline cellulose, Template/structure directed synthesis, Co-precipitation synthesis, Microwave-hydrothermal treatment (MWHT)

Abstract:

Layered double hydroxides (LDH) also known as hydrotalcite clays, are a class of laminar minerals with anions sandwiched in between the brucite like layers. LDHs are useful materials investigated for its use as catalysts, catalyst supports, photo-catalysts, adsorbents, anion exchangers and, medicines. These applications are greatly dependent on their layered structure, regular shape, granular distribution. Traditional methods of producing LDH results in the formation of less ordered crystal growth. This proves that the production of LDH with better-defined geometry, crystal structure, controlled morphology and size still remains as a challenge. This difficulty can be attributed to the high rigidity and lack in the tenacity of LDH layers. Templates such as vesicles, micelles, microemulsions, polymers, are reported in literatures which directs the direct the formation of the target material with specific size, morphology and properties. However, the use of microcrystalline cellulose as a structure directing agent in the synthesis of LDH has not been reported to the best of our knowledge. Therefore, we report here an efficient way of preparing Layered double hydroxides using cellulose as biotemplates. ZnAlCO₃ LDH material was prepared in the presence and absence of microcrystalline cellulose as a stabilizing/structure-directing agent using a Co-precipitation method followed by post Microwave hydrothermal treatment. The prepared material was characterized for FTIR spectroscopy, SEM, TEM and XRD. From the SEM results it was identified that as the cellulose in the system directs rod shaped structures to LDH and this was further proved via TEM analysis. The main aim of this study is to identify cellulose polysaccharide as a structure directing agent and a size controlling agent. The use of cellulose during the synthesis has not hampered the formation of Layered double hydroxides structures which was further confirmed via XRD analysis. The prepared material is anticipated to be used as a catalyst and catalytic supports and in other applications.

Acknowledgement:

We would like to acknowledge NanoTalo, Aalto University, Finland for their help in taking the TEM microscopic images and also NCL, Pune, India for performing the XRD analysis.

Future perspective in PS research:

Exploitation of inexpensive and bio-friendly polysaccharide sources as structure directing agents, stabilizing agents in the synthesis of inorganic materials like LDH particles is a versatile and useful idea to improve their surface area, porosity, etc to enhance their biological, chemical applications.

Photopatterning of Cellulose Thin films - from Transistors to 3-D Microfabrication

Archim Wolfberger¹, Andreas Petritz², Alexander Fian², Jakob Herka¹, Volker Schmidt², Barbara Stadlober², Rupert Kargl^{3#}, Thomas Griesser¹, Katrin Niegelhell⁴, Stefan Spirk^{4#}

stefan.spirk@tugraz.at

¹ Chair of Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, 8700 Leoben, Austria

² Materials-Institute for Surface Technologies and Photonics, Joanneum Research Forschungsgesellschaft mbH, Franz-Pichler-Straße 30, 8160 Weiz, Austria

³ University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers, Smetanova 17, 2000 Maribor, Slovenia

⁴ Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

Member of the European Polysaccharide Network of Excellence

General topic: Polysaccharides in advanced applications

Keywords: Photolithography, Photopatterning, Transistors, 3-D microfabrication, 2-Photon absorption Lithography

Abstract:

In many areas of science and technology, patterned films and surfaces play a key role in the engineering and development of advanced materials. One of the main disadvantages of cellulose, however, is its poor solubility in common organic solvents and therefore its constrained processability, limiting its applications especially in the growing field of organic electronics. In order to overcome these limitations, various procedures for the regeneration of cellulose from organosoluble cellulose derivatives have been developed, paving the way towards novel biodegradable functional materials. A promising cellulose derivative for the preparation of cellulose thin films is trimethylsilyl cellulose (TMSC), which is soluble in several common organic solvents, including eco-friendly solvents such as ethanol and can be regenerated to cellulose by a treatment with vapors or solutions of hydrochloric acid. While such thin films have been widely employed to study and to understand the interaction of a variety of biomolecules with cellulose, micro- and macropatterned cellulose films have been shown to be promising materials for the fabrication of protein microarrays, high protein affinity matrices or for sensitive DNA. Here; we present a versatile toolbox that provides an easy non-destructive patterning method for cellulose thin films by means of photolithography and enzymatic digestion. A patterned UV illumination of trimethylsilyl cellulose (TMSC) thin films containing small amounts of a photo acid generator (PAG) leads to a desilylation reaction and thus to the formation of cellulose in the irradiated areas. Depending on the conditions of development, either negative- or positive-type cellulose structures can be obtained, offering lateral resolutions down to the single-digit micrometer range by means of contact photolithography. In order to highlight the potential of this material for advanced patterning techniques, cellulose structures with sub- μm resolution are fabricated by means of two-photon absorption lithography.

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Future perspective in PS research: In my opinion, polysaccharides will play a major role in the design of components in advanced applications such as transistors, batteries or photonic devices. However, to fully exploit the potential of these materials, more knowledge on the fundamentals of polysaccharides must be gained.



Biomass for cementitious building materials

Loan T. T. Vo^(*)

loan.vo@mines-paristech.fr

MINES ParisTech, PSL Research University, CEMEF - Centre de mise en forme des matériaux, CNRS UMR 7635, CS 10207 rue

Claude Daunesse 06904 Sophia Antipolis Cedex, France

Member of the European Polysaccharide Network of Excellence

General topic: Polysaccharides in advanced applications

Keywords: biomass, concrete, treatment, durability, mechanical properties

Abstract:

The use of biomass for developing energy efficient and low cost construction materials is an emerging field in building construction and civil engineering. Although the biomass-based cement and concrete composites have several advantages, such as low densities, low amount of CO₂ gas emission, good thermal and acoustic insulation etc. the durability in alkaline cement matrix, the high absorption of water and the problem of compatibility deteriorate their mechanical properties. Hence, the surface treatments and modifications of the fibers are required to overcome these drawbacks, to achieve the optimum performances of cement-based materials using biomass, and to improve the durability and compatibility for its use in the building materials. Several methods to modify fibers by chemical treatments or alter the compositions of cement binder have been proposed. A numerous works have been performed to value the use of biomass. However, the development and practical applications of these materials are still under a critical evaluation. Many problems still remain and need further investigations. If the mentioned problems are addressed and overcome, the long term performance is ensured, biomass-based construction and building materials can be industrially developed.

Acknowledgement:

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Future perspective in PS research:

The potential use of biomass to replace conventional materials appears to be feasible solution to solve problem of pollution, to reduce the amount of CO₂ emission from the production and to develop energy efficient and cost effective durable construction materials. Nevertheless, there is a vital need to translate the knowledge into downstream commercial activities.



Chitin nanofillers: from lobster shells wastes to new nanocomposite materials

Asier M. Salaberria, Susana C.M. Fernandes, Jalel Labidi

asier.martinez@ehu.es

University of Basque Country (UPV/EHU), Polytechnic School, Department of Chemical and Environmental Engineering,
Biorefinery Processes Research Group, Plaza Europa 1, 20018 Donostia-San Sebastian, Spain

General topic: Preparation of polysaccharide based materials

Keywords: chitin, nanocrystals, nanofibers, nanocomposites, chemical modification

Abstract:

Recently, increasing interest has been observed in the use of nanofillers from natural resources as structural and/or functional agents in composite materials, due to their unique properties, including renewable character, biodegradability, availability, biocompatibility, environmental friendly, etc.

Among the nanofillers from biopolymers, *i.e.* cellulose, chitin and starch, chitin nanofillers are the most unexploited. Chitin is widely distributed in nature (found in crustaceans, insects and fungi) and considered as the second most abundant natural polymer after cellulose. Like cellulose, chitin is a semi crystalline and high-molecular-weight linear polymer. However, a point of difference from other polysaccharides is the presence of nitrogen in its chemical structure. This particularity, makes chitin an important biopolymer because of its intrinsic biological properties, in particular, antimicrobial activity.

Chitin nanofillers can be obtained by different isolation methods, and depending on the used approach, different morphologies (nanocrystals or nanofibers) can be obtained. The unique properties, of chitin nanofiller, namely small size, low density, large surface, chemical reactivity, biological activity, and non-cytotoxicity make them unique candidates for use in a widespread range of applications (food, medical and pharmaceutical industries).

In this communication a general overview of the work that we have been developing in the Biorefinery Processes Research Group will be presented: (1) isolation of different chitin nanofillers by two different methods: acid hydrolysis (nanocrystals) and high pressure homogenization (nanofibers); (2) development of different types of valuable bionanocomposites (composites, films) using different biodegradable matrices (e.g., starch, chitosan and poly(lactic) acid); (3) characterization of the resulting materials in terms of chemical and crystal structure, morphology, optical, thermal, barrier and mechanical properties, and antifungal activity; (4) evaluation of the role of different chitin nanofiller morphologies on the structural and functional properties of resulting materials.

Acknowledgement: The authors are thankful for the financial support from the European Commission through the project ECLIPSE CP 280786.

Future perspective in PS research: i) Research around the different polysaccharides follows a growing trend, indicating in some way: (1) the growing interest on environmental friendly materials as alternative to fossil resources; and (2) the appearance of a new biopolymer increases the research work to develop; ii) Continued research on the optimization of extraction processes and fabrication of composites and materials, in order to reduce the cost of production, time and pollution. Making the materials from renewable resources more attractive for the big companies; iii) Fundamental research on chitin nanofillers, in order to understand the biological mechanisms of this biopolymer and the influence of their morphology.



Viscoelastic properties of cellulose nanofibril (CNF) hydrogels

Leila Jowkarderis¹, Theo G.M. van de Ven²

leila.jowkarderis@mail.mcgill.ca

¹Department of Chemical Engineering, McGill University, Montreal, Quebec H3A 0C5

²Pulp & Paper Research Center and Department of Chemistry, McGill University, Montreal, Quebec H3A 2A7

General topic: Polysaccharides in advanced applications

Keywords: Cellulose nanofibrils, Suspensions, Rheology, Ionic strength, polyelectrolyte

Abstract:

Increasing environmental concerns have led to efforts to replace petroleum based products with materials from bio-degradable and renewable sources. Cellulose nanofibrils (CNF), produced by disintegration of wood fibers, can be a promising candidate. Cellulose is a linear polysaccharide with a large number of hydroxyl groups. Cellulose nanofibrils (CNF) are long and thin rodlike particles, consisting of aligned cellulose molecules bundled together by hydrogen bonds. Owing to their high aspect ratio and high degree of crystallinity, cellulose nanofibrils in water make viscous suspensions and stiff gels, practical for many industrial applications. For example, CNF has been suggested as rheology modifier in food, paint, cosmetics, and pharmaceutical products. Therefore, knowledge of viscoelastic properties of CNF suspensions is important. In this work, the rheology of CNF hydrogels in dilute and semi-dilute regimes is studied. The effects of ionic strength and polyelectrolyte concentration are investigated by addition of NaCl, CaCl₂, and cationic polyacrylamide (C-PAM). The results show that the primary electroviscous effect significantly increases the intrinsic viscosity of CNF suspensions. Suspensions with higher mass fractions exert higher resistance against deformation and a higher degree of recovery, after releasing the stress, in creep-recovery tests. Low ionic strengths and polyelectrolyte concentrations increase the creep deformation because of screening the surface charge. Higher ionic strengths and polyelectrolyte concentrations lead to fibril aggregation, which stiffens the network structure and decreases the creep deformation. However, cationic polyacrylamide and calcium ions do not significantly affect the recovery response.

Acknowledgement:

NSERC Innovative Green Wood Fiber Products Network is acknowledged for funding the project. Thank to Forest Product Lab (Madison, WI) for providing CNF, and FP-Innovations (Montreal, QC) for providing access to their rheometer.

Future perspective in PS research:

Efforts should be dedicated to decreasing the preparation costs of polysaccharide based products, in order to advance them in industrial applications.

Extraction of maritime pine bark tannins for bio-based adhesives

Chupin Lucie^{1,2}, Charrier Bertrand¹, Charrier – El Bouhtoury Fatima¹

lucie.chupin@mines-paristech.fr

¹ University of Pau, IPREM-EPCP, CNRS/UPPA UMR 5254, IUT des Pays de l'Adour, 371 Rue du Ruisseau, BP 201, 40000 Mont de Marsan, France

² Mines ParisTech, CEMEF – Centre de Mise en Forme des Matériaux, CNRS UMR 7635, BP 207, 1 rue Claude Daunesse, 06904 Sophia Antipolis Cedex, France

General topic: Polysaccharides in advanced applications

Keywords: Extraction; adhesives; sugars; tannins; lignosulfonates.

Abstract:

The biggest maritime pine (*Pinus pinaster*) forest in Europe is located in the Aquitaine region in France. These trees are mostly cultivated for their timber, which are partly used to make particle boards. Even though the bark is rich in condensed tannins, it is not used much. Particle boards are glued with formaldehyde urea adhesives. However, the regulations for formaldehyde emissions are getting stricter, so new formaldehyde-free adhesives must be formulated.

A hot water based extraction was conducted on maritime pine bark, three conditions were tested. The extracts were characterised by their extraction yield, total polyphenols, total sugar content, condensed tannins. The condensed tannins extracted were identified by reverse phase high pressure liquid chromatography. Catechin was the main condensed tannin extracted. Epicatechin and epicatechin gallate were also identified. The thermal resistance of the extracts was determined by thermogravimetric analysis (TGA). The results showed that the extracts are stable up to 170°C.

The maritime pine bark extracts and lignosulfonates were used in wood adhesives formulation to eliminate resins based on formaldehyde. Two ammonium lignosulfonates and two sodium lignosulfonates were glyoxalated to be more reactive. The thermal properties of the cured resins were studied by TGA, differential scanning calorimetry (DSC). The curing temperature of the resins was determined by thermomechanical analysis (TMA). The TGA and DSC results showed that the resin formulations with glyoxalated sodium lignosulfonates were stable up to 200°C. On the other hand, the resin formulations with glyoxalated ammonium lignosulfonates were less stable to temperature and their degradation started at approximately 180°C. The curing of the resins started at 100 – 110°C to reach a peak at 150 – 170°C.

Acknowledgement:

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Future perspective in PS research:

Some trees' extracts are being used today as substitutes for formaldehyde in urea – formaldehyde resins for wood adhesives. Even if these extracts are rich in polysaccharides, only the condensed tannins' reactivity have been studied. Therefore, the implication of polysaccharides in the reactivity of extracts to make bio-based wood adhesives has to be investigated.



Chitin as a resource for production of chemicals

Małgorzata Królicka¹, Carmen G. Boeriu², Gerrit Eggink^{1,2}

malgorzata.krolicka@wur.nl

¹Wageningen University, Department of Bioprocess Engineering, PO Box 16, 6700 AA Wageningen, The Netherlands

²Wageningen UR & Biobased Research, Department of Biobased Products, PO BOX 17, 6700AA Wageningen, The Netherlands

Member of the European Polysaccharide Network of Excellence

General topic: Chemical and enzymatic functionalization of polysaccharides

Keywords: chitin, chitosan, glucosamine, enzymatic depolymerization

Abstract:

Chitin is the second most abundant polysaccharide in nature, after cellulose. Due to its abundance, chitin is a suitable almost unlimited resource for production of important carbohydrate based chemicals and materials. Currently commercial derivatives are chitosan, glucosamine (GlcN) and N-acetylglucosamine (GlcNAc). Their application is multidimensional, such as in food and nutrition, material science, drugs and pharmaceuticals as well as in agriculture. Nevertheless, chitosan, GlcN and GlcNAc are produced by chemical decomposition of chitin under harsh conditions. Because of the high environmental impact and low efficiency of the process, there is need to develop environmentally friendly and more efficient routes to produce sustainable products derived from chitin. In our study, we focus on an alternative process, which is an enzymatic depolymerization of chitin. We aim to apply specific chitinolytic enzymes in production of wide range of high-value chemicals using chitin as a feedstock.

Acknowledgement:

This research received funding from the Netherlands Organisation for Scientific Research (NWO) in the framework of the TASC Technology Area BIOMASS.

Future perspective in PS research:

In the past few decades the biochemical conversion of biomass, in particular the enzymatic conversion of polysaccharides, has received a great interest. In contrast to thermochemical conversion which leads to destruction of the carbohydrates under harsh conditions, enzymatic technology advantageously preserves the original carbohydrate structures and is used under mild conditions. Therefore, the enzymatic methods seem to be the best replacement for currently used chemical methods.



Cellulose nanocrystals used for the immobilization of polymer antioxidants

Sabrina Weigl¹, Klaus Bretterbauer², Christian Paulik¹

Sabrina.Weigl@jku.at

¹ Institute for Chemical Technology of Organic Materials, Johannes Kepler University Linz, Altenbergerstraße 69, 4040 Linz, Austria

² Profactor GmbH, Functional Surfaces and Nanostructures, Im Stadtgut A2, 4407 Steyr-Gleink, Austria

General topic: Chemical and enzymatic functionalization of polysaccharides

Keywords: cellulose nanocrystals, functionalization, antioxidants, immobilization

Abstract:

Cellulose nanomaterials are known as fillers and reinforcements for polymers to increase mechanical, thermal and barrier properties [1]. Their compatibility with hydrophobic polymers can be enhanced by chemical functionalization [2]. Additionally, polymeric materials need to be stabilized against degradation with antioxidants [3]. Commercially available antioxidants are known to migrate within a polymer and subsequently are physically lost and can contaminate its surrounding area [4,5]. This work presents the combination of antioxidant immobilization with the enhancement of polymer properties through cellulose nanocrystals. Antioxidants were grafted to cellulose nanocrystals (CNC), via two different functionalization routes. One was achieved by converting CNC to carboxymethyl cellulose nanocrystals with chloroacetic acid and subsequent amide formation by coupling of an amine functionalized antioxidant. The second was reached by reaction of an antioxidant acid chloride with CNC. The two different products were characterized using fourier transform infrared spectroscopy and nuclear magnetic resonance measurements whereby the covalent nature of the bonds is proved. The degree of substitution was determined through elemental analysis. Antioxidant grafted CNC were mixed to squalane and the oxidative induction time was measured to verify their antioxidant activity. Squalane was used as model substance for polypropylene due to its liquid state and therefore easier handling. Stabilizing activity of these immobilized antioxidants could be shown, however compared to commercially available antioxidants it is a weak effect. This can be explained by reduced mobility and poor dispersion of the antioxidants within squalane. To reduce the mobility was one of our goals and could not be changed. Nevertheless, dispersion could be improved through additional functionalization with aliphatic groups which lead to an extension of stabilization time.

Acknowledgement: The NMR spectrometer was acquired in collaboration with the University of South Bohemia (CZ) with financial support from the European Union through the EFRE INTERREG IV ETC-AT-CZ programme (project Moo146, "RERI-uasb").

Future perspective in PS research: Since polysaccharides are natural products and ubiquitous there will be an increasing interest in the context of environmental protection. Additionally, new PS based materials (inspired by nature) could expand the applications of several products.

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Access to Amphiphilic 4-(Alkyloxy)Aniline-Linked Chitooligosaccharide-2,5-Anhydro-D-Mannofuranose from Chitosan

Emil Salim¹, [Alice Galais](#)², Stéphane Trombotto¹

stephane.trombotto@univ-lyon1.fr

¹ Ingénierie des Matériaux Polymères (IMP, UMR CNRS 5223), Université Claude Bernard Lyon 1,

Université de Lyon, Villeurbanne F-69622, France

Member of the European Polysaccharide Network of Excellence

General topic: Chemical and enzymatic functionalization of polysaccharides

Keywords: chitosan; chitooligosaccharide-2,5-anhydro-D-mannofuranose; 4-(hexyloxy)aniline; nitrous deamination; reductive amination

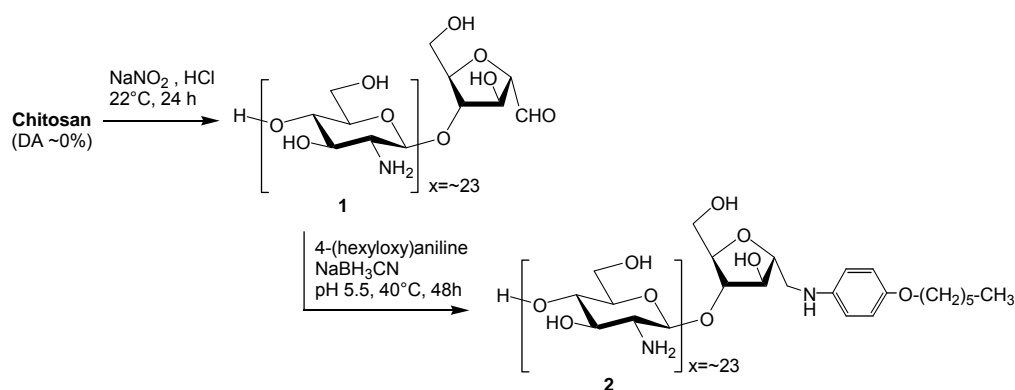
Abstract:

Chitosan is a random linear copolymer of D-glucosamine (GlcN) and N-acetyl-D-glucosamine (GlcNAc) units linked by β -(1 \rightarrow 4) glycosidic bonds. This polysaccharide is generally obtained by N-deacetylation of chitin, the second most abundant naturally occurring polymer produced industrially from shells of crustaceans and squid pens [1]. Chitosan oligomers, also named chitooligosaccharides (COS) have recently received considerable attention as functional biomolecules with a wide range of applications in food, agriculture, medicine, pharmaceuticals and cosmetics. Indeed, COS possess interesting physico-chemical and biological properties, including water-solubility, biocompatibility, antibacterial, antifungal and antitumoral activities [2]. In order to improve the scope of their properties, chemical modifications of COS have been investigated for a decade [3, 4].

In this work, we generated COS with one 2,5-anhydro-D-mannofuranose (amf) unit at their reducing end by nitrous deamination, and took advantage of the reactivity of the amf aldehyde group to obtain new COS derivatives through reductive amination coupling reactions [5].

The main challenge faced when preparing and derivatizing COSamf was to avoid the degradation of the amf unit through a Schiff-base reaction between the amf aldehyde group and the GlcN unit amine [10]. Structural characterizations of isolated COSamf showed the presence of a non-degraded amf unit at the reducing end that an effective control of their molar mass was possible by tuning the quantity of sodium nitrite added. We also show that COSamf can be linked to aniline derivatives in the presence of NaBH₃CN. An example will be presented with the synthesis of the amphiphilic 4-(hexyloxy)aniline-linked chitooligosaccharide-2,5-anhydro-D-mannofuranose. The targeted product, obtained in high yield, was fully characterized by NMR spectroscopy, MALDI-TOF mass spectrometry and size-exclusion chromatography.

This methodology can be applied to a large extent of aniline derivatives and it opens the way to a new generation of modified COS while preserving their inner structure.



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Future perspective in PS research:

I believe that polysaccharide research has a limited potential for the more classical industrial applications such as plasturgy: polysaccharides are difficult to adapt to purposes that oil-derived polymers were designed for, even if huge progress is made in terms of compatibilization, modification of properties, etc... In this context, there are thus little incentives for industrials to develop polysaccharides-based materials and the new production processes that they require. However, with extraordinary intrinsic properties such as bioactivity and biodegradability, and strong potential for chemical modification, polysaccharides (and chitosan in particular) are ideally suited for food and biomedical applications, where industries operate at the forefront of research and continually renew their production processes as new products emerge.

Oxidized Cereal Beta-Glucan and Iron – Reducing Capacity and Complexation Behavior

Samy Boulos¹, Martina Stettler¹, Laura Nyström¹

laura.nystroem@hest.ethz.ch

¹ ETH Zurich, Institute of Food, Nutrition and Health, Laboratory of Food Biochemistry, Schmelzbergstrasse 9, 8092 Zürich, Switzerland

Member of the European Polysaccharide Network of Excellence

General topic: Chemical and enzymatic functionalization of polysaccharides

Keywords: mixed linkage beta-glucan, hydroxyl radicals, Fenton reaction, ferricyanide reducing capacity, iron complexation, antioxidants

Abstract:

Mixed linkage (1->3,1->4)-beta-D-glucan (BG) is a soluble fiber predominantly found in oat and barley grains. Its EFSA and FDA approved health benefits - such as improvement of blood glucose regulation and reduction of cholesterol levels - make BG a promising functional food ingredient. During processing and storage, however, BG can degrade to lower-molecular-weight compounds with diminished viscosity and altered health benefits. Substances commonly present in foodstuff - such as transition metal traces (Fe or Cu) and ascorbic acid in contact with atmospheric oxygen - are enough to degrade the polymer with high viscosity loss in short time through the action of the Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 = \text{Fe}^{3+} + \text{HO}^\cdot + \text{OH}^-$). The degradation can be forced even without the addition of reducing agents to close the catalytic cycle. The aim of this study was to understand the role of the iron(III)-->iron(II) reduction by native vs. oxidized BG involved in the degradation cycle, as well as their iron complexation behavior. Pure BG was oxidized to various degrees with $\text{H}_2\text{O}_2/\text{FeSO}_4$ and then tested in spectrophotometrical assays for their ferricyanide reducing capacity and their iron complexation against ferrozine as ligand. Oat BG showed a slower increase in reducing capacity over oxidation time, indicating that it degrades more slowly than barley BG. Iron complexation, on the other hand, was stronger for oat than for barley BG, and increased slightly with increased oxidation time before diminishing again. The slower reactivity of oat BG could be attributed to the more tightly bound iron, slowing down the hydroxyl radical production in the catalytic cycle. Those results have implications regarding the use of BG as functional food ingredient, and the impact food processing might have on BG's potential antioxidant activity and altered iron bioavailability, especially in the case of oat BG in conjunction with iron fortification.

Acknowledgement: The authors thank Christophe Zeder (Laboratory of Human Nutrition, ETH Zurich) for the transition metal content analysis of oat and barley BG.

Future perspective in PS research:

The trend of raising the level of non-starch PS in food products continues because of their health promoting properties; however, consumer acceptability through changed sensory perception varies. Hence, future perspective lies in establishing structure - function - property relationship of food PS regarding both the technological properties (processing, emulsifying functions, hydration properties/water holding capacity, sensory perception) as well as the nutritional properties (digestion and health; role as prebiotics), ultimately, to reduce occurrence of diet-related diseases (type 2 diabetes, cardiovascular diseases, certain cancers).

Characterization of the chitin-glucan complex extracted from *Komagataella pastoris* cell wall

Inês Farinha¹, Paulo Duarte², Ana Pimentel², Evgeniya Plotnikova³, Bárbara Chagas¹, Luís Mafra⁴, Christian Grandfils³, Filomena Freitas^{1,*}, Elvira Fortunato², Maria A.M. Reis¹

: a4406@fct.unl.pt

¹ REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

² CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa and CEMOP-UNINOVA, Campus de Caparica, 2829-516 Caparica, Portugal

³ Interfaculty Research Centre of Biomaterials (CEIB), University of Liège, B-4000, Liège, Belgium

⁴ CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

General topic: Isolation and production of polysaccharides

Keywords: Chitin-glucan complex (CGC); *Komagataella pastoris*; Characterization; Thermal properties; Molecular Weight

Abstract:

Chitin-glucan complex (CGC) is a natural co-polymer composed of chitin and β -glucan which can be isolated from several fungi and yeast cell wall. To avoid inconsistency between batches, purified chitin-glucan complex (CGC_{pure}) was extracted from *Komagataella pastoris* biomass using an alkaline treatment with NaOH 5 M, at 65 °C, for 2 h, followed by neutralization with HCl 1 M and repeated washing with deionised water. The purified co-polymer had a glucan:chitin molar ratio of 75 : 25 with a low protein and inorganic salt contents (3.0 and 0.9 wt%, respectively). Its physico-chemical properties were evaluated and compared with other chitinous commercial biopolymers. CGC_{pure} had an average molecular weight of 4.9×10^5 Da with a polydispersity index of 1.7 and a crystallinity index of 50%. A degree of acetylation (DA) of 61% was determined by FTIR. X-ray diffraction and FTIR data support the persistence of β -chitin in the co-polymer. CGC_{pure} thermal analysis has highlighted an exothermic decomposition peak at 316 °C which can be assigned to the degradation of the saccharide structures.

CGC has therefore similar properties to chitinous commercial biopolymers and represents an attractive alternative to crustacean chitin derived-products and might be considered as a reliable raw material for the development of new/improved pharmaceutical, cosmetic or food products.

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Future perspective in PS research: Polysaccharides have a large potential in biomaterials research and their main challenges include both production and product development areas. It is increasingly important to develop more productive and cost effective polysaccharides bioproduction processes. Other future potential of polysaccharides research is the development of new polysaccharides-based products, competitive with chemical-based products that are already in the market.

Mechanism of copper adsorption on electrosterically stabilized nanocrystalline cellulose: From star-like bridging to raft-like aggregation

Salman SafariMohsenabad^{1,3*}, Amir Sheikhi^{2,3*}, Han Yang^{2,3}, Theo G. M. van de Ven^{2,3}

theo.vandeven@mcgill.ca

¹ McGill University, Department of Chemical Engineering, Montreal, Quebec H3A 0C5, Canada

² McGill University, Department of Chemistry, H3A 2A7 Montreal, Quebec, Canada

² McGill University, Department of Chemistry, Pulp and Paper Research Centre, H3A 2A7 Montreal, Quebec, Canada

³ McGill University, Centre for Self-Assembled Chemical Structures, H3A 2A7 Montreal, Quebec, Canada

*These authors contributed equally to this work.

General topic: Polysaccharides in advanced applications

Keywords: biodegradable adsorbents, nanocrystalline cellulose, copper removal, wastewater treatment, bridging interactions

Abstract:

Discharge of heavy metal ions such as copper from industrial waste to water poses a threat to aquatic life and has reproduction and developmental toxicity effect on humans. Removal of these ions using an efficient and low-cost method with low ecological footprint is a critical process in wastewater treatment, which can be achieved in a liquid phase using nanoadsorbents such as inorganic nanoparticles. Recently, attention has turned toward developing sustainable and environmentally-friendly nano-agents to remove heavy metal ions from aqueous media. Examples of such biodegradable adsorbents are nanocrystalline cellulose, bacterial cellulose and nanofibrillar cellulose.

In this work, we explore possibility of using electrosterically stabilized nanocrystalline cellulose (ENCC), a new nano-sized derivative of wood fibre developed by the van de Ven group, as a biodegradable nanoadsorbent. It is hypothesized that highly charged dicarboxylated cellulose chains are protruding from the crystalline part, which play a major role in stabilizing the ENCC suspension. Photometric dispersion analysis, a powerful technique to monitor the stability of aggregates, was used to study the strength of ENCC aggregates in presence of copper ions at a constant shear rate (390 S^{-1}). It was found that up to copper/ENCC ratio of $\sim 200 \text{ mg/g}$ the shear rate was sufficiently high to break the aggregates in less than a minute; however, at higher ratios, the aggregates resisted break-up. Transmission Electron Microscopy images of the suspending aggregates at copper/ENCC ratio of 100 mg/g revealed presence of star-like features consisting of a few ENCCs, whereas at copper/ENCC ratios higher than 200 mg/g lateral and head-to-head aggregation of ENCCs led to raft-like features. Furthermore, at pH 4 and copper and ENCC concentrations of 310 ppm and 1000 ppm , respectively, copper removal efficiency as high as $\sim 63\%$ was obtained corresponding to removal capacity of 195 mg/g , which places ENCC among adsorbents with high copper uptake capacity.

Acknowledgement:

Future perspective in PS research:

Nano-sized cellulose products could have potential applications in electronics as high surface area templates, water treatment as nano-adsorbents, and painting as stabilizers, where use of high surface area, biodegradable, and sustainable nano-materials is desired most.

Novel antitumor nanofibrous implants

Containing quaternized chitosan and gossypol with antitumor activity against *graffi* myeloid tumor

Kalin Kalinov¹, Milena Ignatova¹, Nevena Manolova^{1*}, Reneta Toshkova², Marin Alexandrov², Iliya Rashkov^{1*}

kkalinovlbap@gmail.com

¹Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 103A, BG-1113 Sofia, Bulgaria, *e-mail: rashkov@polymer.bas.bg

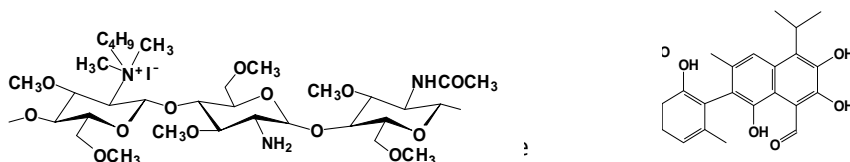
²Institute of Experimental Morphology, Pathology and Anthropology with Museum, Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 25, BG-1113 Sofia, Bulgaria

Member of the European Polysaccharide Network of Excellence

General topic: Polysaccharides in advanced applications

Keywords: Polysaccharides for biomedicine, pharmaceuticals, and healthcare systems

Abstract:



In the recent years there has been an increasing interest in the using of electrospinning for the fabrication of nanofibrous materials loaded with antitumor drugs for local tumor treatment. The specific properties of the electrospun materials related to their nanoscale size provide possibility for sustained release of the active substance leading to diminution of the cytotoxic impact and improvement of the therapeutic effect of the antitumor drugs [1].

Chitosan is a natural polysaccharide that is usually prepared by N-deacetylation of chitin. Chitosan is a polysaccharide non-toxic, biocompatible, biodegradable and non-immunogenic with inherent antitumor and immunomodulating properties [2]. It has been reported that quaternized chitosan derivatives (QCh) exhibit a good *in vitro* antitumor activity [3]. Antitumor implants containing both QCh and GOS gossypol (a plant polyphenolic compound with reported antitumor activity), exhibited higher cytotoxicity against Graffi tumor cells than that of free GOS. The *in vivo* antitumor efficacy of the QCh-coated and GOS-loaded nanofibrous implants was studied in golden hamsters bearing experimental Graffi myeloid tumor. The local postoperative treatment with the implants containing both QCh and GOS led to an increase in the animal survival rate and to a decrease in the percentage of recurrences and metastases of the Graffi tumor cells. These highly efficiency of the novel nanofibrous implants make them perspective for postoperative local application in treatment of solid tumors.

Acknowledgement: The study is partially financed under Grant DO 02-164/2008, Bulgarian National Science Fund.

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Future perspective in PS research: Combination of biodegradability and non-immunogenic with inherent antitumor and immunomodulating properties of polysaccharides like quaternized chitosan derivatives with the therapeutic effect of the antitumor drugs is a perspective strategy for postoperative local tumor treatment.



TEMPO oxidation of polysaccharides as a strategy to modify and enhance functional properties: comparison between chemical and chemoenzymatic approaches

Suse Botelho da Silva, Lambertus A.M. van den Broek, Carmen G. Boeriu

suse.botelhodasilva@wur.nl

Wageningen UR, Food & Biobased Research,

Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands

Member of the European Polysaccharide Network of Excellence

General topic: Chemical and enzymatic functionalization of polysaccharides

Keywords: 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), selective oxidation, chemoenzymatic modification, laccase, chitosan.

Abstract:

Cellulose, chitin/chitosan and starch are the most abundant polysaccharides in nature. They play an important role in the biobased economy, from production of fuels to application in food and pharmaceutical areas. These biopolymers can be used in their native form, or can be hydrolysed or modified in order to improve their functional properties. One of the strategies to modify these biopolymers is the selective oxidation of the primary hydroxyl groups with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a reaction mediator in a co-oxidative system. In the conventional chemical route, sodium hypochlorite and bromide are used as regenerating agents of TEMPO, while oxidative enzymes such as laccase can do the same in the chemoenzymatic approach. This work aims to present a comparison between chemical and chemoenzymatic approaches using TEMPO to oxidize cellulose, chitosan and starch. The work also shows preliminary results of the TEMPO/laccase system for the first time used to oxidize chitosan. Researches have shown in the last ten years that the co-oxidative systems using TEMPO as a mediator have been successful in improvement of the functional characteristics of products. The introduction of aldehydes and carboxyl groups in the structure have been demonstrated by FTIR, NMR and Maldi-Tof-MS techniques. Chemical and chemoenzymatic approaches can generate similar products, but the use of oxidative enzymes leads to a more sustainable process with lower environmental impact and lower waste generation. To the best of our knowledge, the chemoenzymatic approach to oxidize chitosan have not been reported in the literature before. Our first results of chitosan oxidation using TEMPO/laccase system show that it is possible to modify the polymer by introduction of new functional groups. Furthermore it was demonstrated that it was possible to control this process. The next step is to evaluate the functional characteristics of the synthesized products in order to propose some new applications.

Acknowledgement: CNPq-Brazil

Future perspective in PS research: Selective oxidation using TEMPO/laccase system will be a good strategy to enhance functional properties of chitosan in the coming years.



The effect of high pressure homogenization on pectin – Novel information regarding the importance of source dependent variation of pectin structure on the outcomes of processing

Avi Shpigelman^{1*}, Clare Kyomugasho², Stefanie Christiaens², Ann M. Van Loey², Marc E. Hendrickx²

*avis@bfe.technion.ac.il

¹ Technion- Israel Institute of Technology, Dept. of Biotechnology and Food Engineering, Haifa 3200003, Israel

² KU Leuven, Department of Microbial and Molecular Systems (M2S), Laboratory of Food Technology, Kasteelpark Arenberg 22, Box 2457, 3001 Leuven, Belgium

General topic: Polysaccharides in advanced applications

Keywords: pectin, high pressure homogenization, size exclusion multi angle laser light scattering (SEC-MALS), conformational changes

Abstract:

Pectin is a common, heterogeneous, and structurally complex polysaccharide present in plant cell walls that is naturally present in staple foods and commonly used in the food and biomedical industry. Pectin is known to be sensitive to process induced chemical changes that can result in various effects on its functionality. Often in literature the source of pectin is not mentioned or not taken into account when considering the outcomes of processing on its structure. This work aimed at better understanding the effects of high pressure homogenization (HPH), an emerging technology that can be used to influence rheological/textural properties and reduce the microbial activity of liquid food systems in a continuous process, on pectin. Our results show that the previously suggested depolymerization of pectin is dependent on its source, most likely due to the presence of neutral sugar (NS) side chains, a property which varies greatly. While citrus pectin (poor in NS) was depolymerized by HPH, apple pectin (richer in NS and having a more compact structure) was not. The depolymerization only occurred to pectins above a specific molecular weight (Mw) threshold, resulting in the possibility of utilization of this method for the production of a more uniform pectin, a possibly important application for producing low polydispersity polysaccharides for products requiring a high level of molecular weight control. Additionally, an effect for pH was noticed. At pH 6.3, the HPH induced conformational changes resulted in a more compact structure (for both pectins), while at pH 4.4 no conformational changes were noticed. HPH did not result in changes in the degree of methoxylation of both pectins and in the amount of reducing sugars.

Acknowledgement:

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Future perspective in PS research:

From my point of view several topics related to food/biotechnology can be expected to be hot in the next few years: 1) Utilization of natural polysaccharides for delivery. Such topic will require a more in-depth understanding of structural and self-assembly properties of polysaccharides and their derivatives. 2) The interaction of polysaccharides with the gut microbiota and the resulting possible health effects.



Interface science of cellulose and other polysaccharides

Rupert Kargl¹, Tamilselvan Mohan², Stefan Spirk³, Volker Ribitsch², Karin Stana Kleinschek¹

rupert.kargl@um.si

¹ University of Maribor[#], Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers,
Smetanova 17, 2000 Maribor, Slovenia

² University Graz[#], Institute of Chemistry, Heinrichstraße 28/III, AT-8010 Graz, Austria

³ University of Technology Graz, Institute for Chemistry and Technology of Materials,
Stremayrgasse 9, 8010 Graz, Austria

[#] Member of the European Polysaccharide Network of Excellence

General topic: Polysaccharides in advanced applications

Keywords: Quartz-Crystal-Microbalance, wettability, protein and polymer adsorption

Abstract:

The solid-gas and solid-liquid interface of polysaccharide based materials plays a crucial role when it comes to applications such as wound dressings, filtration membranes or biosensor supports. Profound knowledge on surface properties such as wettability, adhesion, topography and protein or polymer adsorption can lead to the improvement of existing, and the development of new materials. Many analytical methods are currently available for the investigation these phenomena. Polymer and protein adsorption for instance can be studied with surface sensitive methods such as a quartz crystal microbalance (QCM-D). This technique requires detailed know-how on the fabrication of thin polysaccharide films that are coated on the quartz sensor disks. These thin films can further be characterized with other surface analytical methods such as infrared or X-ray photoelectron spectroscopy. Available data on charges and contact angles can then be correlated to results obtained from QCM-D measurements. By exploiting the investigated surface phenomena, new applications for polysaccharides can be found. This presentation will give several examples on how cellulose and other polymer surfaces can be studied and modified with the mentioned techniques, in order to influence their protein and polymer adhesion and to selectively immobilize compounds that can be used as biosensor platforms or low-fouling coatings.

Acknowledgement: The research leading to these results has received funding from the European Union Seventh Framework Programme ([FP7/2007-2013]) under grant agreement n° [PIEF-GA-2012-331600] Poly-Inter-Faces.

Future perspective in PS research:

Owing to their natural origin, poly- and oligo-saccharide interfaces are ubiquitously found in living organisms. Glycoproteins, proteoglycans, glycolipids and peptidoglycans are only a few of a great variety that co-determine almost all biological functions. Immunorecognition, cell adhesion, growth or the action of antibiotics are often based on, and guided through, the polysaccharide structure on biointerfaces. These properties are studied in glycobiology and medicine but are almost neglected in material science. A future perspective in PS research is therefore seen in combining research in these areas.



Biocatalyzed esterification of starch in the ionic liquid

Arkadiusz Zarski¹, Sylwia Ptak^{1,2}, Sandra Zdanowska¹, Przemyslaw Siemion¹, Janusz Kapusniak¹

arkadiusz.zarski@ajd.czest.pl

¹Jan Dlugosz University in Czestochowa, Faculty of Mathematics and Natural Sciences, Institute of Chemistry, Environmental Protection and Biotechnology, 13/15 Armii Krajowej Ave., 42-200 Czestochowa, Poland

²Technical University of Lodz, Faculty of Biotechnology and Food Sciences, Institute of Technical Biochemistry, 4/10 Stefanowskiego Str, 90-924 Lodz, Poland

General topic: Chemical and enzymatic functionalization of polysaccharides

Keywords: starch, esterification, lipase, ionic liquids, hydrophobization

Abstract:

Starch – natural, renewable, biodegradable, non-toxic and cheap raw material is of great interest due to its application in food, paper, pharmaceutical and packaging industries. The modified starches are more desirable for the industry than native. Modification of native starch by hydrophobization is carried out in order to improve its mechanical and processing properties (reduction of viscosity, increase in thermoplasticity and moisture resistance). Esterification is one of the most important ways to modify starch. Bio-catalyzed esterification of polysaccharides is relatively environmentally friendly due to lack of by-products and very mild process conditions. Usually, starch is esterified by acid anhydrides or fatty acids. Fatty acids starch esters are among the most important starch derivatives.

The aim of the study was to obtain potato starch oleates by lipase catalysed esterification of starch in an ionic liquid (1-butyl-3-methylimidazolium chloride). *Thermomyces lanuginosus* lipase immobilized on the polymer carrier was used. The esterification was carried out in an oil bath at different temperatures (60, 70, or 80°C) for 4, 6 or 8 hours. Constant molar ratio of starch to oleic acid (1: 3) was used. In order to confirm esterification reaction products were subjected to Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) analyses. Moreover, degree of substitution (DS) was determined by titration method and elemental analysis. Scanning electron microscope (SEM) was used to characterize the morphology of modified starches.

Acknowledgement: Future perspective in PS research: Modifications of polysaccharides for the preparation of biodegradable and functional packaging materials. The use of polysaccharides and their derivatives as bio-active agents or as carriers of these agents.



Structural morphology of cellulose nanocrystals extracted from chili leftover and their reinforcement in cariflex-IR rubber latex

Malladi Nagalakshmaiah^{1,2}, Nadia Elkissi¹, Alain Dufresne²

¹Laboratoire Rhéologie et Procédés, 63 rue de la Chimie- Bâtiment B - Domaine Uni-versitaire - BP 53 - 38041 Grenoble cedex 9.

²Laboratoire de Génie des procédés papetiers (LGP2) Grenoble

nagalakshmaiah.malladi@ujf-grenoble.fr, elkissi@ujf-grenoble.fr, alain.dufresne@pagora.grenoble-inp.fr

General topic: Isolation and production of polysaccharides

Keywords: cellulose nanocrystals, aspect ratio, scanning electron microscopy, dynamic mechanical analyzer and tensile test.

Abstract:

The morphology and chemical composition of chili fibers were investigated. Unusual low lignin content was found when compared to the other annual plants. High aspect ratio cellulose whiskers were prepared from chili fibers by an acid hydrolysis treatment. The length and diameter of the chili leftover whisker were 240-320nm and 4-6 nm respectively resulting in an average aspect ratio of 46. The good aspect ratio ensures the percolation which in turn results in high thermal and mechanical properties of the nanocomposites at low filler content. The whiskers were used as filler in the highly marketing commercial latex called Cariflex-Isoprene (IR) by casting in order to prove their reinforcement. Cellulose nanocrystals from chili left over were characterized using FT-IR, AFM and X-rd to understand functional, structural and degree of crystallinity respectively. Latex composites has improved mechanical properties in both linear and nonlinear ranges when studied by using DMA, Tensile test and their morphology was studied using scanning electron microscopy.

Electrospinning fabrication of bio-based antibacterial and antioxidant materials using olive leaf extract

Zdenka Persin^{1,#}, Manja Kurecic^{1,2,#}, Matej Ravber³, Karin Stana Kleinschek^{1,#}, Zeljko Knez³, Mojca Skerget³

zdenka.persin@um.si

¹University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers,
Smetanova 17, 2000 Maribor, Slovenia

²Center of Excellency PoliMaT, Tehnoloski park 24, 1000 Ljubljana, Slovenia

³University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory of Separation Processes and Product Design,
Smetanova 17, 2000 Maribor, Slovenia

Member of the European Polysaccharide Network of Excellence

General topic: Polysaccharides in advanced applications

Keywords: Electrospinning, oleuropein, hydroxytyrosol, antioxidativity, antimicrobial

Abstract:

Electrospinning is a method of producing ultra-fine fibres with micro and nano range diameter using electrostatic forces. The ultrafine fibres are generated by application of a strong electric field on polymer solution, i.e. using synthetic or natural polymers dissolved in water or organic liquids. The fibre thickness and morphology can be controlled by many parameters, such as solution properties (viscosity, conductivity and surface tension), electric field strength, distance between rotating cylinder electrode and collecting plate, temperature and humidity. By selecting a combination of proper components and by adjusting the components ratio, properties of electrospun nanofibres can be tailored with desired new functions.

In present study we focused on formation of electrospun nanofibres using natural polymers (carboxymethylcellulose and alginate), calcium chloride and olive leaf extract. The extract was obtained by water extraction using olive leaves that present a waste material during tree lopping. Olive tree and its natural products (leaves, oil, and fruits) possess antioxidative and antimicrobial properties due to high content of phenolic groups. Besides taking advantage of the material composition, the electrospinning fabrication process, through which the fibre diameter, morphology and porosity can be manipulated, was evaluated by scanning electron microscopy. The presence of phenolic groups was assessed by High-Performance Liquid Chromatography, while antioxidative activity was determined using DPPH radical scavenging. The antimicrobial properties were tested using pathogen microorganisms, mostly present in spoiled food.

The results show that the electrospinning technology offer versatility and unique nanostructure material with desired properties. The incorporation of olive leaf extract presents a potential packaging material used for food preservation.

Acknowledgement: The authors would like to acknowledge the operation entitled "Centre of Open innovation and ResEarch UM", co-founded by the European Regional Development Fund.

Future perspective in PS research: Our research shows that natural compounds integrated in polysaccharide materials have very good antimicrobial activity they could represent a good possibility to replace the inorganic silver ions, used widely as antimicrobial agents in different fields. Due to the need to replace silver ions used in food packaging materials as well as materials for medical applications, our vision in further research is to exploit the antimicrobial activity of different plant extracts, which will combine the antimicrobial and outstanding antioxidant activity in developed polysaccharide materials.



Functionalization of polysaccharides and their derivatives by multi-walled carbon nanotubes

Sandra Zdanowska¹, Magdalena Pyzalska¹, Damian Kulawik¹, Arkadiusz Żarski¹, Wojciech Ciesielski¹, Józef Drabowicz^{1,2}

sandra.zdanowska@ajd.czest.pl

¹Jan Dlugosz University in Czestochowa, Faculty of Mathematics and Natural Sciences, Institute of Chemistry, Environmental Protection and Biotechnology, Ave. Armii Krajowej 13/15, 42-200 Czestochowa, Poland

²Center of Molecular and Macromolecular Studies Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

General topic: Polysaccharides in advanced applications

Keywords: β -cyclodextrin, starch, esterification, multi-walled carbon nanotubes

Abstract:

Modifications of polysaccharides or their derivatives using carbon nanotubes give hope to create new materials with a wide spectrum of action and huge possibilities of application, e.g., materials capable of storing energy. One of the functionalization methods can be esterification. This reaction is impossible for an unsubstituted multi-walled carbon nanotubes (MWCNTs), but it is possible when MWCNTs contain reactive chemical groups, like carbonyl group. Esterification of native starch by previously oxidized multi-walled carbon nanotubes - can lead to a hydrophobization of a polysaccharide, and can therefore improve its processing abilities. If in the above reaction β - cyclodextrin replace native starch, the solubility of MWCNTs will increase. The aim of study was to esterification of native starch and β - cyclodextrin using oxidized MWCNTs. Reactions were carried out in the following way:

- 1) The reaction with native starch was proceeded in aqua environment. The starch was gelatinized and was added carbon nanotubes in 1:1 weight ratio. After reaction the mixture was cleaned and dried in temperature 500C.
- 2) The reaction with β -cyclodextrin was proceeded in pyridine. This process was carried out 2 days in 100°C. After this time the mixture was cleaned and dried in temperature 500C.

Thermal analysis (TG/DSC) of unsubstituted MWCNTs, oxidized MWCNTs and (starch or β -CD)/MWCNT system were made. The thermal behavior of investigated systems indicates the formation of complexes/systems complexes. The products of esterification were also characterized by scanning electron microscope (SEM) with EDS detector, electrochemical studies and FTIR spectroscopy. This analysis show significant changes and possibility of creation of new structures. Realization of this project will lead to an enlargement of libraries of functionalized nanotubes and show new physico-chemical properties useful when one considers the application of the designed derivatives.

Acknowledgement: This project was financially supported (grant to JD) by the National Science Center fund awarded based on the decision UMO-2011/01/B/ST5/06304

Future perspective in PS research: Battery cells built with the multi-walled carbon nanotubes (MWCNTs) and polysaccharides and their derivatives are currently used competition for gel batteries, which have a higher mass than our cells, and that will translate into better application in automotive and aviation reducing operating costs.



Preparation and characterization of sterically stabilized nanocrystalline cellulose obtained by periodate oxidation of cellulose fibers

Han Yang¹, Dezhi Chen², Theo G. M. van de Ven¹

¹Department of Chemistry, ²Department of Chemical Engineering,

^{1,2}Pulp and Paper Research Centre, McGill University, Montreal, H3A 2A7, QC, Canada

theo.vandeven@McGill.CA

Member of the European Polysaccharide Network of Excellence

General topic: Preparation of polysaccharide based materials

Keywords: Periodate oxidation, Nanocellulose

Abstract:

We produced novel nanocellulose particles made from cellulose fibers by periodate oxidation. For partial oxidation ($DS < 2$), three products were generated after the periodate oxidized fibers were heat treated: fibrous cellulose, rod-like DAC (dialdehyde cellulose) nanofibers which we refer to as sterically stabilized nanocrystalline cellulose (SNCC), and dissolved DAC which is a copolymer of cellulose and DAC which we refer to as DAMC (dialdehyde modified cellulose). The products were separated by centrifugation and cosolvent addition. SNCC has similar dimension as conventional nanocrystalline cellulose (NCC) made by sulfuric acid hydrolysis. Several techniques were applied to characterize SNCC and its properties are compared to NCC. DAMC was found to be soluble in hot water, but was insoluble in most common solvents at room temperature but soluble in a few solvents at elevated temperature. The molecular weight of DAC ($DS = 2$) produced under various conditions (heating time and temperature) was determined by gel permeation chromatography (GPC). It was shown that the molecular weight decreased with heating time and residence time when cooled down to room temperature.

Acknowledgement:

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Future perspective in PS research:

Nanocellulose films have many advantages, including renewable, non-toxic, biodegradable, good barrier property and strength. Nanocellulose films have the potential to substitute the conventional plastics, and will bring lots of benefits to forest-based industry, due to the increasing consuming of packaging materials.



The Formation of Silver Nanoparticles Using Cationic Cellulose Nanocrystals: No Added Reducing Agent or Stabilizer

Wei Chung Chen, Theo G.M. van de Ven

McGill University

Abstract:

Plant-based materials such as cellulose and lignin possess qualities that are beyond renewability. It has been demonstrated by many researchers that plants are great antioxidants, which also suggests the ability to act as a reducing agent. Making use of this notion, in the present work, silver nanoparticles with a narrow size distribution (10nm) were formed by the reduction of silver nitrate using cationic cellulose nanocrystals (CNC). Elemental analysis with electron dispersion x-ray spectrometry (EDX) and x-ray photospectrometry (XPS) suggest the formation of silver nanoparticles of low chlorine content stabilized by saccharides. The yield of the product is 70% based on analysis with inductively coupled plasma atomic emission spectroscopy (ICP-AES). By eliminating the need for reducing agents and stabilizers, this technique is more efficient than current methods of silver nanoparticle production.

Future Perspectives of Xanthan polymer for Enhanced Oil recovery (EOR) application.

Sofia GHOURASSI- BARR¹, Djamel ALIOUCHE⁴, Bruno .Grassl², Sylvie dagreou³

¹Division Technologies et Développement -DTD (ex CRD), Direction Géologie SONATRACH, Avenue du 1er Novembre, Boumerdès, 35000, Algérie (sofiabarr70@yahoo.fr / sofia.ghomrassi@ep.sonatrach.dz)

^{2,3}Laboratoire de Physico-Chimie des polymères, IPREM UMR CNRS/UPPA 5254, Pau, France (bruno.grassl@univ-pau.fr/ sylvie.dagreou@univ-pau.fr)

⁴Directeur de Laboratoire traitement et mise en forme de polymères, Université M'HAMED BOUGUERRA Boumerdès 35000, Algérie (aliouche_dj@umbb.dz@yahoo.fr)

Keywords: Biopolymer –xanthan gum –Rhéological properties - characterization .

Abstract:

Xanthan is a bacterial polysaccharide that is much used in industrial applications as stabilizer and texturant. Xanthan gum is also used in flocculation in food, petroleum (in process of perforations for oil recovery), pharmaceutical, cosmetics, paint, textile and agricultural products (in suspensions, as an agent for stabilizing herbicides, pesticides, fertilizers and fungicides). For this reason the dynamic mechanical properties of xanthan in aqueous solution have been investigated extensively. In this article we are interested in the use of xanthan gum in the oil sector, mainly in the oil recovery. At present, xanthan gum is one of the two commonly water-soluble polymers used for polymer flooding, and makes a more excellent performance in salt resistance than that of hydrolyzed polyacrylamide (HPAM) in EOR. The objective of this study, was first to characterize the xanthan gum and analyze the chemical composition from the data collected by the infrared spectra, ¹H NMR, High-pressure Steric Exclusion Chromatography, Wide Angle X-ray Scattering, thermal properties and obtain information of rheological behavior in order to provide basic data for the application of xanthan gum in EOR.

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