2\textsuperscript{nd} International EPNOE Junior Scientists Meeting

»FUTURE PERSPECTIVES IN POLYSACCHARIDE RESEARCH«

BOOK OF ABSTRACTS

13-14\textsuperscript{th} October 2016

Sophia Antipolis, France

Materials Forming Center (CEMEF) of Mines ParisTech

Organised by:
The meeting was co-funded by the EPNOE CSA and is a European commission funded project that started March 1st, 2012 for a duration of three years (2012-2014). The Cellulose and Renewable Materials Division of the ‘American Chemical Society’, 'Elsevier B.V.', ‘Springer International Publishing AG’, and ‘Lenzing AG’ support the meeting financially.

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INTERNATIONAL EPNOE Junior Scientists Meeting (2 ; 2016 ; Sophia Antipolis)

1. Gl. stv. nasl. 2. Freire, Carmen 3. Cemef
COBISS.SI-ID 88561665
FOREWORD

Dear Students, Colleagues, and Friends,

polysaccharides are fascinating and versatile in many ways. They are the most abundant organic compounds in nature and ubiquitous as major components in many plants and marine organisms. As such, polysaccharides are renewable bioresources of increasing value in the continuous quest for sustainable and carbon neutral alternatives to fossil based materials and energy. Polysaccharide based materials are also indispensable in countless everyday life products; from wood and paper derived products over derivatives like cellulose esters and ethers that are produced in kiloton scale for various applications to high value-added biomedical and pharmaceutical materials. Thus, it’s only natural that polysaccharide research is a diverse area with many facet that brings together scientist from many different branches; from organic chemistry to biology, from applied material sciences to theoretical computational sciences and life-cycle-assessments, from biomedicine to food, agriculture, and forestry sciences.

The “European Polysaccharide Network of Excellence” (EPNOE) is an organization dedicated to promote research in the vast area of polysaccharides. It provides a platform for interdisciplinary discussion and knowledge transfer among companies, academia, and research institutes. One of EPNOE’s main missions in this regard is to organize the education, high-level qualification, and carrier development of young researchers. In this spirit, the “1st EPNOE Junior Scientist Meeting” was held January 19/20 2015 in Wageningen/The Netherlands. It was specifically addressed to PhD students, Post-Doctoral scientists, and junior Professors only and provided a unique platform for about 40 participants to present and discuss their personal visions on future aspects of polysaccharide research among fellow young colleagues. The "2nd EPNOE Junior Scientist Meeting", which will be held October 13/14 2016 at the ‘MINES ParisTech Centre de Mise en Forme des matériaux’ (CEMEF) in Sophia-Antipolis/France, will continue this tradition. Thereby, it was possible to raise the visibility of the meeting within the European Community and beyond resulting in over 80 active oral and poster presentations from over 20 different countries.

This is also reflected by the fact that four renowned sponsors, namely ‘The Cellulose and Renewable Materials Division’ of the ‘American Chemical Society’, ‘Elsevier B.V.’, ‘Springer International Publishing AG’, and ‘Lenzing AG’ were interested to support the meeting financially.

As a final personal remark I would like to emphasize that it is a great pleasure to have the event being hosted in Sophia-Antipolis. Thanks to an EPNOE sponsored student exchange, I had the chance to spend as substantial time of my PhD studies at CEMEF. Thus, I am looking forward to meet you at the upcoming Junior Scientist Meeting at the beautiful French Riviera.

On behalf of the organizing comity

Martin Gericke

Jena, 08.09.2016
Topics and Scientific Program:

Contributions from fundamental, as well as applied research are highly welcomed. The call is open to all polysaccharide related topics including but not limited to:

- **Fundamental polysaccharide research**: theoretical/experimental studies on dissolution/regeneration of polysaccharides, computational analysis of polysaccharide assembling/disassembling, advanced techniques for the characterization of polysaccharides, interaction of polysaccharides with other compounds.

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

- **Biological and pharmaceutical aspects**: biosynthesis of polysaccharides, genetic engineering/characterization of plants with respect to polysaccharide components, application of polysaccharides as pharmaceuticals or cosmetics.

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

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

- **Polysaccharide based materials**: innovative processes for shaping of polysaccharides (e.g., into fibres, films, membranes), “non-classical” polysaccharide shapes (e.g., particles, hydrogels, aerogels), polysaccharide composites with organic/inorganic materials, nanostructured polysaccharide based materials, materials 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.
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Polysaccharide research at Lenzing AG

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Keywords:

Abstract:  
With over 75 years of experience Lenzing AG today is the leading producer of wood-based cellulose fibers. R&D has been an important part of the business ever since and is also an integral part of the new company strategy sCore TEN. Within the frame of this strategy the biorefinery concept will be further exploited as Lenzing AG owns two pulp mills also. Already today Lenzing has a portfolio of co-products (like acidic acid or sodium sulphate) in addition to the core business fibers (like TENCEL\textsuperscript{®}). Regarding wood-based cellulose fibers the whole value chain is covered and developments include technology improvements as well as new applications. All these developments are conducted by a team of 170 dedicated experts from Global R&D located in Lenzing together with other departments like production or business management.

References:

Future perspective in polysaccharide research:  
With sustainability becoming more and more an important topic, for both manufacturers and consumers, and the need for materials from renewable resources there is a bright future for polysaccharide research. And the field is vast, reaching from a renaissance of rather old topics to brand new developments.
Sapperite, six million years old cellulose. Formation, structure and properties

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Keywords:
Cellulose fiber, paleobiology, delignification

Abstract:
Cellulose is the major abundant biopolymer since it has been one of the main components of all higher plants since the Silurian. However, there is a lack of knowledge on very old, rather pure native cellulosic samples available which allows for a deeper understanding of cell wall interactions in a geological context. Here, we describe the properties of a Miocene basaltic mineral, namely Sapperite, which contains native cellulose fibers embedded into an apophyllite, an aluminosilicate, matrix. The incorporated fibers originate from a conifer, which was buried in the course of volcanic activity six million years ago in Southern Austria. We prove that the mechanically extracted fibers in this mineral are not silicified/petrified by a wide range of techniques including soft X-ray tomography, and RAMAN spectroscopy. The fibers are structurally intact as shown in high resolution transmission electron microscopy and they are still bioavailable to cellulose digesting enzymes such as cellulases as proven by real time video-AFM studies. The white fibers do not contain any lignins which probably have been removed by either lignin digesting fungi or via geologic pulping. These results demonstrate that cellulose can be rather resistant against degradation under protective microenvironments and that pure cellulose fibers in their native state can endure for millions of years.

References:

Future perspective in polysaccharide research:

In my opinion, polysaccharides will take a large role in biorefinery processes. However, to be sustainable only waste materials should be used which are neither competing with nutrition purposes nor with other processes where materials are manufactured.
Pulp fines – Investigating the smallest constituent parts of the paper network

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Keywords:
Pulp, fines, cellulosic particles

Abstract:
Pulp fines are a by-product of the pulping (primary fines, mechanical fines) as well as the refining process (secondary fines) [1]. These particles, which are the smallest constituent parts of the paper network, are defined as the pulp fraction which is able to pass through a 200 mesh screen of a so called Bauer McNett fractionator (75 m hole diameter) [2]. The size of this material ranges from the nanometer to the micrometer scale and the morphological as well as chemical properties of fines differ from those of fibers. Fines are also known to promote the mechanical properties of the final product [1]. When adding these cellulosic particles to pulp, paper properties such as tensile strength can be improved. In order to better understand the properties of fines as well as how fines influence paper properties, this material needs to be isolated from the pulp and investigated as a separate material.

In the present study, the properties of fines and their effect on the final product are investigated. Handsheets made of pure fines as well as paper sheets having defined amounts of fines are prepared and their properties are determined. In addition, also the morphological properties of different types of fines are investigated. Knowing the properties of fines will contribute to a better understanding of how these particles influence the final product.

References:


Future perspective in polysaccharide research:

Fines are a by-product of the pulping process and might be an alternative for the production of composite materials. Furthermore, this material can also be used as a potential source for xylan and fatty acids.
Extraction of flax cell wall components and its role on the microstructure and mechanical behaviour of flax fabrics reinforced biocomposites

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Keywords:
Biocomposites; Epoxy; Flax fibres; Cell wall components; Microstructure; Mechanical behaviour

Abstract:
Mechanical and chemical processes used in the separation of flax fibres for the production of technical flax fabrics and other flax products are likely to modify the surface chemistry, and the inter and intra-cellular supramolecular structures of the fibres, in particular by the extraction of some non-cellulosic components. One might wonder about the influence of these treatments on the resulting physical properties of the fibres and their biocomposites. In this work, we investigated the effect of selected chemical extraction treatments on the biochemical composition and physical chemical properties of flax fabrics and their influence on the microstructure and mechanical behaviour of thermo-compressed flax fabrics reinforced epoxy biocomposites. A unidirectional (UD) flax tow woven fabric with minimal processing was chosen in order to retain as much of the original flax cell wall structure as possible. The flax fabrics were treated by various aqueous and organic solvents with increasing solvation capacity, so as to gradually extract inter and intra-cellular non-cellulosic components from the fibres. The treated flax fibre fabrics were characterized in terms of biochemical composition, wettabillity and dimensional characteristics. The influence of chemical extraction treatments and the role of cell wall components on the microstructural and mechanical properties of UD flax/epoxy biocomposites were investigated and discussed by means of Scanning Electron Microscopy (SEM), image analysis, differential scanning Calorimetry (DSC) and transverse tensile tests. Our results demonstrate that the extraction of non-cellulosic cell wall components from flax fibres modifies greatly the dispersion of flax yarns within the epoxy matrix, hence generating a higher specific interface between the fibres and the matrix. The transverse mechanical behaviour related to interfacial adhesion is also significantly influence by the extraction treatments, attesting for the key role of non-cellulosic components in the mechanisms of transfer loading fibre/fibre and fibre/matrix within biocomposites.

Acknowledgement:
The authors gratefully thank ADEME for its financial support, N°TEZ12-26.

References:
Acrera Fernández et al. (2016) Role of flax cell wall components on the microstructure and transverse mechanical behaviour of flax fabrics reinforced epoxy biocomposites, Industrial Crops and Products, 85, 93-108

Future perspective in polysaccharide research:
This research work highlights the need for the development of selective and non-degrading treatments so as to better control the final performances of natural fibres reinforced biocomposites.
Humidity dependent mechanical properties of cellulose materials investigated by atomic force microscopy

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Keywords:
Atomic Force Microscopy; Cellulose; Mechanical Properties; Nanoindentation; Relative Humidity;

Abstract:
The ability of cellulose fibers to change their mechanical properties within about two orders of magnitude due to water uptake [1] is exploited on a daily basis during papermaking. Only when the wood fibers are wet and swollen, it is possible for two fibers to align to each other and form a high area in molecular contact [2]. When a high area in molecular contact is formed, the fiber-to-fiber bond is obviously stronger than one with less area in molecular contact. This means that by tuning the mechanical properties of any cellulose fiber material, the strength of the bond between two fibers can be tuned. Here, an atomic force microscopy (AFM) based nanoindentation method is used to measure hardness and elastic modulus of cellulose materials under controlled relative humidity. The lower these two quantities become in the fully swollen state, the higher the area in molecular contact of a fiber-to-fiber bond can become. These two properties can also be influenced by e.g. changing the ion concentration of the swelling solution or changing the composition of a fiber by, e.g., mixing hemicellulose to the material. Furthermore, the geometrically observed swelling (increase of fiber diameter due to water uptake) could be related experimentally to the decrease in hardness and elastic modulus.

All in all, AFM based nanoindentation in humidity controlled setup proved to be a very useful method to study how the mechanical properties of cellulose materials change with water uptake.

References:

Future perspective in polysaccharide research:

In future and already ongoing research, we will explore the possibility to detect viscoelastic properties using an atomic force microscope with large radius AFM tips. By investigating the time dependent material response, it is possible to extract the materials viscosity in addition to the elastic moduli. Such information is a useful input for, e.g., simulations of paper network mechanics.
Mechanical properties of physically blended cellulose acetate/thermoplastic urethane-blends

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Keywords:
cellulose acetate, thermoplastic urethane, physical blending

Abstract:

Thermoplastic cellulose acetate (CA) as a bio-based polymer exhibits outstanding properties such as high transparency, high stability and stiffness. It is comparable with petrochemical based polymers like acrylonitrilebutadiene-styrene (ABS) or polystyrene (PS) which are mainly used for technical applications. These polymers offer an excellent combination between toughness, stiffness and easy processing. However, these materials are derived from petrochemical resources and non-renewable. CA can be an environmentally friendly and sustainable alternative. It is derived from renewable resources and offers mechanical properties comparable to ABS or PS, except for its low impact resistance and high notch sensitivity. Therefore, research is needed to overcome these deficits.

In the literature it is well described that bio-based stiff polymers like poly lactic acid (PLA) can be toughened with thermoplastic urethanes\textsuperscript{[3,2]}. This is due to the high intermolecular forces which are formed between the hydrogen groups of the PLA and the urethane groups of the TPU. As PLA, cellulose acetate also contains free hydrogen groups, which can interact with the free urethane groups of the TPU. To test this hypothesis, blends of cellulose acetate and thermoplastic urethane (from 2.5 to 15 wt.-%) were physically blended and the effects of TPU addition on notch sensitivity and toughness of CA were studied. The mechanical properties like modulus and tensile strength of the CA/TPU blends decrease with rising TPU content, just like it is expected for these immiscible polymers. To verify if a decrease in notch sensitivity can be achieved by increasing the TPU content charpy notched impact tests were conducted. It was found that the notched impact strength can be slightly increased due to energy dissipation of the TPU up to a content of 7.5 wt.-% in the blends. A further increase of the TPU content in the blend, however, leads to lower notched impact strength values.

References:


Future perspective in polysaccharide research:

The next investigations will be focussing on the compatibilisation of the thermodynamically immiscible CA/TPU blend system. Using appropriate compatibilisers can lead to improved mechanical properties of the materials offering new market opportunities for cellulose acetate in technical applications.
Towards a better understanding of the role of mechanics in enzymatic degradation of plant biomass

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Keywords:
lignocellulose, hydrolysis, mechanics, bioprocessing

Abstract:
For any industrial biorefining process based on degradation of insoluble plant biomass to be economically feasible, the enzymatic hydrolysis step needs to take place at high solids loading [1]. However, absence of free water during saccharification limits the rate of hydrolysis [1], so it is essential to achieve liquefaction during the initial phase of the hydrolysis. Mechanical forces acting on fibers during enzymatic breakdown of biomass have been shown to play a vital role in liquefaction. Research has shown that particle size reduction takes place during liquefaction for several different types of plant biomass, and for different dry matter contents [2]. Specifically, it has been found that the longest dimension of the particles, i.e. the length, decreases as elongated particles break into shorter segments. Further, it has been shown that liquefaction rate is faster when saccharification takes place in a horizontal rotating reactor where agitation is based on gravity, so-called free fall hydrolysis [1]. This study attempts to improve the fundamental understanding of the interrelation between mechanical and biological degradation mechanisms of insoluble plant biomass during free fall hydrolysis. Results show that both reactor parameters (i.e. reactor dimensions) and enzymatic hydrolysis conditions (i.e. enzyme loading and dry matter content) affect the rate of liquefaction and saccharification, and that these effects are furthermore confounded.

References:

Future perspective in polysaccharide research:
These findings suggest that reactor configuration and operation conditions are key to process optimization.
Wettability of cellulosic porous media by capillary impregnation

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Keywords:
wettability, natural fibre, capillary rise method, paper filter, interface.

Abstract:
Biocomposites may be manufactured by liquid composite molding. During impregnation process, the flow of matrix is governed by three phenomena: (1) capillary phenomena, (2) transport phenomena and (3) the mechanics of potential fiber preform deformation [1]. To understand the first phenomena, the interface between fiber and matrix needs to be known. This work is proposed to study the wettability of flax fiber by capillary rise method. Many studies of natural fiber wetting exist in the literature [2]. The fiber scale was mostly studied but not at the yarn scale. But during impregnation, the porous property of yarn plays an essential role in capillary phenomena. The flow in the yarn depends of geometrical properties (tortuosity, shape of pore), liquid properties (viscosity, surface tension, density) and the interface (contact angle).

The capillary rise method is performed on tensiometer K100SF by Krüss. The experimental method is tested on filter paper manufactured by Whatman. This filters are used as porous calibrated materials. Flax bundle come from Groupe Depestele (Normandy) is tested by the same protocol. The principal difficult is the combination between all phenomena during the impregnation process by capillary rise. This difficult induces many differences in calculated surface energy component of flax fiber. The choice of liquid, the conditioning and geometry of bundle are reasons to illustrate the difference between the experiment and the literature.

References:


Future perspective in polysaccharide research:
The knowledge of the interface with contact angle measurement, is essential to understand the affinity between the fibre and matrix during process impregnation of biocomposites.
Influence of anion size on cellulose solution structure in imidazolium-based ionic liquids

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Keywords:
Cellulose, Ionic Liquids, NMR, Rheology

Abstract:
Ionic liquids are powerful solvents for cellulose dissolution, particularly those based on the imidazolium cation. They have generated much interest for use in creating cellulotic films, fibres and aerogels. In previous studies, cellulose, cellobiose and glucose solutions in 1-ethyl-3-methylimidazolium acetate were studied using NMR spectroscopy, diffusion and rheology. We have extended this work to 1-ethyl-3-methylimidazolium octanoate, in order to investigate the effects of a different anion chain length. The 1-ethyl-3-methylimidazolium octanoate systems were examined over a range of carbohydrate (glucose, cellobiose and cellulose) concentrations (0% - 15% by weight) and a range of temperatures (20 °C to 60 °C). In 1-ethyl-3-methylimidazolium acetate, the decrease in self-diffusion coefficient is proportional to the number of hydroxyl groups per anhydrous glucose unit of the carbohydrate (3 for cellulose, 4 for cellobiose, 5 for glucose). However, 1-ethyl-3-methylimidazolium octanoate does not follow this rule. This reveals a different structuring of 1-ethyl-3-methylimidazolium octanoate in relation to the dissolved cellulose. More recently, our work focusses on using conductivity measurements and studying other ionic liquids to further investigate the effect of changing architecture on ionic liquid properties.

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References:

Future perspective in polysaccharide research:
Fully utilising cellulose as a renewable resource requires an efficient, ‘green’ solvent that can dissolve and extract cellulose. Ionic liquids may be the required solvent but there are still many more questions to be answered and problems to solve in the dissolution of cellulose in ionic liquids.
Gelling capacity of diluted alkali soluble pectin in the presence of divalent metal ions (Mg\textsuperscript{2+}, Fe\textsuperscript{3+}, Ca\textsuperscript{2+})

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Keywords:
diluted alkali soluble pectin, rheology, atomic force microscopy, divalent metal ions

Abstract:
Maintaining the correct level of minerals such as calcium, magnesium or iron is necessary for the proper functioning of the human body. Contemporary diet of western countries does not deliver required amount of these macronutrients which need to be supplemented. Pectin can be used as a delivery system of these components due to their ability to bind divalent metal ions. Additionally, cross linking of pectin by such ions as calcium assures an increase of viscosity of pectin solutions which can be applied as thickener or texture stabilizer in food.

The aim of this study was characterization of physical and chemical properties of diluted alkali soluble pectin (DASP) in the presence of divalent metal ions. Solutions of CaCl\textsubscript{2}, MgCl\textsubscript{2} and FeCl\textsubscript{3} were used as cations sources. To determine the rheological behavior of DASP solutions with metal ions flow curves (shear stress to shear rate) were used. Obtained data was analyzed using the Power law model. The size of the hysteresis loop between upward and downward curves was used to evaluate a thixotropic effect. Gas chromatography was used to determine the chemical composition of DASP fraction and atomic force microscopy was applied to characterize a molecular structure of the samples. The content of galacturonic acid was measured using colorimetric method.

All the ions caused an increase of viscosity of the DASP solutions compared to control sample (water + DASP). The study also showed that with increasing shear rate viscosity of the DASP solutions decreased. All experimental solutions were classified to pseudoplastic and dilatant fluids. Rheology analysis showed the differences between the size of hysteresis loop of control sample and hysteresis loop of samples with metal ions. After addition of metal ions an increase of the area of hysteresis loop was observed. Chromatography analysis showed that the main neutral sugars of DASP were arabinose, rhamnose, xylene and galactose. Colorimetric analysis showed the large content of galacturonic acid compared to neutral sugars. Control sample of DASP fraction applied to the mica formed regular interlinked network which was degraded after metal ions addition.

Acknowledgement:
This project was financed by National Science Centre, Poland (project Nr. 2015/17/B/NZ9/03589)

Future perspective in polysaccharide research:
The enzymatic modification of pectin and observation of the chemical modification using the atomic force microscopy is scheduled. The AFM imaging will be used to verify whether the modified DASP fraction forms regular network after removal of a specific sugar fraction. The theoretical basis of the observed phenomena will be carried out on the basis of numerical modelling techniques (density functional theory – DFT and molecular modelling Md)
New Cellulosic Materials for Packaging Applications via Reactive Extrusion of Pulp

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**Keywords:**
thermoforming of paper, reactive extrusion, glycol cleavage, dialcohol cellulose

**Abstract:**
In many packaging applications with complex shape like trays, yoghurt cups or blisters classical plastics like PP, PET or PS are predominant due to their favourable manufacturing and product properties. Here flat films are heated and moulded afterwards to yield three dimensional hollow objects. Unfortunately cellulose based paper boards as a sustainable and cheap alternative could not be thermoprocessed due to the lack of cellulose thermoplasticity.

In general several types of chemical cellulose functionalisation are known to generate thermo-plastic derivatives in a homogeneous or heterogeneous manner. However regarding the production of thermoplastic fibre webs, homogeneous modification processes are not adequate since they convert the formerly rigid architecture of pulp fibres into bulk materials inappropriate for papermaking. To overcome these problems PTS planned to provide pulp fibres with a core-shell architecture in which the core remained cellulosic and the shell is composed of a thermoplastic cellulose derivative in order to change the inter fibre bonding properties.

Within the present work we focus on the surface-selective glycol cleavage of cellulose fibres via reactive extrusion in order to achieve a thermoplastic paper material. The promising applicability of this reaction type has already been shown in laboratory scale. In reactive extrusion technique a compounding extruder is applied as a continuous reactor for carrying out chemical reactions rapidly at high consistency. The simultaneous impact of kneading, shearing, pressuring and heating results in evenly modified products with small amounts of chemicals needed.

It has been recently shown by PTS that reactive extrusion is a sufficient technique for selective homogeneous as well as heterogeneous chemical modifications of cellulose fibres (e.g. acetylation, graft-polymerisation or carboxymethylation) to provide different specific materials with interesting properties such as thermoplasticity or barrier effects. Since upscaling of reactive extrusion is comparatively simple, industrial applicability could be provided for different scales.

**References:**


**Future perspective in polysaccharide research:**

Polysaccharide, especially cellulose, based materials could become a major alternative to oil-based plastics in packaging if material inherent properties could be changed in an eco-friendly and cost efficient way. In this context the above strategy seeks to open a sustainable and convenient way for the production of mass packaging goods.
Development of novel biobased hybrid materials based on nanocellulose and copper nanowires for electrical conductivity applications

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Keywords:
hybrids, nanofibrillated cellulose; copper nanowires; electrical conductivity.

Abstract:
Cellulose fibres have been widely used in the design of hybrid biomaterials due to their renewable and ubiquitous nature, biodegradability and high specific strength. Interestingly, in the last few years nanometric forms of cellulose have attracted great attention, namely nanofibrillated cellulose (NFC), due to their nanosized dimensions that might impart unique features to the ensuing materials, e.g. enhanced mechanical properties, transparency among others.¹

The singular properties and functionalities of NFC based materials can be significantly enhanced through the combination of this biopolymer with diverse inorganic nanofillers. Metal nanoparticles are among the most prominent candidates because of their unique features.

Nowadays, Cu nanostructures appear as an interesting alternative to the design of low-electrical-resistance materials due to the remarkable conductive properties of this metal. In fact, Cu is only 6% less conductive than the most conductive element, Ag, and yet is 1000 times more abundant, making it particularly attractive for a wide range of applications that require high electrical conductivity.²

Contrasting noble metals, Cu is limited by its ease oxidation under ambient conditions, however, there has been done a considerable progress on the morphosynthesis of copper nanostructures that allow overcome this limitation. Some studies demonstrated that, for example Cu nanowires were more resistant to oxidation caused by prolonged air exposure than the common nanospheres opening a new window of opportunities for the conductive applications of these nanostructures.

This communication aims to report the preparation and characterization of novel hybrid materials based on NFC and Cu nanowires. Different compositions were investigated aiming to address their effect on the morphology and stability, as well in the electric conductivity of the final hybrid materials.

References:


Future perspective in polysaccharide research:

Design of NFC/Cu Nws hybrids for application as cheap conducting materials.
Potential application of NFC/copper hybrid materials as humidity sensors.
Short-fiber dispersion approach for making all-cellulose composites

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Keywords:
cellulose, composite, NaOH, short-fiber, dissolution

Abstract:
The improved mechanical properties of polymer composites are typically gained by reinforcing the polymer matrix with dispersed glass or carbon fibers. Recently, natural fibers are considered as promising reinforcing materials for composites. However, the poor interphase between chemically different matrix and fiber materials is leading to bad stress transfer and thus inadequate mechanical properties of the composite material.

These challenges have been overcome by producing “self-reinforced” composites, for example, by reinforcing a polypropylene matrix with polypropylene fibers. The adhesion between the fibers and matrix is then practically perfect due to chemical similarity of the components. Such “one-polymer” composites exhibit significantly improved mechanical properties and substantially simplified recycling. This approach can be applied to cellulose and other natural fibers for producing all-cellulose composites (1). A cellulosic matrix reinforced with cellulose fibers represents a strong self-reinforced cellulose composite, which is completely bio-based, biocompatible and biodegradable.

In our study we used “short-fiber dispersion” approach, which is similar to the preparation of polymer short-fiber composites. Dissolving grade cellulose was dissolved in 8 w-% NaOH-water solution in order to prepare the cellulosic matrix, which was then reinforced with softwood kraft pulp fibers. The evolution of fiber size and dissolution was monitored. The mechanical properties of the composites were controlled by the concentration of the reinforcing fibers and the degree of polymerization of the dissolving pulp. Composite structure-properties relations will be presented and discussed.

References:

Future perspective in polysaccharide research:
Development of polysaccharide based materials. Additionally, the controlling and modifying the properties of the materials will play a significant role.
Effect of agar and algae waste obtained from red algae on the manufacture of films and biocomposites

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Keywords:
agar; algae-waste; injection; compression; functional properties.

Abstract:
The continuous increase in the use of non-biodegradable plastics has generated huge disposal problems and a serious impact on the environmental pollution and climate change. In an attempt to reduce the amount of plastic solid waste and also to reduce the dependency on fossil fuels, a great interest in the manufacture of biodegradable, renewable and cost-competitive materials has grown in recent years. Renewable and biodegradable films can be prepared from mixtures of polysaccharides and proteins. In this context, agar (AG) and soy protein (SPI) contain many reactive groups that can interact to form an interconnected network. Agar is a gelatinous product extracted from red algae. It has excellent film-forming properties and can be used to develop bio-based films. Moreover, the algae waste (AW) obtained in the extraction process of agar from red algae can be used for the development of sustainable biocomposites with lower cost. This algae waste contains mainly protein and lignin free cellulose. Both AG and AW show good compatibility with SPI.

Regarding the manufacture of the materials, thermo-mechanical methods are the most widely used processing techniques in the plastic industry and thus, their use for the production of the bio-based materials would greatly promote their commercial applications. In this work, extrusion and compression moulding were employed to develop SPI/AG films, while extrusion and injection moulding were used to manufacture SPI/AW biocomposites. In this regard, the optimization of the abovementioned processes was analyzed and also the functional properties of the films and biocomposites and their feasibility to be used as packaging materials.

References:

Future perspective in polysaccharide research:
Development of more sustainable composites using by-products or wastes from the agricultural and horticultural industries and processing them using the methods employed in the plastic industry with the aim of bringing environmental and economical benefits.
Development and characterization of polysaccharide blend films and their application for the removal of dyes from aqueous solutions

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Keywords:
Polysaccharides, CA/CS films, CA/CMC films, Dye removal, PS blend films

Abstract:
In this study, polysaccharide (PS) blend films of cellulose acetate/chitosan (CA/CS) and cellulose acetate/carboxymethyl cellulose (CA/CMC) in different compositions were prepared by using solely acetic acid/water mixtures. Cellulose acetate was subsequently deacetylated using potassium hydroxide under optimized conditions. Fourier transform infrared spectroscopy (FT-IR) was used to analyze the presence of chemical moieties in PS blend films. The morphology of the films was studied using scanning electron microscopy whereas hydrophilicity/hydrophobicity was investigated by water contact angle studies. Quantitative charge titration experiments were conducted to determine the number of accessible charges in the PS films. Resulting blend materials containing cellulose and CS or CMC were used for the removal of anionic and cationic dyes from aqueous solutions to demonstrate the applicability of the functional biodegradable material. Kinetic studies were carried out on the adsorption of dyes using UV-Vis spectroscopy. The method presented here allows for the production of cellulose/CMC/CS blends that are otherwise not easily accessible by dissolving all three materials in one proper solvent for cellulose. Several other application scenarios and material properties are therefore anticipated.

Acknowledgement:
This project has received funding from the European Union’s Erasmus Mundus programme, EUPHRATES, Lot 13.

Future perspective in polysaccharide research:
Polysaccharide derivative based blends accessible by using “green” solvents are seen as promising for the development of environmentally friendly materials in bioremediation.
Development and characterization of active edible films based on fish gelatine and Aloe Vera Barbadensis polysaccharide extract

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Keywords:
Active packaging, Aloe Vera, characterization, edible film, polysaccharides.

Abstract:
Fish gelatin (FG) is a major by-product from the fish-processing industry, causing waste and environmental pollution. Due to its film forming capacity, the elaboration of edible films from fish gelatin has been studied. Aloe Vera gel (AV) has been recently used to develop edible coatings for fruits showing antioxidant and antimicrobial effects. The aim of this work is the development and characterization of novel active edible films based on the use of FG and AV. To obtain the AV, the colourless hydroparenchyma of leaves, kindly provided by “Las Coronas” (Spain), was extracted, lyophilized and stored at -21 °C until analysis. Two different hydrolysis procedures were performed to quantify AV polysaccharides, based on the use of trifluoroacetic acid and sulfuric acid, respectively. High-pH anion exchange chromatography with pulsed amperometric detection was used to quantify glucose, mannose, xylose, arabinose, galactose, rhamnose, galacturonic and glucuronic acid compounds. Structural characterization, thermal stability, total phenolics content and antioxidant activity (by ABTS, DPPH and FRAP methods) of AV were studied. Edible films were prepared by the casting/solvent evaporation method with FG (8 %, w/v), glycerol (25 %, w/v) and different AV proportions (0, 1, 4 % w/v). Structural, morphological, and thermal characterization of films was carried out. Barrier properties were evaluated in terms of water vapour permeability and oxygen transmission rate. Thickness, transparency, solubility, tensile properties and disintegration behaviour of films were also determined. Antimicrobial activity of AV and films was evaluated against E. coli and S. aureus bacteria. In addition, oxidation induction temperature, initial degradation temperatures and DPPH, FRAP and ABTS were studied to evaluate the antioxidant activity of films. Crosslinking between protein chains from FG and AV polysaccharides (mainly mannose) and polyphenols resulted in a reduction in crystallinity degree, increasing thermal stability of active films; obtaining some antioxidant and antimicrobial effect.

References:

1 S. F. Hosseini; M. Rezaei; M. Zandi; F. Farahmandghavi. Food Hydrocolloid. 2015, 44, 172-182.


Future perspective in polysaccharide research:
The development of innovative active edible films based on FG and AV could extend polysaccharide applications by improving food products in terms of quality, freshness and safety.

New active environmentally friendly materials based on antioxidant and/or antimicrobial extracts from polysaccharides, such as AV gel, could be considered promising sustainable food packaging systems to extend the shelf-life of packaged foodstuff.
The influence of CNC content on the water sorption properties of some biocomposite films

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**Keywords:**
water sorption, biocomposite films, NIR spectroscopy

**Abstract:**
Water molecules can be adsorbed in different ways on the polymer matrices. It can be molecularly dispersed in the matrix (random dispersion in the bulk of the matrix) or can interact with specific sites from the macromolecular backbone, when present. Both sorption mechanisms induce changes in the physico-chemical and mechanical properties of polymeric matrix. Since the plasticization extent is related to the type of interaction that water molecules establishes with the matrix, its extremely important to investigate the state of water molecules sorbed into the polymers. A very effective technique is the NIR spectroscopy which allows the detection of differently interacting water molecules. In an NIR spectrum, the band at 1930 nm is assigned to a combination of O-H stretching vibration and O-H deformation of water molecules.

The purpose of this study is to evaluate the interactions that occur between water molecules and some polymeric systems containing polyvinyl alcohol (PVA)/starch (S) and cellulose nanocrystals (CNC) in different concentrations by gravimetric and near infrared (NIR) spectroscopy. In this context, PVA/S/CNC samples were exposed to ten different RH values media, and thereafter the NIR spectra were recorded and the integral area of the 1930 nm spectral band with the content of water adsorbed were evaluated. It was observed a modification in the water adsorption properties with the modification in the samples components concentrations.

**Acknowledgement**

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**Future perspective in polysaccharide research:**
Effects of the nature of atmosphere during thermal treatment on chemical compositions and properties of miscanthus. Application to miscanthus-filled concrete

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Keywords:
Miscanthus, thermal treatment, concrete, chemical compositions, hydrophilicity

Abstract:
Among the difficulties of preparation of ligno-cellulosic biomass-filled concrete are its hygroscopicity, its sensitivity to degradation in strong alkaline media and its probable low resistance to micro-organisms. Among the many methods have been explored and tested to solve these difficulties. We are reporting here the use of high temperature thermal treatment. We applied heat on miscanthus with the hope to reduce hygroscopicity, enhance alkali resistance and dimensional stability, without using any chemical treatment. The effects of heat treatment atmosphere on chemical modifications and behaviours of treated miscanthus were investigated. The parameters which were varied were atmospheres (vacuum and nitrogen), time and treatment temperature. Mass loss, with closely related to the degree of miscanthus modifications is the parameter used to control the treatment conditions.

At the same treatment intensity, miscanthus treated under nitrogen has lower mass loss than those treated under vacuum. Under vacuum, volatile degraded products are continuously removed, which can help to stop their recondensation or cross linking reactions occurring on the surface of miscanthus stems. Reductions in water absorption and in mass loss in alkali medium with thermally treated Miscanthus are observed. The hydrophilicity of treated miscanthus is expected to decrease. The resulting products likely have an improvement in decay resistance due to the removal of hemicelluloses which are low stability and are mostly degraded during treatment. At elevated temperature, cellulose and lignin are also modified.

After thermal treatment, miscanthus chips were used to prepare lightweight concrete blocks with a common Portland cement as a binder. The amount of sugars released during concrete preparation process, which can contribute to the inhibition of cement hydration or delay in cement setting time, was determined. The interactions between miscanthus chips and cement were characterised. We will evaluate the potential of this method for improving concrete preparation.

References:

Future perspective in polysaccharide research:
Crystallization of polypropylene in the presence of Miscanthus x giganteus stems fragments

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Keywords:
Crystallization; DSC

Abstract:
Miscanthus Giganteus – reinforced polypropylene composites have been prepared by internal mixing. The effect of the size of the miscanthus fragments used as fillers onto the thermal properties of composites has been evaluated by differential scanning calorimetry (DSC) and polarized light optical microscopy (POM). The kinetics of the crystallization processes have been evaluated by isothermal methods. The influence of the fiber-matrix interface onto the melting/crystallization processes has been evaluated by adding a maleic anhydride–grafted polypropylene (MA-g-PP) coupling agent. A clear acceleration of the crystallization kinetics was observed in the presence of miscanthus stem fragments. However, the results showed that, for non-coupled composites, the size and aspect ratio of those fragments had no significant influence onto the crystallization kinetics of polypropylene. The presence of the MA-g-PP coupling agent increased the kinetics and reduced the crystallization activation energy. Although relatively small, if a good fiber-matrix interface is achieved, the size of the filler plays a significant role onto the crystallization kinetics of the matrix, with smaller fragment leading to faster kinetics and reduced activation energy.

References:

Future perspective in polysaccharide research:
Effect of processing conditions on the mechanical properties of flax fabrics reinforced polypropylene composites

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Keywords:
Flax fibres, thermocompression, process-microstructure-property relation

Abstract:
Natural fibres such as flax are a promising replacement for synthetic fibres in polymer composites and achieve comparable specific properties due to their low density. Flax fibres derive their good mechanical properties from their secondary wall which is mostly made of crystalline cellulose microfibrils (75%), held together by amorphous hemicellulose (20%) and a matrix of pectin, with a small amount of lignin (1%). Extruded and injection molded composites with short fibres of flax and jute are already used in automotive applications for semi-structural and interior parts. However, it is possible to achieve higher mechanical performance with long continuous flax fibres. Recent developments in the production of technical flax fabrics allow their use in the manufacture of structural composite parts with thermoset and thermoplastic matrices. Commingled flax / polypropylene (PP) fibres developed by Composites Evolution and produced in 2x2 Twill preforms of 400 gsm was chosen for this study. The melting point of PP makes it a suitable matrix for flax fibres which begin to degrade at temperatures higher than 200°C. Many articles have been published concerning modifications of flax fibres to improve the interface adhesion with a polymeric matrix. However, the effect of processing conditions on the microstructure and mechanical properties is not fully explored. In this paper, the effect of different processing parameters on the mechanical properties of a laminated flax fabrics reinforced PP composite produced by thermo-compression is studied. Temperature, pressure and consolidation time were the chosen parameters and composite plates were manufactured with combination of different conditions. Uniaxial tensile tests and flexure tests were carried out and the effects of the processing parameters on the modulus and strength of the composite were studied. The microstructure of the biocomposite was also investigated using an optical microscope to observe matrix-fibre cohesion, porosity, dispersion of fibres in the warp and weft directions.

References:
2. Lu Zhang, Menghe Miao, Commingled natural fibre/polypropylene wrap spun yarns for structured thermoplastic composites, Composites Science and Technology, Vol.70, 2010

Future perspective in polysaccharide research:
Understanding the effect of processing conditions on the microstructure and mechanical properties of flax thermoplastic composites is necessary to optimise the industrial manufacturing process for structural applications.
Properties of lyocell-polypropylene composites

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Keywords:
Composite, Lyocell, Polypropylene, Sorption-Isotherms

Abstract:
During the last decade cellulose fibre based composites were investigated with intensity, as such lightweight materials are expected to contribute substantially in energy and material savings in mobility application. High performance and lightweight composites were prepared through thermal shaping of intermingled polypropylene-lyocell fibre slivers. The concept of intermingled fibres results in composites with superior mechanical properties compared to composites prepared by extruder, because the fibres are oriented along the direction in which the drawing process was performed. The lyocell fibres function as reinforcement and influence the mechanical properties. Three different types of fibre slivers were used with different share of lyocell. The tensile strength and E-modulus were determined as function of the lyocell share in the composites, which were also tested in water saturated state. The share of lyocell influences the ability of the composite to sorb water. In water saturated state, the ultimate tensile strength was reduced from 160 MPa to 90 MPa, which can be explained by the deteriorated adhesion between the lyocell fibres and the polypropylene matrix. Thus attention was directed towards moisture sorption of the composites. Lyocell has benefits such as low density and sustainability, but its reinforcing properties are reduced in presence of water. Moisture sorption isotherms were recorded through measurement of the dynamic water vapour sorption. Results were analysed using the “Parallel Exponential Kinetics” (PEK) model. The results given form a scientific basis for a more detailed understanding of the behaviour of cellulose reinforced composites in lightweight materials.

References:

Future perspective in polysaccharide research:
Lyocell, which is a refined cellulosic fibre, has a high potential in future composite materials, because it belongs to the group of renewable resources.
Characterisation of cellulose hydrogels synthesised by different *Komagataeibacter* strains

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Keywords:
bacterial cellulose; *Komagataeibacter*; cellulose production; microstructure; mechanical properties.

Abstract:
Bacterial cellulose (BC) is an insoluble exopolysaccharide generated by fermentation of bacterial species, which has the potential to be an environmental friendly biomedical material. Generally, *Komagataeibacter* (formerly *Glucanacetobacter*) strains can produce high amounts of BC. The possible diversity of BC synthesised by different *Komagataeibacter* strains is a worthwhile research direction. Our study investigated cellulose production, microstructure and mechanical properties variation from six *Komagataeibacter* strains (ATCC 53524, ATCC 10245, ATCC 23769, ATCC 700178, NBRC 13693 and KTH 5655). Phylogenetic analysis of the 16S rRNA gene indicated that these strains shared a high level of genetic similarity (ranging from 88% to 98%). Strain KTH 5655 produced the highest BC yields (20.39 g/l) after 9 days cultivation compared with the other five strains. Nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction (XRD) revealed that strain ATCC 23769 synthesised cellulose with the lowest crystallinity and decreased ratio of I / I  allomorph, whilst strain KTH 5655 produced a relatively ordered BC structure. However, the average widths of cellulose ribbons were similar (30-50 nm) for all types of BC. The mechanical properties of BC synthesised by these six *Komagataeibacter* strains were investigated in terms of their ductility, toughness, poroelasticity, and swelling abilities. High extensivity, toughness and elasticity were characteristic of those BC hydrogels which contained higher amounts of cellulose, especially those produced by strain ATCC 53524 after long term fermentation. Comparatively, strain 5655 synthesised a relatively open-structure BC, whose original structure was retained well after having been freeze-dried and showed a superior water absorbing ability (70% weight recovery). Additionally, BC hydrogels showed apparently anisotropic mechanical behaviours, which may due to their ‘scaffold’ architecture. Our results illustrate the diversity of structures and properties available from bacterial cellulose and provide guidance for the selection of cellulose-producing strains for specific biotechnological and research applications.

References:


Future perspective in polysaccharide research:
Bacterial cellulose has the potential to play an important role in medical applications like tissue-repair and blood vessel replacement. Additionally, current applications in food fermentation could be expanded, particularly given the ability of bacterial cellulose hydrogels to immobilize proteins and phytochemicals for nutritional benefits. For all these applications, the knowledge developed in this study concerning the relationships between bacterial strain, cellulose hydrogel production, structure and application properties will be useful.
Structural characterization of Hyaluronic acid hydrogels by NMR

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Keywords:
Hyaluronan, hydrogels, NMR, LC-MS, cross-linking

Abstract:
Cross-linked polysaccharide hydrogels can have very different physical properties depending on the characteristics of the cross-linked network. Parameters which describe these networks are therefore important to understand the differences in properties as well as to facilitate the design of hydrogels with desired properties. One important parameter that describe such a network is the degree of cross-linking which combines the degree of modification and the effective cross-linker ratio. Another parameter that might influence the physical properties of the hydrogel is the substitution position of the cross-linker on the polysaccharide. Using NMR spectroscopy and LC-MS/MS, we have analysed the substitution pattern in hyaluronic acid (HA) hydrogels cross-linked with 1,4-butanediol diglycidyl ether (BDDE), one of the most commonly used cross-linkers for HA hydrogels. HA-BDDE hydrogels are highly viscous so to enable the analysis the hydrogel was first degraded by chondroitinase ABC and the digest was subsequently separated into size dependent fractions by preparative HPLC. Structural analysis of the mono-linked di-, tetra- and hexasaccharide fragments demonstrated that all four hydroxyl groups of the HA repeating disaccharide could be substituted by BDDE and not predominantly position 6 of N-acetylglucosamine (GlcNAc-OH6) as previously often assumed. The most favored substituted position was GlcNAc-OH4 followed by GlcNAc-OH6 and GlcA-OH2. Substitution at GlcNAc-OH4 in the tetrasaccharide prevented chondroitinase ABC from cleaving down to disaccharides. Diastereoisomers derived from the chirality of BDDE were identified from LC-MS analysis. NMR analysis of cross-linked fragments showed that, as for the mono-linked fragments, substitution occurred only on the reducing and non-reducing end sugar and the same substitution position chemical shift reporters of could be used independently of the size of the fragment. Using the enzymatic digest of HA hydrogels, 1D NMR methods that can be used to determine both the substitution pattern and the degree of cross-linking without any chromatographic separation step have been developed.

References:


Future perspective in polysaccharide research:

Being able to modify polysaccharides to receive desired properties will be beneficial to many fields that utilize polysaccharides such as medicine, cosmetic, food or energy. Development of new advanced methods for analysing the structures of these polysaccharides is very important to be able to relate them to the physical and biochemical properties.
Quality control of natural polymer chitosan

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Keywords:
Chitosan, Biopolymer

Abstract:
A major hurdle for market success of many natural polymers like chitosans is often a problem of lack in reproducibility, i.e. batch-to-batch differences and, thus, non-satisfying functional reliability. In fact, most of the chitosan preparations offered on the market are analytically highly undefined. Today, even the best characterised chitosans available in the market are usually described only concerning their ash and heavy metal content, the (near) absence of contaminating bacteria, their viscosity and their average degree of acetylation. However, one of the key parameters in characteristics and functionality relevant for the development of new commercial applications of chitosans are their molecular weight (Mw) and the polydispersity index (Ip). While viscosity and Mw correlate to some extent, the viscosity alone does not disclose any information on the polydispersity of the sample. We explored the relationships between the viscosity and the Mw using 36 chitosans with defined viscosities produced in different ways by BioLog Heppe GmbH. Mw and Ip were determined in collaboration with our partners from the University of Münster using a SEC-MALLS-RI system according to the ASTM method F2602-13. The results obtained open up new perspectives to make chitosan preparation more reliable for both chitosan producers and chitosan users. Using this method of quality control, the producer can influence the production to improve quality and reduce material costs (energy, chemicals, time). Moreover, he can provide the customer with reliable and well documented material with defined quality. In this way, biopolymers such as chitosans can be used as reliably as synthetic polymers in different areas of industry and agriculture as well as medicine.

References:

Future perspective in polysaccharide research:
A simple extraction method to obtain chitin from squid pen: characterization and environmental assessment

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Keywords:
Squid pen, extraction method, β-chitin, protein, LCA.

Abstract
Food processing generates large quantities of unavoidable wastes that lead to environmental and human health problems. These wastes contain several substances that could be extracted to obtain added value-compounds with remarkable properties for a wide range of applications whereas waste amounts would be reduced. Among them, squid pens can be considered as a novel source of chitin. Chitin is a nitrogenous polysaccharide that has been extracted from many natural sources, such as crustaceans, molluscs, fungi, insects, and annelids. Chitin is known as a highly hydrophobic polymer and thus, insoluble in water; however, its excellent properties, such as biocompatibility, biodegradability, non-toxicity, and film forming ability, make it an excellent raw material for applications in packaging, biotechnology, pharmaceuticals, and environmental sectors.

β-chitin could be extracted from squid pens through an alkali treatment at ambient temperature, which avoided degradation processes. In addition, extraction at ambient temperature is a more environmentally friendly process. Furthermore, chitin could be obtained by one-step-extraction (deproteinization) due to the low content of inorganic components in squid pens. The chitin obtained was characterized by UV spectroscopy, which showed the deproteinization process. Life cycle analysis (LCA) evidenced that this extraction method was a less contaminating process than the three step-method (demineralization, deproteinization, decoloration) usually employed to obtain chitin from other natural sources. In addition to environmental concerns, the simplification of chitin extraction reduced the production cost. Furthermore, proteins could be isolated from the extraction process and the amino acid composition of the protein obtained in this work was determined.

References:

Future perspective in polysaccharide research
Assessment of the deacetylation process of β-chitin to obtain chitosan and the potential applications of both polysaccharides for biomedical and food applications, such as drug delivery, tissue wound healing and food packaging.
Characterisation of a thermostable chitinase from *Myceliophthora thermophila* and its potential for production of *N*-acetylchitooligosaccharides

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Keywords:
chitinase, *M. thermophila*, chitosan, *N*-acetylchitooligosaccharides

Abstract:
In recent decades, oligosaccharides derived from chitin and chitosan have gained much attention in many fields i.e. biomedical, pharmacology, agriculture, and biotechnology. Common procedures for the production of chitooligosaccharides rely on acid catalysis, which is characterised by a low yield and high environmental impact. The use of enzyme catalysis for depolymerisation of chitin and chitosan is a promising alternative to the chemical methods because it allows the production of specific chitooligomers in a controlled way and in an environmentally friendly process. Nevertheless, development of an efficient enzymatic process requires fundamental knowledge of the catalytic mechanisms of enzymes and understanding the interactions between enzyme and their substrate.

In our study we over-expressed and characterised a chitinase from the fungus *Myceliophthora thermophila* C1. It was found that this chitinase is very thermostable and can depolymerise both chitin and chitosan. The degree of acetylation and the Mw of the substrates influenced the chitinase activity and the composition of released oligomers. These oligomers were identified as hetero-oligomers by MALDI-TOF-MS. The chitinase was able to degrade fully-acetylated chitooligomers, which were attacked from their non-reducing end. Due to the high thermostability and specific mode of action, the chitinase seems to be a promising tool for production of *N*-acetylchitooligosaccharides at industrial scale.

References:

Future perspective in polysaccharide research:

Enzymes are promising tools for production of high-value chemicals and materials from polysaccharides. Therefore, it is important to characterise new enzymes and develop processes based on enzymatic catalysis.
Levan from *Bacillus licheniformis*: Structural characterization and novel applications

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**Keywords:**
levan, *Daphnia magna*, graft copolymer

**Abstract:**
Levan is a fructose based polymer present in several microorganisms as exopolysaccharide and a few plant species as non-structural storage carbohydrate. Numerous uses have been identified for levan in personal care and cosmetics, medicine and food industry which included moisturizers of the skin, healing damaged tissue, increasing obesity and hyperlipidemia, food packaging and functional food [1]. Apart from the fine structural characterization of microbial levan the aim of this study was to propose two novel applications for this polysaccharide. Levan was isolated from *Bacillus licheniformis* NS032 [2] after cultivation on sucrose medium and characterized by 2D-NMR spectroscopy, methylation analysis and determination of molecular mass. Its ability for reducing copper toxicity and affecting activity of oxidative stress enzymes in *Daphnia magna* juveniles was investigated. Also levan-polystyrene copolymer was synthetized by the free radical reaction using potassium persulfate as initiator and influence of reaction time on grafting reaction at 70 ºC was studied. Molecular mass of levan obtained after cultivation at 200 g/L sucrose (~10^6) was higher compared to those cultivated at 400 g/L sucrose (~10^5). 2D-NMR spectra of obtained polysaccharide and GC-MS spectra of partially acetylated alditol acetates confirm that the obtained polysaccharide containing only β-(2→6) linked β-D-fructofuranose units in backbone and occasional β-(2→1) branches. Acute toxicity of copper on *D. magna* in presence of levan was decreased from 0.14 to 0.44 g/L and activity of oxidative stress enzymes in these animals was also lower. Grafting reaction between natural polysaccharide levan and polystyrene was successful and maximum percent of grafting (57.7 %) was achieved after 45 minutes of reaction time.

**References:**

**Future perspective in polysaccharide research:**
The utilization of polysaccharides in medicine and pharmacy requires synthesis of novel derivatives, testing their biological activities and functional characteristics. Also, preparation of new copolymers for use in food packaging and environmental protection in order to replace of petroleum-based products is a desirable approach.
Starch based thermoplastic resins by radical graft copolymerization of styrene and butyl acrylate: synthesis, characterisations and film formation

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Keywords:
starch, graft copolymerization, film properties

Abstract:
Research toward bio-based and biodegradable polymers has received a lot of attention these last years, due to environmental concerns and the need to replace fossil resources. In this context, starch which is an abundant and cheap starting material becomes more and more attractive. Native starch displays however poor mechanical properties and has little resistance to water. New starch-based thermoplastic materials were prepared by grafting. A large range of polymers can be grafted on starch by radical polymerization in order to modulate the properties of the final product. The synthesis of starch-graft-poly(styrene-co-butyl acrylate) was performed with different radical initiators on native,1 acetylated or oxidized starch,2 these copolymers being used as sizing for cotton or yarn fibers. In this contribution, we report on the synthesis of dextrin-graft-poly(butyl acrylate) and dextrin-graft-poly(styrene-co-butyl acrylate) in comparison to their starch homologues. The use of dextrin instead of native starch could improve the grafting efficiency on low molar weight carbohydrate and could give rise to thermoplastic films displaying new properties. Moreover adding butyl acrylate increases the strain and styrene increases the rigidity. The mix of both monomers allows to obtain a good compromise between ductility and strength.

References:

Future perspective in polysaccharide research:
Different parameters will be studied to improve the grafting efficiency and the mechanical properties such as the influence of the length of the alkyl group of four acrylates (methyl to hexyl acrylate) and the influence of radical monomers (acrylate vs. methacrylate).
Synthesis of modified potato starches as supramolecular device for aqueous solubilization of benzo[a]pyrene

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Keywords:
Potato starch, Benzo[a]pyrene, surfactant-like, nanostructure

Abstract:
This project concerns the devising of an innovative method for the remediation of historically contaminated soils with persistent organic pollutants (POPs) by using the supramolecular chemistry principle. Indeed, polycyclic aromatic hydrocarbons (PAHs) or dioxins are pollutants which tend to persist in the environment because of their high stability, low water solubility and their tendency to be adsorbed onto soil organic matter. Among the processes available for soils rehabilitation, the surfactant-enhanced remediation has emerged as a promising technology especially for biodegradation involving saprotrophic soil fungi. Therefore, in contaminated soil ecosystems, POPs biodegradation requires their transfer from the solid phase (soil) to the aqueous one in order to be available to fungi and therefore to be degraded by them. For this purpose, polysaccharides like starches represent a material of choice owing to their abundant, renewable and biodegradable nature. This approach takes advantages of the hydrophobic cavities presence in starches in order to increase the solubilization of hydrophobic pollutants [1]. Nevertheless, the weak aqueous solubility of starch is also known to be a major constraint that seriously limits the development of starch-based materials. Thus, starch derivatives were difunctionalized by 1,4-butane sultone (BS) and 2-octen-1-ylsuccinic anhydride (OSA). In comparison with native starch, the best obtained compound (B) increased starch apparent aqueous solubility by a factor of 10 and also stimulated 77-fold aqueous solubilization of benzo[a]pyrene underlining its very high surfactant-like property [2]. We have determined the critical aggregation concentration (CAC) and average diameter of the starch nanostructure (AB) using fluorescence spectroscopy, dynamic light scattering experiments, respectively and transmission electron microscopy. Finally, we have shown that the reversible complexation phenomenon can be controlled by temperature underlining the supramolecular device.

Figure 1. Schematic representation of the self assembly of modified starch with a guest molecule.

References:

Future perspective in polysaccharide research:
To our point of view, the obtained compound is the most promising candidate for the elaboration of surfactant-enhanced remediation of POPs contaminated soils. Further research will be oriented towards the scale up synthesis of this compound for using it in combination with chemical oxidation and fungi-based remediation. This method could accelerate degradation processes while preserving as much as possible the integrity of the soil.
Molecular characterization of grafted starches for bioplastics application

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Keywords:
grafted starches, ToF-SIMS, solid-state NMR, size-exclusion chromatography, thermogravimetric analysis

Abstract:
Starch is a renewable glucopolymer, composed of amylose and amylopectin, organized in semi-crystalline phases. Designing starch-based bioplastics could be upgraded by the understanding of structure-properties relationships. Alkyl or vinyl monomers polymerized onto starch are expected to improve properties of starch-based bioplastics. The aim of this work is to characterize grafted starches at the molecular level by combining various analytical methods. We focus on three parameters: degree of substitution, localisation of grafted groups and macromolecular size distribution.

Chemical composition, grafted groups positions and grafting ratios were investigated on grafted starches in bulk by solid-state Nuclear Magnetic Resonance (Zhang, Xu & Wang, 2008). Thermal degradation was studied by thermogravimetric analysis and surface chemistry of films obtained by casting was characterized by Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS). After solubilisation and specific preparation of grafted starches, their macromolecular size and molar mass distributions were determined by means of size-exclusion chromatography (SEC) and asymmetrical flow field flow fractionation (AF4) coupled with multiangle laser light scattering (MALLS), whereas extremities and sequences were studied by Matrix-Assisted Laser Desorption Ionisation-Time-of-Flight Mass Spectrometry (MALDI-ToF).

Solid-state NMR allowed to determine the chemical composition of these starch-based copolymers. Thermal degradation of grafted starches was dependant of degree of substitution and of the polymers grafted on starch. The specific fragments observed for all copolymers studied by ToF-SIMS indicated that films surfaces were composed of both polymers. Grafted starches exhibited smaller macromolecular size compared to native starches which means that the grafting process induced an hydrolysis of the starch chains. The MALDI-ToF mass spectra profiles were similar in spite of degree of substitution.

In conclusion, by using specific analytical methods for the analysis of chemically-modified starches, we were able to characterize grafted starches and to provide some hypotheses about structure-properties relationships.

References:

Future perspective in polysaccharide research:
Our perspective in polysaccharide research will be to characterize other types of grafted starches. The choice of starches and monomers used as plasticizers will be based on the hypotheses emitted above.
Modified Starches for Concentrated Water-Based Binder Systems with Application in Paints and Varnishes

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Keywords: Modified starch, binder, coating, paints and varnishes

Abstract:
Our work aimed at the optimization of the structure of native starch for the preparation of concentrated water-based dispersions with film forming properties for the application in paints and varnishes.

Potato and smooth pea starches were degraded via ManOx and hypochlorite conversion (9.4–0.2·106 g/mol) and used as starting materials for esterification and etherification reactions with different chain lengths (C2-C6) and varied degrees of substitution (DS) / molar substitutions (MS) (0.05-1.1) for an increase in their hydrophobicity.

The applied modification conditions led to cold water soluble or dispersible products with concentrations between 30 and 45% (w/w) and viscosities in the range of 102 – 103 mPa·s (300 s-1). The most samples had a newtonian flow behaviour and showed viscoelastic properties with higher values for the loss modulus (G”) than the storage modulus (G’). Continuous films were observed with starch esters in the DS range of 0.1-0.8 and in the case of the starch ethers with MS values of 0.7-0.9. Wet and dry layer thicknesses of 25-50 µm and 7-12 µm were obtained (doctor blade: 100 µm). In the cross cut test on glass plates the esters had clearly better results with values of 0 and 1 (ISO class), in contrast to the tested ether with values of 4.

The compatibility tests with 3 commercial binders showed that two Acronal binders (A 754 and S 559) (42%) showed compatibility with the modified starches (58%).

Selected starch esters showed also good adhesion (class 0 and 1) on aluminium plates while the tested ether could be classified in the worst class (5). In the short-time corrosion stability tests which were evaluated by electrochemical impedance spectroscopy, the barrier properties corresponded to the hydrophobicity of the starch ethers and esters. The starch butyrate with a DS of 0.65 had the best performance.

Future perspective in polysaccharide research:

According to our experiments, in particular to the results of film formation, cross cut tests and corrosion stability tests the starch esters rather than the starch ethers are the preferred materials for a potential application in the coating sector with a focus on metal substrates as alternative to synthetic polymers. Additionally, the film forming starch esters could be useful for film applications when water-based solutions or dispersions are needed and no external plasticizers are desired, for example in the pharmaceutical or food industry.
Hydrophobic starch derivatives for packaging industry - opportunities, limitations and challenges

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Keywords:
esterification, unsaturated fatty acids, 1-butyl-3-methylimidazolium chloride, extrusion

Abstract:
Native starch is characterised by high fragility, incompatibility with hydrophobic polymers and low moisture resistance. Because of high viscosity and hydrophilicity, native (unmodified) starch shows very poor processability. Therefore, different types of modifications have been implemented to improve its mechanical properties and hydrophobisation. Esterification is one of them. Usually, in order to enable an esterification reaction with the acids, a starch is first dissolved in common organic solvents as DMSO, DMF or pyridine. However, the use of such solvents also has some limitations and disadvantages - volatility, flammability and high levels of toxicity. A few years ago, scientists discovered the some ionic liquids (ILs) have the ability to dissolve carbohydrate polymers. Moreover, it was found that biocatalysed esterification in an ionic liquid provided the possibility for the relatively rapid hydrophobisation of starch. Materials based on such modified starch could be used in the production of cheap and biodegradable packagings.

In present study, potato starch was esterified with oleic acid, using an immobilized lipase as a catalyst and an ionic liquid as a reaction medium. Degree of substitution (DS) of starch oleates was determined by the volumetric method and method based on results of elemental analysis. The effect of the reaction temperature and time, on the DS was studied. In order to confirm esterification reaction, products were subjected to Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Moreover, the thermal analysis (TG) was performed. In order to determine the usefulness of starch oleate in the packaging industry - the material was plasticized at the mixer (30% w/w glycerin). Then, the film was extruded using a laboratory extruder. The mechanical strength at static tension and tensile strength (Elmendorf method) were examined. Additionally, water absorption and hydrophobicity (sitting drop method) were determined.

References:

Future perspective in polysaccharide research:
The use of unsaturated fatty acids in the starch esterification, which may allow to conduct further modification and functionalization of esters - eg. by the addition to the double bond in the carbon chain (acyl residue) of acid. The use of polysaccharides and their derivatives for the preparation of biodegradable and functional packaging materials.
Structural and morphological evaluation of biodegradable PVA/Starch/CNC films

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Keywords:
structural properties, morphology, biocomposites

Abstract:
For a long period of time, the petroleum based polymers like polyethylene, polypropylene, polyethylene terephthalate, polystyrene, polycarbonate, etc., have been widely used in every field of human activity. These materials are regarded as non-degradable and caused, along time, serious environmental problems. The limitation on petroleum resources, and the growing interest in environmental protection, lead to the development of renewable and environment friendly polymers (such as polyesters, polysaccharides, gums, proteins or lipids) with similar properties and low costs. In this context, PVA, which is a water soluble polymer, in combination with different polysaccharides are good candidates to replace the petroleum polymers. Moreover, an association between eco-friendly biopolymers and nano-materials, with the aim to obtain synergic effects, is one of the most innovating routes to enhance the properties of these bio-matrices.

The aim of this work is to evaluate the structural and morphological properties of PVA/S and PVA/S/CNC composite films. For the structural characterization, IR, UV-Vis spectroscopy and X-Ray diffraction were used. The morphological aspects of the films were analyzed by AFM. The influence of the blend components on the thermal stability of the films was studied by TG/DTG analysis.

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Future perspective in polysaccharide research:
Non-thermal atmospheric plasma treatment of inulin in liquid media

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**Keywords:** non-thermal plasma, depolymerisation, polysaccharides

**Abstract:**

Within the specific realm of polymer science and technology, the exploitation of renewable resources in the form of monomers, oligomers and natural polymers has become a worldwide practice. The research activities related to polysaccharides are currently spanning many new avenues, for the development of novel materials to be implemented in a large number of domains [1]. However, it is generally necessary to functionalize them and current pre-treatment methods (acidic or basic treatment, chemical modification, ionic liquids use or strong mechanical treatment) are either expensive or require synthesis chemistry that is hard to transpose at the industrial scale and leads to the loss of the bio-sourced character of the polysaccharides.

Compared to current biomass valorisation methods, the non-thermal atmospheric plasma (NTAP) technology is a flexible, efficient and low polluting technique which uses highly reactive species (such as ions, free radicals, electrons, excited molecules) for the modification of surface properties and functionalization of polysaccharides. Among the different types of available plasma discharges, we focus on the dielectric barrier discharge in water. In order to characterize non-thermal plasma in liquid media and to study the different plasma parameters (signal, voltage, frequency) inulin has been chosen as a model molecule. Inulin is a well-defined oligosaccharide (DP30) composed of linear chain of fructose units connected by β-(1→1) glycosidic bonds and terminated by one glucose.

The results have shown that plasma plays an important role in oligosaccharides transformation, leading to obtain fructose, glucose and other fructo-oligosaccharides with a degree of polymerization lower than 5. This lead to a better understanding of the depolymerisation mechanism of inulin in water and of the plasma reactive species involved in this reaction.

**References:**


**Future perspective in polysaccharide research:**

The study on inulin has proved the efficiency of the reactor design for non-thermal plasma. It can now be applied to the treatment of other biopolymers, such as cellulose nanocrystals.
Water and heat treated cellulose thin films - The impact of increased humidity

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**Keywords:**

Cellulose, Humidity, Thin Films

**Abstract:**

Cellulose, the most abundant biopolymer on earth, features a wide range of industrial applications in a variety of fields. Particularly, in papermaking, textile and fiber spinning processes the influence of different parameters (e.g. heat treatment, swelling with water) on the final properties of the cellulosic materials is essential but still not completely understood due to the complexity of real cellulosic substrates.

In this contribution, we will present the consequences of increasing humidity (0%RH \(\rightarrow\) 70%RH \(\rightarrow\) 0%RH) on amorphous cellulose thin films which serve as model systems for regenerated cellulose. The films were prepared by spin coating and converted to cellulose by simple hydrochloric acid vapor hydrolysis. As precursor two different trimethylsilyl cellulosates were used. Afterwards different physical treatments are performed and the consequences on the swelling behavior are investigated. This process was investigated in real time with XRR, GI-SAXS and QCM-D equipped with a humidity module to obtain information about changes of the thickness, roughness, electron density and pore size of the films.

**References:**

**Future perspective in polysaccharide research:**

Cellulose and other polysaccharides, due to their variety of properties, will also be in the future an important component for the development of new materials (e.g. optoelectronic devices, medicine hygienic and life science). Beneath the better knowledge about modification and processing of polysaccharides also the reduced availability of fossil resources is an important factor for the increasing amount of research in the field of polysaccharides and other renewable resources.
Selective C6 oxidation of cellulose with oxone in water

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Keywords:
Oxone; C6-carboxyl cellulose; Cladophora nanocellulose; Cellulose pulp; low-cost method

Abstract:
A novel method for selective C6 primary alcohol oxidation of cellulose, as an alternative to TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), was developed. Cellulose pulp and Cladophora nanocellulose were selectively oxidized in a one-pot procedure by Oxone (2KHSO\textsubscript{5}-KHSO\textsubscript{4}-K\textsubscript{2}SO\textsubscript{4}) and efficient reaction conditions were investigated. The effects of the reactions on the morphology, viscosity and chemical structure of the products obtained were studied. The C6 primary alcohol groups were selectively oxidized to carboxyl groups, as testified by solid-state CP/MAS \textsuperscript{13}C NMR and FTIR, and the content of carboxyl groups was determined by conductometric titration. SEM, capillary-type viscometry and XRD were applied to characterize the products and to investigate the influence of the oxidation. For the first time, low-cost and stable Oxone was used as a single oxidant to oxidize cellulose into C6-carboxyl cellulose. The oxidation is an inexpensive and convenient process to produce carboxylic groups on the surface of the cellulose fibers and to make the cellulose fibers charged. Particularly, this method can avoid the use of halogens and toxic radicals and constitute a green route to access C6-carboxyl cellulose. Further, sodium bromide could be used as a co-oxidant to Oxone and increase carboxylic acid content by 10\% to 20\%. The Oxone oxidation is a promising alternative to the frequently employed TEMPO-mediated oxidation of cellulose, which might increase the possibility to develop and improve applications of cellulose.

References:

Future perspective in polysaccharide research:
Polysaccharide is a rich source for develop functional materials compared to the industrial manufactured polymers. It is a carbon source for its application in energy area.
Iodine complexes of chemically modified natural polysaccharide: Gum arabic

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Keywords:
Gum arabic, chemical modification of gum, acetyl chloride, degree of substitution, microspheres

Abstract:
Acetylated gum Arabic (AGA) derivatives with different degrees of substitution (DS 0.97-2.74) were synthesized using acetyl chloride and a base under varying reaction conditions. The AGA derivatives were obtained in the form of microspheres and thereafter stable iodine products were prepared by doping the microspheres with an iodinating agent, iodine monochloride (ICl). The reaction between electrophilic iodine and polar carbonyl groups was studied by FT-IR, 1H-NMR, and UV-VIS spectroscopies. The products were also characterized by DSC, TGA and SEM studies. The incorporated iodine was released in aqueous medium as iodide ions (I−). A reaction scheme has been proposed for the iodination and deiodination of the gum derivatives. This work suggests that the iodine derivatives of modified gum Arabic could be used as a source of iodide ions which is the nutritional form of iodine.

References:

Future perspective in polysaccharide research:
Chemical Modification, Complexation of modified polysaccharides with various bioactive molecules
Hyaluronic acid-cyclodextrin crosslinked fibers for biomedical applications

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Keywords:
Nanofibers, electrospinning, hyaluronic acid, cyclodextrin

Abstract:
Hyaluronic acid (HA), a polysaccharide naturally found in the human body is crucial for many cellular and tissue functions and has been used in medicine for decades. A HA-based nanofibrous scaffold was successfully fabricated by electrospinning, using exclusively water as a solvent. Electrospinning is a technology which has gained much attention in the last decades; it utilizes electrical forces to produce polymer fibers with diameters ranging from few tens of nanometers to few micrometers using polymer solutions in semi-dilute entangled regime\textsuperscript{1}. Suitable blending of HA with a template polymer and a modified cyclodextrin (hydroxypropyl-β-cyclodextrin: HPβCD) allowed an efficient electrospinning of this polysaccharide and thereby providing fibers in nanometer range (300-500 nm depending on the processing conditions). HPβCD, a nontoxic cyclic oligosaccharide, is a compound of interest by its ability to encapsulate hydrophobic molecules\textsuperscript{2}, moreover we also demonstrated its role as a processing aid in the fiber formation. For medical purposes, the pre-formed mats require to be treated to exert water resistant feature. Crosslinking conditions (addition stage, concentration and annealing time) were then investigated and optimized using N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) as biocompatible crosslinking agent. To validate the encapsulation properties of embedded HPβCD, nanofibers with HPβCD complexed with small molecules with anti-inflammatory properties will be produced. Finally, the release kinetics of the active compound will be characterized for these obtained functional fibers.

The use of biocompatible products and the absence of harmful solvents make this nanofibrous scaffold a material of choice for biomedical applications in tissue engineering or wound healing. Furthermore, the combination of intrinsic characteristics of HA and encapsulating properties of HPβCD enables the development of a bioactive material.

References:

Future perspective in polysaccharide research:
Other polysaccharides like chitosan, carboxymethyl cellulose or alginate display interesting properties for applications in wound healing (antibacterial activity, haemostatic function...). Similarly to the electrospinning of HA, the blending of these polysaccharides with HPβCD could facilitate the fiber formation, which could be a future research area to investigate.
Enzymatic polymerization of rutin and its interaction with cellulose

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Keywords:
rutin, enzymatic polymerization, cellulose, adsorption, anti-oxidant properties

Abstract:
Rutin is one of the major flavonoids and also known as vitamin P. It has been shown to exert anti-oxidant, anti-inflammatory and wound healing activities [1]. With regard to this, our study examines rutin as potential naturally active substance for local healing of chronic leg ulcers. However, depending on its structure, the processibility of this compound is limited by its low solubility in water [2], making it difficult to adsorb on cellulose materials to obtain a wound dressing with antioxidant properties. With the target to increase the solubility of rutin, an aqueous based enzymatic polymerization was performed and water soluble polyrutin isolated. The aim of this work was to study the chemical structure, anti-oxidant activity, cytotoxicity and interaction properties of rutin and polyrutin with surfaces of cellulose thin films, representing a model for a cellulose wound dressing. Rutin and polyrutin were investigated with UV-Vis, FT-IR and 1H-NMR spectroscopy. The charging behaviour of the substances was studied by potentiometric charge titration. To study the interaction of both substances with cellulose surfaces a quartz crystal microbalance was used to detect the amount of deposited rutin and polyrutin on the cellulose thin films. The morphology of the coatings was additionally characterized by atomic force microscopy. For a possible biomedical application, the antioxidant activity of rutin and polyrutin was determined photometrically in solution and on surfaces. Biocompatibility and cytotoxicity testing of both substances were performed using human skin-derived fibroblasts.

Acknowledgements:
The research work was financially supported by the Slovenian Research Agency in the frame of the programme group for Textile Chemistry P2-0128 and the research training program for Junior researchers. such as anti-inflammatory, anti-oxidant and wound healing properties.

References:

Future perspective in polysaccharide research:
My future perspective in polysaccharide research lies in the functionalization of polysaccharide materials with a natural active substances to produce a new, safe, and environmentally friendly materials, with specific properties.
Nanocellulose hydrogels for wound-healing applications

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Keywords:

wound healing, nanocellulose, hydrogel

Abstract:

Nanocellulose (NC) is an emerging biodegradable, recyclable and renewable biopolymer of enormous industrial importance. In recent years, NC has been identified as a promising candidate for biomedical applications.1,2 NC based materials are generally regarded as biocompatible, however the interactions with biological systems can be affected by the physicochemical properties and the nano-structure of the studied material.3 It is therefore of great importance to evaluate the biocompatibility of novel NC based materials as a complement to the physicochemical characterization.

In the present work, ion cross-linked hydrogels of NC were prepared to be further evaluated for wound healing applications. Anionic wood-based NC (a-NC) prepared through TEMPO-mediated oxidation as well as cationic wood-based NC (c-NC) modified by EPTMAC condensation were prepared. Through ionic crosslinking with calcium, self-standing hydrogels of two compositions were obtained: the pure a-NC hydrogel and the composite ac-NC hydrogel consisting of a-NC and c-NC fibers. Rheological measurements confirmed successful ionic cross-linking of the gels while water retention tests brought clarity to the distinct water conservation abilities of the two products. Biocompatibility tests using the monocyte-like THP-1 cell line, human dermal fibroblasts and blood-isolated monocytes were performed, revealing that no toxicity was introduced during the preparation of the two NC materials and that the cells maintain their viability and normal pro-inflammatory cytokine production.

Due to the demonstrated biocompatibility, the ability to maintain a moist environment and the observed mechanical stability, we believe that the studied hydrogels are suitable candidates for further work towards specific wound-healing applications.

References:


Future perspective in polysaccharide research:

Testing the ability of the hydrogels to promote wound-healing ex vivo and in vivo, as well as further improvement and characterization of the material compositions.
Isolation and characterization of glycosaminoglycans from pathologic human and animal tissues

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Keywords:
glycosaminoglycans, Multiple Osteochondromas, Cystic Fibrosis, HPLC-MS

Abstract:
Glycosaminoglycans (GAGs) are linear sulphated polysaccharides involved in a variety of cellular processes and implicated in severe pathologies, e.g. Multiple Osteochondromas (MO), tumors, Alzheimer’s disease, Cystic Fibrosis (CF). Many studies of the last decades proved correlation between GAGs, especially the ubiquitously expressed heparan sulphate (HS) and human disorders, thus underlying the importance of a better understanding of the complicate network of interactions and of the structure/activity relationship of HS. Its role in two rare genetic disorders has been investigated: MO and CF. MO[1] is characterised by the formation of multiple cartilage-capped bony outgrowths along long and flat bones during human development due to mutations in the EXT1 and EXT2 genes, responsible for heparan sulfate biosynthesis. CF[2] is a multifaceted disease caused by mutations in the CFTR chlorine channel and in which vicious cycles of infection by Pseudomonas aeruginosa and other bacteria and subsequent immune response cause prolonged and sustained inflammation that first involves lungs and then expands to other organs. While the link between HS and MO is clear, although a clear understanding of the structural changes that HS undergoes was lacking until now, less is known about its contribution to CF. Starting from the hypothesis that HS could have an important role in tissue remodelling, we isolated and characterised GAGs from lung tissues of healthy and CF mice during Pseudomonas aeruginosa infection. HPLC-MS analysis of enzymatic digestion products showed an increased level of HS in CF mice compared to controls. Using a similar approach we isolated and characterized HS from human healthy and pathologic cartilage to investigate the structural changes of HS in MO. A higher degree of sulfation of pathologic HS, which actually resembles heparin, was discovered.

References:


Future perspective in polysaccharide research:

Better understanding of the contribution of GAGs to tissue remodelling and of the structure requirements necessary for proper activity could help the design of HS analogs that compete with endogenous HS for example to mitigate inflammation or tumor progression.
Functional polysaccharide nanoparticles - From polymer synthesis to advanced applications

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Keywords: polysaccharide derivatization, cellulose esters, functional nanoparticles, lateral-flow immunoassays, dye incorporation

Abstract:
Hydrophobic polysaccharide (PS) derivatives can self-assemble into spherical nanoparticles (NP). These PS-NP are biocompatible and selectively taken up by cells. By introducing desirable functional groups such as dyes, affinity ligands, and drug molecules, advanced nanomaterials for specific applications can be prepared. This can be achieved by two different approaches. Functionalities can be linked chemically to PS-NP prior or subsequent to the particle formation. Favourable in this regard is the introduction of highly reactive moieties at the PS backbone that enable an efficient functionalization.

Physical entrapment of functional compounds within PS-NP is a highly desired alternative approach, e.g., for drug delivery. By using different dyes, it is demonstrated how hydrophobic compounds can be incorporated into composite particles derived from cellulosic esters and how the particle properties are affected by the composition. The dye loaded NP are studied by electron microscopy and UV–vis spectroscopy to gain insight in the interaction of the hydrophobic compounds with the cellulosic matrix. By using functional cellulose derivatives, in particular carboxylate group bearing acetate phthalates, it is possible to introduce reactive moieties on the NP surface that can be exploited for coupling additional functionalities such as antibodies. By this approach, NP can be obtained that are well suited as dye labels in immunoassay applications.

Reference:

Future perspective in polysaccharide research:
Functional nanomaterials on the basis of polysaccharides have a unique potential for biomedical and biotechnological applications. A key aspect of current research is to find efficient ways to tune the material properties and to introduce functionalities. Advanced polysaccharide chemistry offers a vast variety of possibilities in this regard.
Biocompatible bacterial nanocellulose/poly(N-methacryloyl glycine) nanocomposites as pH-sensitive systems for controlled release of diclofenac

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Keywords:
bacterial nanocellulose, diclofenac, drug delivery, nanostructured composites, poly(N-methacryloyl glycine)

Abstract:
Cellulose, the most abundant natural polymer, is regarded as a never-ending source of new functional and sustainable materials. Although most of the cellulose available on earth is produced by photosynthesis in green plants, some non-pathogenic microorganisms, such as bacteria belonging to the \textit{Glucanacetobacter} genus, among others, are also able to produce an extra-cellular form of cellulose, known as bacterial nanocellulose (BC).\textsuperscript{3} The high purity, biocompatibility and unique physical and mechanical properties arising from its three-dimensional nano- and micro-fibrillar structure, generated considerable interest on this biopolymer in the biomedical area, for example as drug carrier for both oral and transdermal drug delivery systems.\textsuperscript{3}

The aim of the present study is to design pH-sensitive nanocomposite materials of poly(N-methacryloyl glycine) (PMGly) and BC in order to modulate the controlled delivery of diclofenac, a typical non-steroid anti-inflammatory and analgesic agent. Thus, a series of PMGly/BC nanocomposite membranes were prepared by the \textit{in situ} free radical polymerization of MGly within the BC 3D network under green reaction conditions.

A thorough characterization of the structure, morphology, thermal, viscoelastic and mechanical properties is presented. \textit{In vitro} biocompatibility assays were performed, demonstrating the potential of these PMGly/BC nanocomposite membranes for biomedical applications. Their applicability as pH-sensitive diclofenac carriers and delivery systems was also tested under different simulated body fluids for dermal and transdermal applications.

References:

Future perspective in polysaccharide research: Notwithstanding the multitude of investigations carried out in recent years, there are plenty of possibilities in terms of R&D in the domain of polysaccharides. These biopolymers due to their availability, multiplicity of structures, biocompatibility and eco-friendly connotation, will continue to be widely used for biomedical applications. In the particular case of BC, or materials prepared from it, the research should move towards the design of smart functional materials, including drug delivery systems with stimuli-responsiveness (e.g. pH, temperature, light, etc.), allowing target oriented drug release and dose reduction while achieving the same therapeutic effect.
Preparation and Properties of Fibrous Materials Based on Chitosan

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Keywords:
chitosan, fibers, coagulation method of spinning, mechanical properties, medical application

Abstract:
Chitosan is a product of partial deacetylation of chitin, a polysaccharide. The aim of this work was to develop a method for processing chitosan fibers, monofilament and polyfilament, as well as modification of these fibers by different additives as nanoparticles or water soluble polymers to improve their mechanical propeties. The chitosan fibers were spun from 4% chitosan (Fluka Chemie, Japan) or 6.5% (Bioprogress, Russia) solution in 2% acetic acid solution by coagulation method. It was shown that the shear rate during spinning process of the polymer solution through a spinneret strongly affected the strength of the spun fibers. The fibers were drawn during the coagulation, and the drawing ratio was varied from 150% to 150%. The increasing of drawing ratio leads to an exponential increasing of fiber's strength and modulus without noticeable decreasing of their elongation at break. The optimal drawing ratio was about 100%, here the fibers strength, tensile Young modulus were the highest.

To improve the mechanical properties of fibers a different type of additives were incorporated into chitosan solution. The greatest increase in strength and tensile Young modulus on the ready-made fibers was observed with the addition of chitin nanofibrils. This is due to the orientation along the fiber axis of the filler and good interaction with chitosan molecules. Meanwhile the addition of polyvinyl alcohol (PVA) leads to a substantial increase in elongation at break and decrease of tensile Young modulus, while the strength remains constant, the optimum ratio of chitosan/PVA is 80/20 and 70/30.

The experimental samples of needle-punched nonwoven materials were also prepared. The studies have shown good biocompatibility, bactericidal action, bioresorption ability and the the absence of cytotoxicity of obtained materials. These properties of chitosan fibers and materials based on them make the chitosan as a promising polymer for the medical application.

Acknowledgement:
Financial support of this work by the Russian Foundation of Basic Research under contract grant number 14-33-00003 is gratefully acknowledged

Future perspective in polysaccharide research:
The obtained results allow using of the chitosan fiber as the matrices for cell and tissue replacement technologies as well as for the creation of muscle, cartilage tissue and serve as the basis for blood vessels and nerves. Polyfilament may be used to produce new biodegradable surgical suture materials while nonwovens based on chitosan to receive hemostatic material.
Quantitative determination of degree of modification in cross-linked hyaluronic acid hydrogels by $^1$H-NMR

- the importance of sample preparation

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Keywords:
Hyaluronic acid, Hydrogel, BDDE, NMR, Quantitativity

Abstract:
In this work the importance of proper and careful sample preparation for the quantitative determination of the degree of modification (MoD) in cross-linked hyaluronic acid (HA) hydrogels with $^1$H-NMR is presented. A clear definition of MoD in cross-linked HA hydrogels have previously been outlined (Ref 1). The MoD is defined as the stoichiometric ratio between the sum of mono- and double-linked linker residues and HA disaccharide units. In order to determine this ratio correctly a quantitative NMR spectrum must be obtained. As is known high molecular weight molecules and polymers, like HA and HA hydrogels, give $^1$H-NMR spectra with large linewidths due to fast spin-spin relaxation (short $T_2$). The large linewidths result in incorrect integration of the signals in these spectra. In order to decrease linewidths and enable correct integration of HA signals the polysaccharide backbone has to be degraded into smaller oligosaccharides. To highlight the importance of degradation MoD has been determined for a number of cross-linked HA hydrogels in their original state, partly degraded and fully degraded. The resulting MoD values are then compared and the results discussed. MoD and its correct determination can be an important contribution in attempts to find relationships between chemical modifications/cross-linking, mechanical and physico-chemical properties as well as to biocompatibility of HA hydrogels.

References:

Future perspective in polysaccharide research:
The correct determination of MoD for cross-linked or otherwise modified HA hydrogels is of outmost importance since MoD data is often used as a means to understand and predict other data generated regarding these materials such as physico-chemical properties or biological activities.
Homogeneous modification of cellulose in the new solvent triethyloctylammonium chloride in combination with organic liquids

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Keywords:
cellulose solvents, triethyloctylammonium chloride, cellulose acetate, cellulose derivatization

Abstract:
Recently, it was found that triethyloctylammonium chloride (N[2228]Cl) bears astonishing properties regarding cellulose dissolution.[1] On the one hand, it is possible to completely dissolve cellulose within the molten ammonium salt. On the other hand, dissolution can be achieved by combination of N[2228]Cl with certain organic dipolar aprotic solvents. The most surprising finding was that the salt dissolves cellulose in presence of acetone, which is usually used as precipitation agent in polysaccharide chemistry. Additionally, cellulose can be dissolved within a short time (2 h) in a mixture of N[2228]Cl and N,N-dimethylacetamide(DMAc) or dimethylsulfoxide(DMSO) without prior activation.

In the present study, the novel solvents were investigated regarding homogeneous cellulose derivatization reactions. One important cellulose derivative is cellulose acetate that is of great industrial interest. Therefore, the reactivity of different acetylation agents in N[2228]Cl/acetone and N[2228]Cl/DMAc under comparable reaction conditions has been examined.[2] The degree of substitution (DS) was used as indicator for the progress of the reaction. The same set of acetylations has been performed in common cellulose solvents like LiCl/DMAc and butyl-3-methylimidazolium chloride (BMIMCl) to verify the results received for the N[2228]Cl containing solvents. Furthermore, the novel solvent has been investigated regarding silylation and tosylation of cellulose. The silylation of cellulose is commonly used to achieve products that form ultrathin films by spin-coating, which are useful as model surface. Tosylcellulose is an important intermediate for nucleophilic displacement reaction.

References:

Future perspective in polysaccharide research:
Currently, self-healing polymers are of great interest in research and up to now polysaccharides are quite unexplored regarding this topic. In this context “Click-reactions” are an important tool to connect single polymer chains with each other and bear great perspectives in polysaccharide research. Moreover, fiber-spinning applying these solvents are under investigation.
Meltable Magnetic Biocomposites for Remote Melting

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Keywords:
Dextran ester, biocomposite, controlled release, alternating magnetic field

Abstract:
Dextran esters of fatty acids were synthesized that are thermoplastic. The melting temperature may be in the range from 30 to 140 °C that can be adjusted by degree of substitution (DS), molecular weight of dextran, and chain length of fatty acid [1]. A method for the preparation of magnetically responsive bionanocomposites was developed consisting of combined dissolution/suspension of the dextran ester and hydrophobized magnetic nanoparticles (MNPs) in an organic solvent followed by homogenization with ultrasonication, casting of the solution, drying and melting of the composite for a defined shaping. This process leads to a uniform distribution of MNPs in nanocomposite as revealed by scanning electron microscope. The thermoplastic magnetic composites have a melting range close to human body temperature. Samples of different geometries were exposed to high frequency alternating magnetic field. It could be shown that defined remote melting of such biocompatible nanocomposites is possible for the first time [2]. This may lead to a new class of polysaccharide based magnetic remote control systems, which are suitable for controlled release applications or self-healing materials.

References:

Future perspective in polysaccharide research:
In the third and fourth year of the project, the focus of the work is structuring of this magnetic biocomposite. It will be investigated how a local enrichment of particles and a structural i.e. magnetic anisotropy, respectively, can be generated.
On the role of CO₂ in dissolution of cellulose in the NaOH(aq) system

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Keywords: cellulose dissolution, cold NaOH(aq), CO₂, carbonation

Abstract:
Given the unsustainable character of cotton cultivation, there is an urge to meet the increased textile consumption by wood cellulose based textiles, capable of gradually replacing the less sustainable fibers. This undoubtedly implies a strong need to search for new solvent systems for cellulose. Today there are only few solvents capable of dissolving the intricate cellulose structure while being environmentally friendly and industrially viable. One of them, experiencing a renewed interest and intense research efforts is undoubtedly cold NaOH(aq). It employs benign and easily available components and is as such a very plausible alternative to the existing concepts. However, due to specific requirement on the hydration level of the NaOH along with the long range organization of cellulose chains, favorable interactions in this system are restricted to a very narrow window, implying need for either appropriate additives or modifications of cellulose structure in order to promote the dissolution process. High alkalinity along with the low temperatures required in the processing window render also solubilisation of substantial amounts of CO₂ in the system. In this work, a previously unexplored role of solvated CO₂ on the course of cellulose dissolution has been investigated. Our preliminary results indicate a partial carbonation of cellulose as an intermediate step facilitating dissolution. In order to promote and further explore the assumed carbonation route, a group of tertiary amines with the reported CO₂-capturing ability have been investigated as potential catalysts. Cellulose/CO₂ interactions were studied as a function of dissolution conditions by FTIR and NMR spectroscopy, including mechanistic investigations on low molecular model compounds. The effect of these interactions on cellulose dissolution in cold NaOH(aq) was evaluated in terms of solubility, solution stability and chemical stability of the generated intermediates under different dissolution conditions using gravimetric, spectroscopic and microscopy methods. Possibilities of governing dissolution conditions by choosing appropriate carbonation parameters have been investigated. Furthermore, the appealing idea of utilizing the reversibility of the carbonation reaction to control the regeneration process has been explored.

References:


Future perspective in polysaccharide research:

Well characterized polysaccharides (in terms of structure and interactions) as building blocks for future bio-based materials and chemicals developed at the intersection of fundamental and applied research.
Novel laboratory methods of fines separation and thickening

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Keywords:
Separation of fines, thickening of fines, dissolved air flotation, pressure screening

Abstract:
In the papermaking process, fines are defined to be fine cellulosic particles, which are able to pass through a 200 mesh screen having an equivalent hole diameter of 76 μm [1]. Common laboratory fractionation devices such as the Bauer Mc-Nett Fractionator (BMN) or the Britt Dynamic Drainage Jar Tester (BDDJ) are limited in production volume if higher amounts of fines are needed for research and lab activities i.e. for evaluation of technological properties of the fines fraction. The main problems when using these devices are that only a small amount of pulp can be fractionated (10 g BMN, 0.5 g / 5 g BDDJ) and the fine fraction is suspended in a huge amount of water. In order to overcome this problem, a laboratory pressure screen was implemented at the Institute of Paper, Pulp and Fibre Technology at Graz University of Technology in collaboration with the Department of Paper Technology and Mechanical Process Engineering at the Technical University in Darmstadt.

The device is equipped with a perforated strainer with a hole diameter of 100 μm separating the fines from the fibre fraction and can produce amounts up to 100g of oven dried fines within reasonable time. Still, when using this device the low consistency of the produced fines suspension is a problem for further application when it comes to transportation and dosage. Depending on the type of pulp, the feed consistency and the process parameters (e.g. accept-reject ratio, feed volume flow, internal pressure, rotor speed) the consistency of the obtained fines suspension ranges from 0.01 to 0.1%.

To overcome this limitation, a new method for thickening of the fines suspension based on flotation was developed. In general flotation is a process for selectively separating hydrophobic from hydrophilic particles. Dissolved air flotation is widely used in the process industry and especially in the paper industry for cleaning of process water or separation of printing particles (DIP). In this work, a flotation cell based on micro bubbles for thickening the fines suspensions with a clear focus on thickening efficiency has been developed. One important aspect for the development of the flotation procedure was the operation without use of chemical agents (e.g. flocculation agents, oils etc.) to avoid contamination of the material. Only water and air are used during the thickening of fines. Investigations regarding bubble size distribution and internal flow pattern were carried out in order to enhance the efficiency of the process. With this new technique it is possible to concentrate fines suspensions from –0.01 up to 4 %.

References:

Future perspective in polysaccharide research:
With the current separation and thickening method, fines can be processed easily and might be an alternative for the production of composite materials.
Understanding and improvement of mechanical properties in plasticized cellulose acetate polymers

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Keywords:
Cellulose derivate; mechanicals properties; dynamical properties; reinforcement

Abstract:
The development of thermoplastic based on cellulose by “melt processing” is a real challenge, not only for the mode of transformation of these systems but also for the properties of the final material. As the degradation temperature of cellulose acetate is very close to its melting point, its processing can be envisaged only with a sufficient amount of external plasticizer. The corresponding polymer/plasticizer blends are mainly governed by a “network” of very strong polar interactions. The strength and density of these networks depend on three specific parameters: the substitution (or acetylation) degree of cellulose acetate, the type and the amount of plasticizer. As it is really important to understand the dynamical properties of these systems, a PhD thesis has already studied their thermos-mechanical relaxations and the dependence of these properties with respect to the type and plasticizer content [1].

To complete this research thematic, our laboratory started to characterize the linear mechanical properties (tensile and compression testing) of plasticized cellulose acetate with an amount between 15 and 30% by weight of two different plasticizers which give an access to the influence of the composition on the mechanical performances (Young modulus, yield stress, rubbery plateau stress, failure deformation, etc...).

The goal of this study is to compare the different already accessible thermo-mechanical relaxations of these systems (primary α and secondary β relaxations) with the main deformation areas of the plasticized matrices (elastic, inelastic and plastic deformations). For this purpose we used the formalism developed by Halary et al [2]. We also used the Eyring formalism for accessing to the activation energy of the main mechanical relaxations (tensile testing experiment at different speed).

At this stage of our research we found for the whole set of compositions a linear dependence between modulus (and yield stress) with the “normalized” temperature. We also identified (by comparison between tensile and compression testing) the critical stress and the ductile-fragile temperature for each composition and the fact that the secondary β transition is always involve in these deformation mechanisms.

References:


Future perspective in polysaccharide research:

In complement we will characterize the microscopic mechanisms of damage during fatigue and tensile testing experiments at different steps of the deformation. The goal of this study will be to describe all the critical steps of the damage (critical stress, size of voids or crazes ...).

At a second step we plan to reinforce these systems with an adapted strategy depending on the typology of the damage we will observe, the response of the matrix and the application field we will investigate.
Advanced structural characterization of Ioncell-F fibres,

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Keywords:
Regenerated cellulose fibres, X-ray scattering, cellulose structure

Abstract:
Cellulose is a non-meltable biopolymer which is not soluble in conventional organic solvents. Recent studies on the application of ionic liquids (ILs) in cellulose chemistry have attracted a lot of commercial interest, including the production of regenerated and modified cellulose fibres. Ionic liquids have excellent solvation characteristics, in general a low toxicity and a low vapor pressure. The ionic liquid 1,5-diazabicyclo[4.3.0]non-5-ene acetate ([DBNH]OAc) was recently identified as an excellent cellulose solvent for dry-jet wet fibre spinning. Fibres spun from cellulose-[DBNH]OAc solution have shown very high tenacities and elastic moduli. The tensile properties of the Ioncell-F fibres are significantly affected by the draw ratio in the dry-jet wet spinning process.

The objective of this study is to elucidate the influence of the supramolecular structure on the mechanical fiber properties, thus establishing a structure-property relationship.

X-ray scattering techniques such as small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) can be utilized to reveal the fibre structure. WAXS measurements provide access to the fiber crystallinity, crystallite dimensions and the degree of crystal orientation, while SAXS measurements reveal the dimensions of microvoids and the length dimension within the elementary fibrils.

In this study X-ray scattering techniques have been employed in wet and dry state for an in-depth structural characterization of the Ioncell-F fibres. WAXS pattern of the ioncell fibres has shown the prominent lattice planes of the cellulose II structure. High crystalline orientation has been observed already for low draw ratios. SAXS scattering curves show enhanced reflections from the swollen fibres. This observation can be the evidence for long periods, however further studies are needed. Complementary analysis such as TEM, solid state NMR, dynamic moduli analysis and water retention are necessary to reveal the supramolecular structure of the Ioncell-F fibres. This study can help us to increase the spinning efficiency and tailor the properties of the Ioncell-F fibres.

References:

Future perspective in polysaccharide research:
Ioncell-F process has been recently developed at Aalto University, Finland, for production of regenerated cellulose fibres. These fibres has shown excellent properties compare to commercial fibres, for further development of this new technology, structural characterization of these fibres is necessary.
Mille-feuille paper: a novel type of filter architecture for advanced virus separation applications

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Keywords:
Cladophora Cellulose; Paper Making; Virus-retentive Filtration; Size-exclusion filtration

Abstract:
Viral contamination of drinking water and protein based pharmaceutics is a huge problem for countries and drug companies alike. Affordable filtration solutions where the viruses can physically remove a generally considered safer due to no residue of inactive virus or virus like particles. We will present a new type of filter, created from nano-cellulose from the filaments green algae Cladophora, with the ability to remove even the smallest viruses with a log. reduction factor of >5.51. The filter composes of a unique stratified structure of nano-cellulose fiber sheet, each with a defined pore size distribution forming the filter membrane. The pore size distribution can of the filter can be controlled by altering the drying temperature2 and will also be presented.

References:
(2) Gustafsson, S.; Mihranyan, A., Strategies for Tailoring the Pore-Size Distribution of Virus Retention Filter Papers. ACS Applied Materials & Interfaces 2016, 8, 13759-13767, 10.1021/acsami.6b03093.

Future perspective in polysaccharide research:
Filters used today are made of plastics or regenerated and modified cellulose, there are no commercially available filters of natural made cellulose fibrils. Our filters are wet-laid using the same principle as regular paper production, all though a lot of research into upscaling the production of our filter it is the main challenge we are facing now.
Paper-based sensing device for determination of contaminants in drinking water

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# Member of the European Polysaccharide Network of Excellence

Keywords:
paper-based, sensor, hydrophobic pattern, colorimetric indication

Abstract:
Paper as one of the most abundant products made of polysaccharides is due to its low cost, sustainability, bio-degradability and unique wetting properties a very promising substrate for sensor creation. Paper sensors can be used in many different fields, but in our work we focused on preparation of an inexpensive, disposable colorimetric sensor for detection of contaminants in drinking water, which is becoming a more and more pressing issue around the world, not only in third world countries, but also in developed parts of our planet.

We prepared the hydrophilic/hydrophobic patterns on the paper substrate using standard paper-making sizing agents, namely alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) and the piezoelectric ink-jet printing technique, which is a simple and effective way to prepare paper-based materials for advanced applications. The advantage of such system is that it requires a small sample volume only.

We studied the prepared patterns in terms of wettability (static water contact angle measurements), interactions between the hydrophobic agents and model cellulose surfaces (quartz crystal microbalance with dissipation - QCM-D; ATR-IR analysis, potentiometric titrations), topography (optical microscopy, SEM) and resistance to time and humidity – “ageing” process.

We applied colorimetric indicators inside the hydrophilic/hydrophobic pattern on the paper substrate in order to simultaneously detect a larger number of different contaminants in drinking water. We detected different pH values, the presence of metal ions, namely copper, chromium and nickel and the presence of E.Coli bacteria, and all that simultaneously with a small sample volume.

In our work we have shown that paper is even with its heterogeneity a very promising substrate for creation of a novel sensing device, especially combined with a reliable and reproducible ink-jet technique for high resolution pattern fabrication.

Acknowledgement:
We would like to acknowledge the funding of the Slovenian Research Agency (ARRS) in the frame of programme group for Textile Chemistry P2-0118, and in the framework of Junior Researchers training.

Future perspective in polysaccharide research:
I believe that polysaccharides are a very interesting and quite diverse group of renewable, biodegradable, sustainable and environmentally friendly materials that are also (mostly) in great abundance on our planet, that is why it is necessary to at least try and replace with polysaccharide materials the petroleum products that are to blame for most of the destruction of our planet. Besides that they are also a very promising material for preparation of novel sophisticated products in advanced applications, eg. sensing systems, electronics, magnetic materials etc.
Polysaccharide flat surfaces for biomolecule interactions

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Keywords:
polysaccharides, proteins, cells, DNA, adsorption, lithography

Abstract:
Given the various functionalities, different physicochemical properties and biochemical similarity with living extracellular matrix components, polysaccharides hold a great potential in numerous applications such as biosensors, immunoassays, drug delivery, tissue engineering, etc. For such applications, flat polysaccharide surfaces featuring smooth morphology, thickness and wettability are of high interest and offer many advantages compared to materials with less defined surface properties. Further, the whole set of advanced characterization techniques can be employed and they enable to perform all possible solid-liquid interface studies under various external stimuli (e.g., ionic strength, pH, etc.). The knowledge gained from these methods can lead to the fabrication of tailored cellulose-based interfaces by polymer blending and soft-lithography [1-3]. The interfaces designed in this way yield spatially resolved structures, wettability, charges and chemical composition, which subsequently allow to create a targeted adsorption of DNA, proteins and cells, leading to highly functional polysaccharide materials. In this presentation, new structuring methods and their resulting surface properties, and site-specific interactions with biological molecules will be presented.

References:

Future perspective in polysaccharide research:
Isolation and characterization of xylans cell wall from *Argania spinosa* leaves

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**Keywords:**
*Argania spinosa*, leaf, Xylan, MALDI TOF/TOF-MS/MS.

**Abstract:**
Hemicellulose-type polysaccharides were isolated from *Argania spinosa* (L.) Skeels leaf cell walls, collected from Tindouf area in the southwest of Algeria, by sequential alkaline extractions. Xylans fractions were obtained, purified and by size-exclusion chromatography on a Sepharose gel CL-4B column. The structure was investigated by acid and enzyme degradation with specific endo-β(1→4)-xylanase obtained from *Thermomycens lanuginosus* followed by analysis of the resulting fragments by size-exclusion chromatography on a Biogel P2 and characterized by sugar analysis and matrix-assisted laser desorption ionisation-time of flight mass spectrometry (MALDI-TOF MS). The results show that *A. spinosa* xylan is composed of a β(1→4)-linked-D-xylopyranose backbone substituted with 4-O-methyl-D-glucuronic acid residues.

**References:**

**Future perspective in polysaccharide research:**
Evaluations of antioxidant properties of xylans against the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) by electronic spin resonance (ESR).
Optimizing the spruce galatoglucomann-rapeseed oil ratio for superior emulsification

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Keywords:
Spruce galactoglucomannans, emulsion stability, polysaccharide characterisation

Abstract:
Plant polysaccharides form a structurally and functionally diverse group of molecules which are easily accessible in nature in abundance. The food and pharmaceutical industries are seeking for safe, cost-effective, sustainable, and functional alternatives to current hydrocolloids used as emulsifiers, for example. As an approach to develop novel hydrocolloids that fulfil all the above-mentioned requirements, we characterise wood hemicelluloses as emulsifiers and stabilisers. Spruce galactoglucomannans (GGM), which can be recovered at high yield from forest bio refinery processes, stabilise O/W emulsions more efficiently than the well-known food hydrocolloid, gum Arabic, and its potential replacer, corn fiber gum. Additionally, GGM efficiently inhibits lipid oxidation in emulsions, manifesting itself as multifunctional bio based stabiliser2. In our previous work, the GGM to oil ratio was standardized as 1:5, which enabled the formation of small oil droplets and stabilised them against coalescence. To systematically map the functioning component ratios in the present work, we used 1 wt.-% GGM to emulsify varying amounts of oil. O/W emulsions were prepared by high pressure homogenisation using micro fluidizer. To quantify the GGM adsorbed at droplet interface and continuous phase, the fresh emulsions were separated into the cream phase and continuous phase by centrifugation. The extracted GGM from both phases were characterised for molar mass and total polysaccharide content to understand the role of macromolecular distribution of this polysaccharide on emulsion stabilisation. Furthermore, the emulsions were stored at 40 °C for an accelerated storage test during 6 weeks. The physical stability of the stored emulsions was studied by droplet size distribution and optical microscopy. The results will enable systematic mapping and optimization of the functional component ratios to produce a physically stable emulsion using the promising novel hydrocolloid, GGM.

References:

Future perspective in polysaccharide research:
Hemicelluloses biomass streams can be valorised to develop efficient bio-based stabiliser progressing the society towards bio-economy and sustainability.
Production of furfural from xylose using solid acid catalysts

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Keywords:
Xylose, Furfural, Solid catalyst, Forest Biorefinery

Abstract:
Recent years have witnessed much activity to upgrade sugars contained in side-streams from the pulp and paper industry into ethanol and other value-added chemicals. An interesting catalytic route, namely the dehydration of sugars to furans, is considered one of the most promising routes for the production of platform chemicals and fuels. Furans such as furfural are highlighted in the “Top 10 + 4” by the United States Department of Energy list as the most rewarding bio-based platform molecules (1).

The current furfural production uses mineral acids at approx. 200 °C, providing around 50 mol% yield. These mineral acids possess several drawbacks, e.g., high toxicity, corrosiveness, difficult recovery and large salt waste after work-up. The purpose of this study is to replace the mineral acid with solid acid catalysts. This approach may offer several advantages over current processes in the conversion of pentosan derivatives e.g. xylose into furfural: high yields, facile separation and reusability of the catalyst. In the present study, different solid acid catalysts developed for this purpose (sulfated zirconia, alumina and Al-MCM-41), as well as commercial polymers have been tested to find a selective and stable catalyst. The results of this work could be used to produce platform chemicals from sugar-based side-streams in the forestry industry, in particular from the pre-hydrolysate liquor for dissolving pulp. These obtained value-added products have applications in a wide range of industrial branches (biofuel, pharmaceutical, agrochemical, petrochemical and chemical industry, among others).

References:

Future perspective in polysaccharide research:
Progress in this research field can be expected to occur in valorization of sugar-based side-streams into processed products such as solvents, resins, pesticides and biofuels.
Extraction, characterization and modification of flaxseed mucilage

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Keywords:
mucilage, flax seed, enzymatic esterification

Abstract:
Mucilage is an exopolysaccharide secreted by the seed or soft-stem plants (i.e. okra, psyllium and tamarind) as a by-product of the metabolism. It is a water-soluble fibre of viscous nature, and can be described as a mixture of condensation biopolymers containing one or more monosaccharides usually combined with uronic acids. Like pectin, chitosan and alginate, mucilage is widely employed as non-toxic, biocompatible, biodegradable and renewable raw material for a large number of industrial applications, such as binding, thickening, emulsifying, gelling and as controlled release agent. Among biomass residues from agri-food industry, the mucilage of flax seeds (Linum Usitatissimum L.) has not yet found large applications and deserves further valorisation. Flaxseed mucilage occurs in the outermost layer of the seed coat and can be easily extracted with water from the whole seeds or the residual seed cake after the extraction of the oil. This fiber is a mixture of two main polymers. An acidic pectin-like ones, named as rhamnogalactuoranan, containing a backbone of L-rhamnose and α-D-galactosyluronic acid with side chains of L-fucose and L galactose, and a neutral ones (about 75%), named as arabinoxylans, containing a β-D-xylan backbone with side chain of L-arabinose and L-galactose. However, both the procedure of extraction and the variety of the flax crop affect the yield, chemical composition and physicochemical properties of the final product.

Mucilage was extracted from flax seed by water-soaking followed by precipitation with ethanol. The product was characterized by NMR, ATR, and TGA analyses. The viscosity, solubility, foaming ability, and stability were also investigated. Currently, we are planning to synthesize flaxseed mucilage-based conjugates, consisting of a hydrophilic polysaccharides backbone and a hydrophobic fatty acid side chain (i.e. lauric, palmitic or oleic acid) by enzymatic catalysis.

References:

Future perspective in polysaccharide research:
The esterification would change the interactions between the polymers, as well as the physicochemical and functional properties of the starting material. The modified mucilage might find manifold applications as food-grade, biodegradable and non-toxic amphiphilic stabilizer in several industrial formulations in substitution of the hazardous synthetic polymers.
Purification and characterization of fucoids from *Bifurcaria bifurcata* seaweed

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**Keywords:**
Polysaccharides, Fucoids, *Bifurcaria bifurcata*.

**Abstract:**

In recent years the search for new active ingredients has led to an increased interest in marine resources. Algae are an important source of bioactive components. Previous studies have shown that brown seaweeds are characterized by their high content of antioxidants like phlorotannins, phenolic compounds and fucoids. Fucoids are natural polysaccharides present in the cell walls of brown seaweeds like *Bifurcaria bifurcata* where it can be found in great amount (Mian et al., 1973). The fucoids generate great interest because of its anticoagulant, antioxidant, anti-inflammatory and immunomodulatory properties (Bo et al., 2008).

This study is based on the extraction, purification and characterization of fucoids from *Bifurcaria bifurcata* seaweed. Fucoids extraction from *Bifurcaria bifurcata* seaweed was done using water as solvent extraction resulting in a high quality fucoid. Further purification and fractionation was carried out by Diethylaminoethyl (DEAE)-Sepharose CL-6B ion-exchange chromatography. The upward gradient elution with sodium chloride revealed six fractions of fucoid according to their sulphate content. The different fractions and fucoid were subjected to tests using the 2,2-diphenylpicrylhydrazyl (DPPH) antioxidant activity assay and the ferric reducing antioxidant power (FRAP) assay method. The results showed that only sulphated fractions had significant antioxidant activity, elucidating the role having sulfated molecules in development activity. Structural determination of the different fractions by Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) concluded that only the crude extract and the 6th fraction were constituted by hexanes. For future prospects the use of higher concentrations of crude extract will be relevant to increase the concentration of the isolated fractions and thereby obtain better mass spectra that allow a better structural resolution.

**Acknowledgement:**

This work was partly supported by the Ministry of Economy and Competitiveness of Spain and European Regional Development Fund (project CTQ-2013-43616/P).

**References:**


**Future perspective in polysaccharide research:**

For future prospects, the determination of fucoids fractions will be the first step for the future investigation about the different applications of these polysaccharides based on their bioactivity.
Ternary systems of carbohydrate, lipid and protein

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Keywords:
starch, lipids, proteins, complex, ternary systems

Abstract:
Among numerous factors promoting retrogradation of starch temperature, gelatinization and storage times, amylose/amylopectin ratio in starch granules, length of the chains of both these components, content of phosphorus, protein and lipids, availability of water, concentration of the gel are the most essential. The aim of study was create of a ternary type systems: potato starch/stearic acid/albumin from egg, potato starch/albumin from egg/stearic acid and stearic acid/albumin from egg/potato starch at 7% concentration of systems. The reactions with potato starch were proceeded in aqua environment. The starch was gelatinized in the ternary system. The systems were reacted in 1:1:1 weight ratio. Thermal analysis (TG/DSC) of ternary systems were made. The thermal behavior of investigated systems indicates the most stability of the system: potato starch/stearic acid/albumin. Also scanning electron microscope (SEM) with EDS detector and FTIR studies were carried out. These analyzes show possibility of creation of new structures/complexes. The typical structures of studied systems show figures.

References:

Future perspective in polysaccharide research:
The conducted analysis confirm the interesting physicochemical properties of tested systems, which will allow for their potential use as environmentally friendly “green cells”. Potentially complexes of ternary systems with multi-walled carbon nanotubes are interesting in composition of electrodes in batteries.
Water vapor permeability and mechanical properties of edible films on native starch from improved cassava variety in Côte d’Ivoire

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Keywords:
Cassava variety, native starch, edible packaging, mechanical properties and water vapour permeability

Abstract:
A study in Côte d'Ivoire entitled "artisanal and industrial valorization of native cassava (Manihot esculenta Crantz) and yam (Dioscorea sp)" starches showed that the film produced with starch cassava and vegetable oil showed the most promising coatings capabilities. This film was designed without plasticizer and showed mechanical limits. So, the presence of plasticizer could overcome the fragility of the film, with a commonly used slurry of 15-40 g of glycerol in 100 g of starch. The properties of starch films can be further improved by producing composite films with incorporation of functional additives. Thus, in this present study, starch-based films have been strengthened with addition of a plasticizer (glycerol), an emulsifier (soy lecithin) and a preservative (potassium sorbate). Films were prepared with 5 % oil, 25 and 30 % glycerol, 0 and 5 % soy lecithin and 0.2 g potassium sorbate. Mechanical (Tensile strength and Elongation at break) and water vapor properties of native cassava starch improved variety Olekanga films were determined. Increasing glycerol concentration and soy lecithin addition had no significant effect on water vapor permeability of all films. In opposite significant difference (p <0.05) of glycerol concentration was observed on tensile strength and elongation at break of films. Which was not the case when soy lecithin concentration is increased from 0 to 5 %. Tensile strength decreased with increase in glycerol concentration. Opposite behavior was observed for elongation at break. Films on native starch from improved cassava variety Olekanga in Côte d'Ivoire were less resistant, very elongable with acceptable water vapor permeability

References:

Future perspective in polysaccharide research:
The variety of starch based edible films improved cassava will be strengthened to improve their poor mechanical properties. Natural and biodegradable materials such as fibers and yam starches of high amylose will be used.
Integrated strategies for the production of starch-enriched microalgal biomass for bioplastic resins

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Keywords:
microalgae, starch productivity, metabolic kinetics, bioplastic

Abstract:
Plasticized starch, eventually blended with other biobased polymers such as aliphatic polyesters, is now established as a reliable alternative to petroleum-based polymers for biodegradable packaging films or injection-molded parts. The occurrence of massive non-food/non-feed applications of traditional starch crops creates new competition and increased tension on global markets. Besides being well-known lipids producers, various microalgae strains have also proven to be powerful starch producers. They display a greater productivity than terrestrial crops such as corn and potato (the current main sources of starch for the industry) and don’t interfere with food & feed markets. This study first focuses on exploring both the microalgal diversity and their growing conditions to select strains with high potential for starch accumulation. Different biotechnological strategies are then envisaged to optimize the production, at both lab (200mL) and small pilot scales (30L). Early results hold the promise of a 40% to 60% w/w starch ratio in the harvested biomass. Direct plasticization assays will confirm its ability to be transformed into an innovative bioplastic material, with properties fitting the current industrial standards.

Acknowledgements:
This work received support from the French National Agency for Research under the program "Investissements d’Avenir" (reference ANR-10-LabX-05-01).

References:

Future perspective in polysaccharide research:
Finding renewable resources non-competing with food & feed crops for the development of polysaccharide based products is a critical issue. The production of specific microalgal biomass with controlled biochemical composition and structure should allow the development of microalgae based materials.
Starch aerogels

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Keywords:
Aerogels, Starch, Thermal Super-insulating Material

Abstract:
Bio-aerogels are a new generation of porous materials made from polysaccharides. Their porosities make them lightweight (density around 0.1 g.cm-3) with a high specific surface area (200-300 m².g-1). With such properties, they can be used as drug carriers, in engineering applications (for thermal super-insulation, pectin aerogels [1]) and in electro-chemical (when pyrolysed, cellulose aerogels [2])

For this work, starches from different sources were used to prepare aerogels via dissolution-retrogradation-coagulation and subsequent drying with supercritical CO2. The goal was to study the influence of starch type (amylose/amylopectin ratio), concentration and processing parameters (retrogradation time, type of coagulation bath) on aerogels properties and morphology.

It was observed that the higher the amylose content, the less the shrinkage after drying, it thus resulted in a lower density. Higher amylose content also led to higher specific surface area. However, it was not possible to prepare pure amylose monolithic aerogels because no mechanically stable network can be obtained. This result showed the importance of amylopectin network formation during retrogradation.

Finally, the thermal conductivity of starch aerogels was investigated. Pea starch aerogels (amylose/amylopectin ratio = 40/60) fell in the region of thermal super-insulating materials, with the thermal conductivity around 0.021-0.022 W.m-1.K-1 which is lower than that of air (0.025 W.m-1.K-1), showing some similarities with pectin-based aerogels [3]. Pea starch-based aerogels have a low density (around 0.1 g.cm-3) and a high specific surface area (up to 250 m².g-1). Their mechanical properties improved with the increase of retrogradation time.

Acknowledgements:
We thank Suzanne Jacomet (CEMEF, MINES ParisTech) for SEM analysis, Nela Buchtova (CEMEF, MINES ParisTech) for guidance in specific surface measurements, Gilbert Fiourucci (CEMEF, MINES ParisTech) for the help in mechanical measurements and Pierre Ilbizian (PERSEE, MINES ParisTech) for supercritical drying.

References:

Future perspective in polysaccharide research:
This study shows that starch can be used to make new versatile materials for various applications, from engineering (thermal super-insulation) to biomedical (matrices for controlled release).
**Abstract:**

Aerogels are lightweight materials with outstanding structural properties like high surface area and open porosity, suitable for thermal insulation or loading active compounds. Using polysaccharides like pectin to produce bio-based aerogel is especially attractive due to their biodegradability and biocompatibility, essential for food and pharmaceutical applications. In this work, pectin was used to produce aerogels called Aeropectins [1]. The goal of our work was to understand the influence of pectin type (Degree of Methylation, DM), concentration and gelation mechanism (physical or Ca2+ induced) on Aeropectin morphology and properties. Aeropectins were prepared by polymer dissolution, gelation (in some cases gelation did not occur) followed by coagulation in ethanol and drying with supercritical CO2. Three pectins with DM varying from 35% to 70% were kindly provided by Cargill. Solution gelation was controlled by varying pH and calcium concentration. In certain conditions gelation did not occur (for acidic conditions without calcium) and pectin was coagulated directly from solution. In all cases monolithic highly porous samples (porosity around 97%) were obtained. The influence of pectin DM and preparation conditions on Aeropectin density, specific surface area, morphology and thermal conductivity will be presented and discussed. For example, the DM of pectin did not seem to significantly impact the morphology and thermal properties of the pectin aerogels prepared in acidic conditions (pH 1.5).

The so-obtained aerogels are thermal super isolating materials with thermal conductivity from 0.18 to 0.22 W.m⁻¹.K⁻¹. As Aeropectins are highly porous materials with open porosity and a high surface specific area (>300 m²/g), they are promising degradable carriers for drug delivery systems.

**References:**


**Future perspective in polysaccharide research:**

This study shows that pectin can be used to produce new versatile materials with high potential for various applications, from engineering (thermal super-insulation) to biomedical (matrices for controlled release).
Mixing and thermal behaviour of gluten free flour doughs supplemented with natural biopolymers

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Keywords:
Chestnut flour, Guar gum, Kappa/iota-hybrid carrageenan, Mixolab®, Starch

Abstract:
Gluten-free doughs must exhibit appropriate nutritional and technological aptitude to enhance the acceptance by the consumer of the final product. As consequence, it could be interesting to assess the effect of addition of natural biopolymers or the increment of mixing temperature, which could help to agglutinate doughs and get optimal bakery formulations. This work is focused on mixing and thermal characteristics of home-made chestnut flour (CF) doughs supplemented with 2% (flour basis, f.b.) of kappa/iota-hybrid carrageenan (KI) or guar gum (GG) and 1.8% f.b. of NaCl. CF doughs without biopolymers were employed as control sample (CS). The mixing and thermal tests were performed at least in duplicate using Mixolab® apparatus following standard protocols for wheat flour (Moreira et al., 2011). A proposed three-step protocol (1: 5 min, 50°C; 2: 10 min, 50-90°C (4°C/min); 3: 4 min, 90°C) was also conducted to study the influence of mixing temperature increase.

Results showed that CS-dough was not able to complete the mixing/thermal tests using standard protocols. Additive supplementation allowed completing these tests. Namely, water absorption of all studied doughs varied in a narrow range (55.5 ± 2.5 % f.b.). The addition of KI or GG in the presence of salt improved the mixing behaviour, mainly in terms of stability (from 0.4±0.1 (CS) to 2.2 ± 0.3 (KI) or 3.9 ±0.7 min (GG)). The proposed protocol allowed enhancing stability of KI-dough (3.4±0.2 min) whereas no changes were observed for GG-dough. The starch heat resistance to dough processing was also improved with additive supplementation, allowing leading to complete the mixing/thermal test. The use of KI promoted lower gelatinization temperatures (around 3°C) compared to GG for both standard and proposed protocols. These initial and final gelatinization temperatures (from 53.9 to 76.1°C) nicely match with those reported for commonly used gluten-free flour dough (Moreira et al. 2015).

Acknowledgement:
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References:

Future perspective in polysaccharide research:
Future works will be focused on improving the technological aptitude of gluten free doughs based on chestnut flour supplemented with antioxidant properties. To this end, the effect of extracts with high polysaccharide and bioactive compounds content from several spices of brown seaweeds will be studied.
Enzymatic treatment for patterning of bicomponent biopolymer thin films

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Keywords:
poly-3-hydroxybutyrate (PHB), cellulose, thin films, phase separation, enzymatic degradation

Abstract:

The utilization of phase separation in order to generate patterned polymer surfaces is of high interest, especially concerning thin film applications in various fields such as optics, electronics and biotechnology. A variety of surface morphologies, ranging from smooth to extremely rough or specially patterned, is required in this wide spectrum of applications.¹,²

In this contribution, we show the bio-orthogonal enzymatic patterning of blend thin films, composed of PHB (poly-3-hydroxybutyrate) and cellulose. Blend thin films were prepared in different ratios via spin coating of PHB/TMSC (trimethylsilyl cellulose) solutions and regeneration of TMSC to cellulose afterwards. Thickness, surface free energy, surface roughness and morphology of the films were investigated. Enzymatic structuring was performed with either PHB‐depolymerase or cellulase. Atomic Force Microscopy investigations of enzyme treated surfaces reveal complete removal of PHB respectively cellulose and display features in the nano and micro size range depending on the blend ratio. Additionally, enzyme‐substrate interaction of PHB‐depolymerase was studied by means of Multi‐Parameter Surface Plasmon Resonance, showing extremely fast PHB degradation compared to other enzymes of this kind.

References:


Future perspective in polysaccharide research:

In my opinion, the gain of significance for polysaccharide research in the future will be accompanied by the rising demand of the replacement of petrol derived polymers due to environmental and economic reasons. In addition to that, polysaccharides feature remarkable properties regarding biodegradability and biocompatibility, that fossil based polymers do not provide, leading to an even greater variety of future applications. The herein presented work depicts one of the ever‐expanding number of examples for the utilization of bio‐instead of petrol‐based polymers.
Reactive cellulose-based thin films - a concept for multifunctional polysaccharide surfaces

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Keywords:
thin films – cellulose – post-modification – QCM-D – CDI activation

Abstract:
Polysaccharide thin film coatings can serve as a model for bulk materials or can subsequently be surface modified by a large number of chemical reactions depending on the targeted application. Surface reactions give accessibility to derivatives that are difficult to produce under homogeneous conditions in solution due to cross-linking, which hampers subsequent processing into thin film coatings. An advanced approach is the design of reactive thin film based platforms allowing post-modification after coating the polysaccharide derivative on a substrate. This includes reversible crosslinking reactions or immobilization of e.g. biomolecules and nanoparticles. This work therefore aims at combining the advantages of polysaccharide derivatization in solution with the post-modification of thin films. Reactive coatings of hydroxyethyl cellulose furoate in the form of thin films, suitable for the covalent immobilization of functional molecules or nanoparticles, were developed and characterized in this work. The cellulose furoate derivatives were synthesized under homogeneous conditions by esterification of hydroxyethyl cellulose with 2-furoic acid. Reactive platform layers of these furoates were obtained by chemical surface modification of spin coated thin films with N,N'-carbonyldimidazole. This chemistry allowed the covalent immobilization of functional molecules bearing primary and secondary amines on the films. The degree of substitution of the furoate thin films and their amino functionalized counterparts was determined gravimetrically by a quartz crystal microbalance (QCM-D) and correlated with infrared and X-ray photoelectron spectroscopy and zetapotential measurements. Scanning electron- and atomic force microscopy confirmed changes in the morphologies that were influenced by the chemical reactions on the surface. The concept presented can be seen as a versatile method for immobilizing amine-containing (bio-)molecules and nano-objects to polysaccharide surfaces with the furoates having the potential for further reversible cross-linking in Diels-Alder reactions.

Acknowledgements:
The support of the German Research Foundation (DFG, Research Fellowship EL843/1-1) and the European Union’s Horizon 2020 research and innovation programme (grant agreement No 665172) is gratefully acknowledged.

Future perspective in polysaccharide research:
The biopolymer derivative could be cross-linking by (Retro)-Diels-Alder reaction with bismaleinimides and thus, these films are promising in field of self-healing materials. Beyond cross-linkable furfuryl moieties 1H-imidazole-1-carboxylate groups provide a reactive platform coating for various multiresponsive materials by aminolysis.
Development of innovative bionanocomposites based on polysaccharides and protein nanofibers

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Keywords:
Protein nanofibers, Polysaccharides, Bionanocomposites

Abstract:
The production of chemicals, materials, fuels and energy is nowadays progressively moving in the direction of renewable resources, and there is a growing interest on the use of polysaccharides, such as cellulose, pullulan and chitosan for the development of new sustainable materials with distinct functionalities and applications. Proteins are also gaining increasing attention as singular components for multi-functional biomaterials. The assembly of proteins into long and insoluble ordered fibrillar structures (protein nanofibers) is a very recent and promising strategy for the development of nanosized reinforcing elements for bionanocomposites, with applications ranging from medicine to soft matter and nanotechnology.

In this project, proteins, such as insulin, β-lactoglobulin and hen egg white lysozyme, were fibrillated and combined with different polysaccharides, namely gelatin, pullulan and cellulose (both vegetal and bacterial forms) to develop new functional biomaterials for application in the biomedical field. These new functional biomaterials were characterized in terms of morphology, mechanical properties and biocompatibility, as well as cell adhesion and proliferation and its potential to be used as scaffolds in the biomedical field.

References:

Future perspective in polysaccharide research:
The use of protein nanofibers with different polysaccharides is opening a promising range of new perspectives in the biomedical field.
Coating of cellulose fibers with inorganic nanoparticles in the course of the Viscose process

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Keywords:

Abstract:
Shortly after the production of man-made cellulose fibres started in the late 19th century, the fibres obtained by a variety of different processes, conquered the markets and replaced natural fibers made from cotton, jute and flax. One of the oldest, but still most successful processes for the production of man-made cellulose fibers is the so called viscose process, developed by Cross, Bewan and Beadle.¹ ² Although the viscose process is already in practice since 1900, still some unsolved problems exist in this process and there is even more space for product development in this heavily used industrial process. One of the most interesting areas in the product development of artificial fibers is the design of new product properties and therefore the use of cellulose based fibers in new applications. In this contribution we will present our latest results in the synthesis of inorganic nanoparticles and the fiber coating with these particles in the course of the viscose process.

References:

1) Klare, H.; Acta Pol.; Bd. 36; S. 347-352

Future perspective in polysaccharide research: In my opinion, the increase in the use of polysaccharide based materials in its classical applications will continue. In addition many today rather unexpected areas, for example electronics, composite materials or smart functional materials, will become possible fields of applications for polysaccharide based materials in the next decades.
Cellulose fibre – silica aerogel thermal superinsulation composites

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Keywords:
Cellulose, silica, aerogel, composite, superinsulation

Abstract:
Thermal superinsulation materials (typically aerogels, with thermal conductivity below that of air: 0.025 W/m.K at room conditions) are usually fabricated from mesoporous alcogels with the use of supercritical (sc) CO₂ for drying. By use of supercritical fluid, the mesoporous structure of the wet matrix, is preserved as the pore liquid is removed. This process is, however, cost prohibitive and involves specific process parameters (e.g. high pressure) which make it difficult to up-scale. Ambient pressure drying therefore is much preferred. The challenge is preserving monolithic shape of the sample which is stressed due to the high surface tension of pore liquid during evaporative drying. We propose that this could be addressed by incorporation of short cellulose fibers into silica alcogels allowing making monolithic, not brittle and thermally superinsulating aerogels via ambient pressure drying instead of sc drying.

We used Tencel as model fibers. The aerogels with 0.5 to 3 final vol% of fibers were synthesized and hydrophobized before drying. Fiber presence allowed fabrication of monolithic aerogels via ambient drying. The effects of different cellulose fibers on the properties of silica-based composite aerogels produced both via ambient drying and the sc CO₂ drying methods are compared. Thermal conductivity of composites was typically below 0.018 W/m.K for composites containing <2 vol% fiber fraction and increased slightly with increasing fiber concentration. The bulk densities of ambient and sc CO₂ dried aerogels were similar (typically in the 0.1 – 0.125 g/cm³ range). The addition of cellulose fibers significantly increased the Young’s modulus of both the sc dried aerogels and ambient-dried aerogels. This original aerogel preparation method was also successfully demonstrated with natural fibers from wood with different lignin content and flax.

Acknowledgements:
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Future perspective in polysaccharide research:
This application may be particularly interesting for the pulp and recycled fibre industries because they produce short fibers (elementary fibres with <10 mm length). Additionally similar composite approach could be potentially applied for polysaccharide based aerogels as well for their reinforcement.
Measuring fiber size in polymer-lignocellulosic fiber composites: advantages and limitations of 2D scanner, automated analysis, microtomography methods

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Keywords:
Natural fibers, Polymer-matrix composites, Microstructure, Statistical properties/methods

Abstract
The mechanical properties of biomass-reinforced composites are influenced by the efficiency of the stress transmission between the matrix and the lignocellulosic fragments. During the compounding, the local thermomechanical conditions influence the fragments dispersion and distribution in the matrix, but also they may lead to severe biomass degradation, with a global diminution of the geometrical characteristics (length, diameter, aspect ratio). Lignocellulosic fragments, which are usually bundles of elementary fibers, can break and fibrillate at the same time. The quantification of the fragments size is therefore crucial to predict the mechanical properties of a composite. The lack of an international standard for the measurement of the biomass morphology opened the way to the development and the utilization of several different methods. In this work we investigated the advantages and the limitations of three different techniques that are commonly employed for the measure of lignocellulosic fragments in polymer composites, i.e. high resolution 2D scanner, automated dynamic fiber analyzer, and X-ray microtomography. Two types of biomass of different morphology and composition, hemp and miscanthus, are chosen. Composites are prepared by using a laboratory-scale co-rotating twin-screw extruder, at two feed rates and constant screw feed. We show that the analysis of the morphology of lignocellulosic fragments is still complex and does not allow an objective estimation of the sizes. Each method has its own advantages and disadvantages. Overall, the three methods are complementary and the use of each depends on the goal of the work.

References:

Future perspective in polysaccharide research:
Studies on biomass size measuring techniques are necessary to improve the assessment of lignocellulosic fragments’ morphology. A customized analysis strategy can be developed to benefit from the strengths of different methods in order to make the measurements more precise and faster.
Layering of polysaccharide and synthetic materials for preparation of an optimal wound dressing

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Keywords:
wound healing, pain, alginate, viscose, polyethylene terephthalate

Abstract:
Among the most important conditions affecting wound healing are clean, adequately perfused wound environment free from infection, necrotic tissue and foreign material. Therefore effective wound management support wound healing by maintenance of moisture balance and prevention of infections, as well as appropriate exudate management. Pain was proven to causes delay in wound healing. It has been demonstrated that patients with wounds experience most pain during dressing changes. Therefore, effectively alleviating pain and also providing patients with less painful wound healing environment should be a topic with more attention. For effective pain relief appropriate dressing materials are needed and also support of analgesic active substances. We combined polyethylene terephthalate, as inert layer that does not damage the newly formed tissue, alginate as an effective absorbent and moisturizer of wounds and viscose as the secondary layer for alginate into one wound dressing. Wound itself and dressing changes cause severe pain, where just selected material can’t be enough for a sufficient pain relief. Mostly non-steroid anti-inflammatory drugs (NSAIDs) are taken in the form of pills and as such they have severe adverse side effects especially on the gastrointestinal tract. The latter can be bypassed by local administration direct into the wound. Their effect starts after 30 minutes and therefore they are not the drug of choice for relieving pain, caused by dressing changes. Therefore, we prepared a multilayered wound dressing with incorporated drugs, where NSAID diclofenac was used for relief of pain, present due to wound, where pain, caused by dressing changes

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References:
MAVER, Tina, HRIBERNIK, Silvo, MOHAN, Tamilselvan, SMRKE, Dragica, MAVER, Uroš, STANA-KLEINSCHEK, Karin. Functional wound dressing materials with highly tunable drug release properties. RSC advances, ISSN 2046-2069, 2015, vol. 5, iss. 95, str. 77873-77884

Future perspective in polysaccharide research:
Wound healing is a very broad scientific field where polysaccharide materials will always have an important role. With available advanced techniques in our laboratory we have possibility to prepare several new materials and through their exact characterisation we can define those that can contribute to a better life of patients with wounds.
Novel textile materials for prophylactic treatment of the diabetic foot

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Keywords: probiotics, nanofibers, advanced materials, diabetic feet

Abstract:
Diabetes has a growing negative impact on healthcare systems around the world with an annually increasing number of patients around 0.5%. Amongst the more frequent complications of diabetes with significant implications on the patient quality of life is the diabetic foot. Since related consequences can be severe, different preventive measures have been considered over the last years to either improve early detection or to prolong the time until the diabetic foot can arise. Over the past decade, a lot of work has been conducted to improve efficiency of antimicrobial agents, their selectivity, and even specificity. Yet there are still no products available, dealing with prevention or disturbance of pathologic bacteria growth by using the body’s natural allies that form the healthy skin microbiome. To the best of our knowledge, using the promotion of “healthy bacteria” growth to hinder habitation by pathologic bacteria, is something new even in research. Based on the mentioned, our main goal will be the preparation of novel textile materials for prophylactic treatment of the diabetic foot. A specially designed approach will be used for functionalization of commercial fibers, where we will use methods for increasing the electrostatic interactions between bacteria and fibers. Novel textile materials will be developed also by using the environmentally friendly technology electrospinning, where careful design of nanofibers with tuned size and chemistry, will enable the incorporation of beneficial microbiota and add to the function of the final product.

Acknowledgement: We would like to acknowledge national project No. L2-5492 and programme group for Textile Chemistry P2-0118, from the Slovenian Research Agency, as well as Woodwisdom programs (Aerowood and PShapes) co-financed by Ministry of education, science and sport.

References:


Future perspective in polysaccharide research:
The combination of bacteria and polysaccharides to prepare novel therapeutic solutions in treatment of diabetes, could be a new niche in the field of polysaccharides for biomedical applications with high potential for future commercialization.
Carboxymethyl chitosan nanoparticle dispersions as coatings for improved antimicrobial and antifouling properties of silicone surfaces

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**Keywords:**
Carboxymethyl chitosan, Silicone, Antimicrobial, Antifouling, QCM-D

**Abstract:**
Antimicrobial and antifouling materials are of great importance in the medical field and the development of natural-based advanced medical materials has gained a lot of attention in the last few decades. In particular, antimicrobial polysaccharides prosper especially as alternative materials for medical applications, since a wide variety of common antimicrobial chemical agents used in the medical field, such as metals and metal salts, iodophors, phenols and thiophenols, and antibiotics, are toxic to humans and harmful to the environment.

Chitosan, a derivative of chitin, is a natural, biodegradable, biocompatible amino-polysaccharide which exhibits antimicrobial properties. It is therefore highly desired in medical applications. Nevertheless, its drawback is its high fouling and protein adsorption. The advanced derivative carboxymethyl chitosan, which also contains carboxyl groups, possesses a zwitterionic character. Zwitterionic polymers are known to exhibit good antifouling properties. Having both, antimicrobial and antifouling properties in one polymer is of great advantage when considering its use as a coating of medical implants.

In this work, the polysaccharide carboxymethyl cellulose was used to prepare aqueous nanoparticles dispersions which exhibit both antimicrobial and antifouling properties. The particles were adsorbed on flat silicone surfaces. Silicone is known for its application in medical implants where antimicrobial and antifouling properties play a major role and a simple and cost effective coating would drastically change the lifetime and comfort of such implants. Interaction studies between the solid surfaces and the nanoparticle dispersions were conducted using a quartz crystal microbalance (QCM-D), confocal microscopy, atomic force microscopy, and potentiometric titrations. The antimicrobial properties were evaluated using the standard test ASTM E-2149-10 and the antifouling properties on silicone were conducted by protein adsorption studies using QCM-D.

**Acknowledgement:** The financial support in the frame of programme group for Textile Chemistry P2-0118, financially supported by Slovenian Research Agency. The European Union’s Horizon 2020 research and innovation programme under grant agreement No 665172 and the WoodWisdom programs Aerowood and Pshapes.

**References:**

**Future perspective in polysaccharide research:**
The use of natural and biodegradable zwitterionic polysaccharides as coatings for medical implants can open a whole range of new ideas and use of other polysaccharides in this field. The zwitterionic coating of silicone surfaces by carboxymethyl chitosan allows one to explore other fields as well, besides the medical one. It can be used as a final coating or as a functional layer used to covalently attach other substances.
Barrier properties of chitosan coated poly (ethylene terephthalate)

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Keywords
Chitosan, PET, Barrier properties, Food packaging, coating

Abstract:
The remarkable properties of water tightness of the PVDC (poly (vinylidene chloride)) make it perfect for food packaging. It is applied in the form of a coating on other plastic films such as poly (ethylene terephthalate) (PET) for barrier properties. However, serious safety and environmental issues must be considered with the use of this polymer. Several studies [1] analyzed the contribution of the PVDC of dioxin formation during incineration: all show that the presence of PVDC increases the amount of dioxins formed in the incinerator of household wastes due to the presence of the chlorine in PVDC.

In order to solve this problem, many solutions are already implemented such as the use of a polymer resulting from shellfishes, chitosan, which has a polysaccharide structure and presents good gas barrier properties due to the high amount of hydrogen bonds in the polymer [2]. Moreover this material shows good film forming properties; one can thus manufacture a film while using the fewer additives possible.

In this work, coating of PET films by chitosan is studied. An acidified aqueous solution of chitosan (1 wt. %) is coated with different bar coaters on 130 μm corona-treated PET films. Thicknesses of the resulting chitosan layers obtained are measured through scanning electron microscopy and are in a range from 1 to 6 μm. Then, helium and dioxygen permeability’s of the PET coated films are measured with dry gases. Oxygen transmission rate (OTR) of the PET films, expressed in cm3/m².s can be decreased from 1.27×10⁻⁴ to only 5.59×10⁻⁶ with a layer of 3 μm of chitosan under dry conditions which is close to PVDC-coated PET films under similar conditions.

References:

Future perspective in polysaccharide research:
Chitosan is very sensitive to moisture which limits its use in the field of food packaging. To limit the impact of moisture, the addition of clay nanoparticles and/or chitosan crosslinking will be attempted to increase the hydrophobicity of the polymer and increase the gas barrier properties.
Hydrogels based on Beetosan – chitosan originating from naturally died bees

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Keywords:
Beetosan, hydrogels, biocompatibility

Abstract:
Chitin and chitosan belong to the group of natural polysaccharides and due to their high biocompatibility and biodegradability, they are applied in medicine, pharmacy and cosmetology. In this study we describe the preparation of chitin and chitosan from naturally died honeybees. This process is multi-step and requires appropriate parameters on each stage. In the first step, waxes were eliminated using extraction with ethyl alcohol. Then, the mineral salts were removed by immersion of died honeybees in various concentrations of HCl. Subsequently, obtained dried material was subjected to the removal of proteins that was carried out using various concentration of NaOH solution. Ultimately, attainment of the chitin and chitosan from honeybees requires removal of natural pigment-melanin using 25% of H2O2. Finally, all received intermediate products were analyzed by means of FT-IR spectroscopy and X-ray Diffraclometry (XRD). Moreover, content of toxic metals such as: As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sn, Zn in naturally died honeybees was analyzed using ICP-OES method. Subsequently, Beetosan based hydrogels were synthesized under UV radiation in the presence of diacrylate poly(ethylene glycol) as crosslinking agent and 2-hydroxy-2-methylpropiofenone as photoinitiator. The attained hydrogel materials were subjected to the determination of swelling ability and incubation studies in distilled water, artificial saliva and simulated body fluids. The morphology of hydrogels was evaluated using SEM equipped with EDS analysis. Furthermore, the thermal stability of obtained materials was determined using thermogravimetric analysis (TG).

Acknowledgements
“The authors would like to thank The National Centre for Research and Development (Grant no: LIDER//033/697/L-5/13/NCBR/2014) for providing financial support to this project”.

References:


Future perspective in polysaccharide research:
In the future we are going to continue our investigations containing synthesis of hydrogel materials based on Beetosan. Moreover, we plan to carry out more specific research such as cytotoxicity by means of XTT and MTT assays using accordingly epidermal CD 1106 KERTr an dermal BJ, ATCC CRL-2522 cell lines.
Characterization of Beetosan based hydrogels modified with magnetic nanoparticles

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Keywords:
Beetosan, hydrogels, magnetic nanoparticles

Abstract:
In this study synthesis and properties of Beetosan based hydrogels modified with magnetic nanoparticles were presented. Magnetic nanoparticles are very interesting compounds for many scientists from a wide range of disciplines including magnetic fluids, catalysis, biotechnology/biomedicine, magnetic resonance imaging, data storage and environmental remediation. Beetosan is known as a form of chitosan after chemical treatment of naturally died honeybees. Initial stage of this research was preparation of magnetic nanoparticles developed by Massart in 1981. This method involves addition of FeCl3·xH2O and FeCl3·6H2O with the Fe3+/Fe2+ (in molar ratio equal 2:1) to previously boiled solution of 1.5 M NaOH. However, magnetic nanoparticles very rapidly form agglomeration. Therefore, preparation of nanosilver or nanogold by chemical reduction in the presence of hydroxylamine, gum arabic and magnetic nanoparticles was carried out. Consequently, core-shell structures (nanoFe3O4/Ag or nanoFe3O4/Au) were obtained and they were analyzed by means of the following methods: UV-Vis, XRD, DLS. After that, synthesis of Beetosan based hydrogels containing magnetic nanoparticles was conducted. The crosslinking reaction was carried out under UV radiation in the presence of diacrylate poly(ethylene glycol) as crosslinking agent and 2-hydroxy-2-methylpropionophenone as photoinitiator. The prepared hydrogel materials were physicochemically analyzed in order to determine their swelling ability and stability in distilled water and in simulated biological fluids. Moreover, chemical structure of these hydrogels was defined using spectroscopic methods (FT-IR) and morphology was determined using Scanning Electron Microscopy (SEM).

Acknowledgements
This research was financially supported by Grant no 0489/IP3/2015/73.

References:


Future perspective in polysaccharide research:
In the future we are going to continue our investigations containing synthesis of hydrogel materials based on Beetosan. Moreover, we plan to carry out more specific research, such as cytotoxicity by means of XTT and MTT assays using accordingly epidermal CD 1106 KERTr an dermal BJ, ATCC CRL-2522 cell lines.
Composite fibers based on chitosan and chitin nanofibrils for medical application

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Keywords:
chitosan, chitin nanofibrils, composite fibers, wet spinning, bioresorption, toxicity

Abstract:
Nowadays tendency in the material science is the development of biomaterials for medicine. Different kind of polymers are used for this purpose. One of the most promising polymer which possesses the combination of the necessary properties is a polysaccharide like chitosan. However, chitosan based materials have several disadvantages as brittleness, low moisture resistance. To control or even improve the mechanical properties of chitosan based materials chitin nanoparticle can be incorporated into the chitosan matrix.

The composite chitosan fibers filled with anisotropic chitin nanofibrils were spun from 4% chitosan (Fluka Chemie, Japan) or 6,5% (Bioprogress, Russia) solution in 2% acetic acid solution by coagulation method. The concentration of the chitin nanofibrils with respect to dry chitosan was changed in the range of 0.05-20 wt%.

The good interaction of the chitin nanofibrils with chitosan macromolecules was proved by rheological studies, scanning electron microscopy (SEM), x-ray diffraction analysis (XRD) and Dinamic Mechanical Analysis (DMA).

It was shown that the incorporation of the chitin nanofibrils into chitosan improves the spinning process and contributes to better orientation of the chitosan macromolecules. The both components (chitin and chitosan) of these composite fibers were well-oriented. At the same time the incorporation of the chitin nanofibrils (0.1 – 0.3wt%) leads to an increase in strength and Young modulus of the composite fibers.

It was shown also that the incorporation of the chitin nanofibrils contributes to improved adhesion of dermal fibroblasts PFC-M to surfaces of the composite materials and these cells had normal morphology. The absence of cytotoxic properties of composite fibrous materials was confirmed by the results of research conducted by the method of immunofluorescence staining of protein H2AX-γ using of dermal fibroblasts PFC-M.

Acknowledgement:
Financial support of this work by the Russian Foundation of Basic Research under contract grant number 14-33-00003 is gratefully acknowledged

References:

Future perspective in polysaccharide research: The proposed results allow using of the chitosan fiber as the matrices for cell and tissue replacement technologies as well as to prepare a fibrous material for traumatology, orthopaedics, etc.
Supramolecular chitosan hydrogels via reversible imine linkage

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Keywords:
chitosan, hydrogels, biomedical application

Abstract:
Chitosan based hydrogels are a class of materials intensly studied due to their high potential of application in biomedical field. Usually, chitosan based hydrogels are obtained by covalent crosslinking with dialdehydes. We proposed a new pathway of obtaining chitosan hydrogels, which exploit the imine forming reversibility to generate dynamic supramolecular hydrogels with special morphology and properties. As a proof of concept, cinnamaldehyde has been used to obtain stable hydrogels with high rate of recovery. FTIR, NMR and X-ray measurements proved a dual physico-chemical crosslinking, with consequences on the self-assembling at nano- and micro-level.

Acknowledgement
This study was financial supported by the Dynagels: PN-II-RU-TE-2014-4-2314 Project.

Future perspective in polysaccharide research:
Hygroscopic properties of kappa/iota-hybrid carrageenan extracted from *Mastocarpus stellatus* seaweed

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**Keywords:**
Equilibrium moisture content, Water activity, Red seaweed, Sorption heat, Temperature

**Abstract:**
Food, pharmaceutical or cosmetic industries demand natural biopolymers as kappa/iota-hybrid carrageenans (KI) like solid powders or splits to be added during processing to different systems. The understanding of water exchange between valuable solids and surroundings is critical to select drying or storage conditions (Moreira et al., 2016). In this context, water adsorption and desorption isotherms of KI (average molecular weight: 2.3·10⁶ g/mol) extracted from *Mastocarpus stellatus* red seaweed were determined at different temperatures (5, 25, 45, and 65°C) using a gravimetric static method. Several saturated salt solutions were selected to obtain different water activities (aw, from 0.09 to 0.89). Biopolymer was extracted (Torres et al. 2016) and dried up to 0.02 kg/kg dry basis in order to ensure the water adsorption during equilibrium experiments. Triplicate samples (around 0.5 g) were stored into different atmospheres with constant relative humidity and periodically weighed until to reach constant weight (±0.0005 g). Eight weeks were necessary to achieve the equilibrium. Moisture content (Xw) was obtained after determination of dry matter of each sample using a vacuum oven (70°C, 15 kPa).

All systems exhibited a concurrent increase in Xw with increasing aw following a sigmoidal curve, suggesting type II isotherms according to the BET classification. At constant aw, Xw decreased with increasing temperature, except at 5°C where a cross-point with 25°C isotherm was observed at large aw (> 0.5) for both sorption processes. The observed hysteresis loops between desorption and adsorption isotherms can be classified as type H3 according to IUPAC classification. The calculated net isosteric heat of water adsorption decreased with Xw increase. Modelling of experimental sorption data was satisfactorily conducted using BET, GAB and Caurie models (R²>0.97). The most suitable air conditions (relative humidity around 30% for adsorption and 40-50% for desorption processes) for storage of this biopolymer at tested temperatures were established.

**Acknowledgement:**
This work was partly supported by the Ministry of Economy and Competitiveness of Spain and European Regional Development Fund (project CTO-2013-43616/P). MD Torres also acknowledges the financial support (POS-A/2012/116) from Xunta de Galicia (Spain) and the European Union’s European Social Fund.

**References:**


**Future perspective in polysaccharide research:**
Future works will be directed to extend the current knowledge on hygroscopic properties of different natural biopolymers. Extraction and processing conditions could modify the water sorption characteristics and its evaluation is critical to improve stability.
Bioprocessing of bran with exopolysaccharide producing microorganisms as a tool to improve expansion and textural properties of extruded cereal foams with high dietary fibre content

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Keywords:
Extrusion, high dietary fiber, bioprocessing, exopolysaccharides, texture, structure

Abstract:
High dietary fibre (DF) levels, especially insoluble DF that is typical for cereal bran, have been associated with poor structural, textural and sensory properties in extruded products. The effect of fermentation with baker’s yeast, fermentation with a mixture of Kazachstania exigua and Lactobacillus brevis with and without added hydrolytic enzymes, as well as with Weissella confusa, on the structural and textural properties of high DF extrudates (ca. 6-14 % added fibre) in extrusion was studied. Superior structural and textural extrudate characteristics were achieved by fermentation of bran with dextran producing W. confusa. At 40 % addition of W. confusa -treated bran (i.e. 12 % DF content) radial expansion was the same as for the 100 % rye endosperm flour control prepared without bran, while density was 35 % lower. Hardness (54.1 N → 16.3 N) and crispiness work (4.11 Nmm → 0.45 Nmm) were reduced, while the crispiness index was significantly higher (0.002 → 0.05) than that of the control extrudate. Bioprocessing with mixed fermentation, containing K. exigua and L. brevis, together with hydrolytic enzymes also improved the structural and textural characteristics of the bran in extrusion, while fermentation with baker's yeast did not significantly improve expansion or textural characteristics.

References:
Markus Nikinmaa, Syed Ariful Alam, Mari Raulio, Kati Katina, Ilkka Kajala, Emilia Nordlund, Nesli Sözer, Bioprocessing of bran with exopolysaccharide producing microorganisms as a tool to improve expansion and textural properties of extruded cereal foams with high dietary fibre content, 2016 (submitted manuscript)

Future perspective in polysaccharide research:
Indigestible carbohydrates have potential for formulation of novel food foam structures and to improve palatability of high-fibre food foams.
Ultrasound-assisted synthesis of oligo-isosorbide glycidyl ether: Towards greener epoxy resins

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Keywords:
Isosorbide, epichlorohydrin, ultrasound, epoxy resins

Abstract:
Epoxy resins are polymers with a wide range of applications such as paints, adhesives, coatings, electronic components and materials. The majority of resins consist of toxic precursors from the oil industry such as Bisphenol A, and many studies are currently done in order to replace these precursors. Otherwise, isosorbide represents a promising alternative due to its rigidity and the presence of two reactive hydroxyl groups. Moreover, the production of the latter via renewable resources (glucose derivative) and its non-toxicity provides a promising alternative to Bisphenol A. Its reaction with epichlorohydrin, also biosourced via EPICEROL® process, under basic conditions leads to isosorbide diglycidyl ether or a dimer. [1] Nevertheless, this reaction is generally time consuming and presents a significant part of hydrated non-reactive forms leading to low composite properties. In this context, the aim of this study is to optimize this key reaction using sonochemistry. An increase of yields up to 20% was observed and the reaction time was divided by 15. [2] Further optimization of reaction parameters dramatically reduces the parasitic reaction of opening the epoxy ring by water molecules, and allows the delivery of highly functionalized polymer precursors (Figure 1) with epoxy equivalent weight (EEW) similar to commercial Bisphenol A diglycidyl ether. As a consequence, the experimental procedure provides a promising bio based epoxy resin for the production of new composite materials.

![Figure 1: Ultrasound assisted synthesis of oligo-isosorbide glycidyl ether (left). HRMS spectra of products obtain following literature conditions (profile 1) and optimized conditions from this work (profiles 2-3) (right) (Image)](image)

References:

Future perspective in polysaccharide research:
Following this work, the oligo-isosorbide glycidyl ether will be cured with primary amine like isophorone diamine in order to obtain new materials. Those materials will be characterized and compared to existing ones.
Silica-supported biosorbents for sorption of metallic ions from aqueous solution

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Keywords:

Abstract:
Submicronic particles, functionalized by grafting or by encapsulation with bio-polyelectrolytes, open potential applications in applied sciences and diverse industrial sectors (use as composite coatings, as adsorbents, as water purification materials...).

Organo-mineral composites allow combining the properties of a mineral skeleton with the chemical reactivity of the organic functions present in abundant and low-cost biopolymers such as chitosan. The aims of this research are (i) to functionalize and characterize submicronic composites by grafting or encapsulating colloidal silica (Figure 1) and (ii) to study the capacities of these hybrid materials for the adsorption of diverse divalent metal ions from aqueous solutions.

The composition and physicochemical properties of these materials were characterized by means of elemental analysis, nitrogen adsorption–desorption and FT-IR spectroscopy. The analytical data confirm the successful grafting of the biopolymers CS and CM-CS on colloidal Aerosil 200 silica.

Nickel ion, Ni²⁺, was chosen as model for divalent metal ion to evaluate the effectiveness of the new sorbents for wastewater treatment. The influence of hybrid particles doses, buffer pH, contact time and nature of the counter ion was assessed through batch experiments. The results point out a high capacity of the hybrid particles to complex Nickel (> 200mg.g⁻¹ of adsorbent). The best interpretation for the equilibrium data is given by the Sips and Redlich-Peterson isotherm models. The adsorption kinetics follow the mechanism of the pseudo-second-order equation for the systems studied.

Future perspective in polysaccharide research:
Green composite - wood in cellulose

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Keywords:
wood, cellulose, composite, ionic liquids

Abstract:
Ionic liquids (IL) are universal solvents of organic compounds. Due to their low toxicity and vapour pressure they are considered “green solvents”. Because of their properties IL’s are successfully used in recent years as solvents of cellulose. By the use of the suitably selected IL’s cellulose could by dissolved and formed in to foil or other shape. IL’s may be used for degradation of cellulose. Process condition determine whether the cellulose would be regenerated in intact form or degraded.

Another application for IL’s is dissolution of wood. Because of the specific construction of lingo-cellulose materials, wood is extremely hard to dissolve and decompose. IL’s suitable for cellulose dissolution do not dissolve lignin or do it slightly. For this reason wood need to be pre-treated, or composition or several IL’s need to be applied to dissolve wood. Anyway process requires considerable amounts of energy.

Due to different reactions for dissolution in IL’s of wood and cellulose it is possible to create composites of both. Cellulose provide the component with structural foundation while added wood may bring extra toughness to the composite. Wood may have a significant role in strengthening the composite when process of dissolution is carried out in extreme conditions and cellulose starts to depredate.

Presented studies contain selection of IL suitable for cellulose-wood composite, choice of the conditions for composite creation and studies of the physical properties of obtained composites.

References:
2. Dariusz Wawro, Witold Madaj, Włodzimierz Stęplewski, Herbert Sixta, Monica Ek, Cellulose Film Cast from Ionic Liquid Solutions, 18th International Papermaking Conference PROGRESS’14, 23-25.09.2014, Łódź, Poland

Future perspective in polysaccharide research:
Creation of composites from range variety of polysaccharides materials with the use of ionic liquids. Potential applications for cellulose-wood composites.
Phase separation of cellulose with covalently or non-covalently bound fatty acids in thin films

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Keywords: phase separation, cellulose, fatty acids, thin films

Abstract: (max 300 words)
In the recent years, phase separation of polymer mixtures has received considerable attention, because it is a bottom-up process to build nano patterns, which allows the production of new materials with fascinating features. In this contribution, we explore the phase separation behavior of cellulose with fatty acids in thin films. The investigated films were constructed in a single-step process by spin coating mixtures of trimethylsilyl cellulose (TMSC) and palmitic acid (PA) or cellulose stearoyl ester (CSE) in different ratios from a common solvent. Atomic force microscopy revealed a nano- and micro-scale phase separated structure. For characterization of the underlying correlation between the surface morphology and the chemical composition, the blends were analyzed in terms of infrared spectroscopy, stylus profilometry for thickness determination, and contact angle measurements resulting in the surface free energy. Additional real time experiments with multi parametric surface plasmon resonance spectroscopy were realized at the example of Bovine Serum Albumin in order to gain information on the interaction of proteins with the herein examined surfaces. Results display, that PA acts as a sacrificial compound inhibiting protein adsorption at all ratios, whereas CSE influences the amount of adsorbed protein depending on the cellulose:CSE ratio.

Future perspective in polysaccharide research:
The diversity of properties in polysaccharide materials leads to usage in various fields of applications such as medicine, biochemistry and technology. Especially applications with protein microarrays for monitoring biological and chemical processes or the design of surfaces that prevent fouling due to proteins or bacteria are of great interest for the industry and will gain even higher significance in the future.

References:
Fibres Recherche Développement © - The project engineering platform of biobased fiber materials

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Keywords: Cellulose, Promotion of natural fibers, Materials, Studies

Abstract: (max 300 words)
Fibres Recherche Développement (FRD®) is a research and innovation company:

- Dedicated to the promotion of natural fibers for use in materials (insulation, concrete, composites, etc.).
- Established in 2008 by 11 shareholders, either producers of natural fibers (together, accounting for 15% of total domestic production with flax, hemp, miscanthus, linseed flax, and wood) or actively working to promote bioresources (ARD, Sofiprotéol).
- Working within the “Industries et Agro-Ressources” competitiveness cluster (Picardy and Champagne-Ardenne).

FRD is an engineering platform for projects that favors the design and development of innovative materials thanks to its skills:

- Multi-scale expertise in agro-material
- Project engineering
- Technical center

Thanks to FRD-Lab, the first French technological platform dedicated to the extraction and characterization of natural-based pellets and fibers for material end-uses, FRD is able to:

- Supply manufacturers with materials, pellets and fiber samples with application-specific characteristics
- Characterize fibers and aggregates (chemical composition, morphology...) and provide technical data sheets
- Enhancing material performance: fractionation, functionalization, characterization
- Find out the potential value of plant resources by upgrade-potential diagnostics on materials to demonstrate the interest of agricultural co-products and plant fibers
- Offer support to formulate materials that incorporate natural fibers
- Offer technical support to producers by helping them to adapt their fiber production to industrial needs for material applications, optimize their quality approach and prepare technical data sheets for their products
- Provide baseline studies (resource availability1, market studies2...)
- Help partners develop R&D programs.

Future perspective in polysaccharide research: (max 2-3 sentences)
We are involved in several applicative projects and based on material qualification. Our R&D work has a strong focus:

- On mastering the fractionation and functionalization of natural fibers
- On understanding the keys properties of fibers and the correlations between their quality and the microstructure and mechanical properties of biocomposites.

References: (max 2)