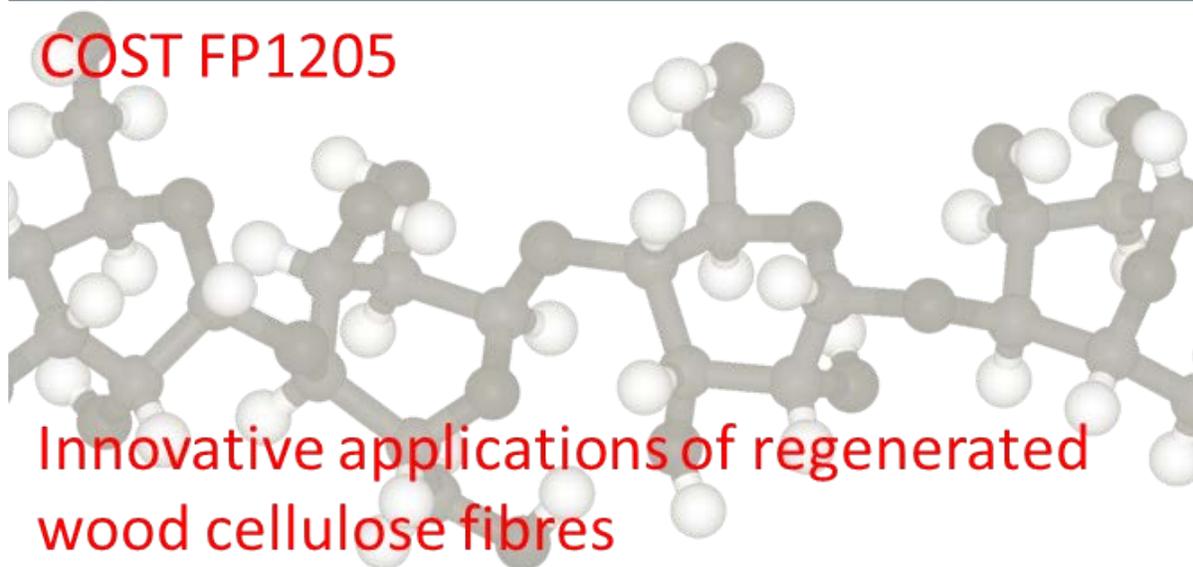


2013



EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

COST FP1205



Innovative applications of regenerated
wood cellulose fibres

[ABSTRACTS, 4TH OF DEC 2013, GOTHENBURG]

Cellulose dissolution and regeneration

Presentations 4th of December 2013

Influence of water on dissolution and swelling of cellulose in EMIMAc

Carina Olsson

In this study the effect of residual coagulation medium (water) on cellulose dissolution in ionic liquids is discussed. Solubility of dissolving grade pulp; HWP and SWP, and microcrystalline cellulose in binary solvents, mixtures of 1-ethyl-3-methyl-imidazolium acetate and water, was investigated by turbidity measurements, light microscopy, rheometry, and CP/MAS ¹³C-NMR spectroscopy. The viscoelastic properties of the cellulose solutions imply that residual water affect the cellulose dissolution. However, it is not obvious that this always necessarily poses serious drawbacks for the solution properties or that the effects are as severe as previously believed. Turbidity measurements, viscosity data and crystallinity of the regenerated cellulose correlated well and an increased conversion to cellulose II was found at low water and cellulose contents with an apparent maximum of conversion at 2–5 wt% water. At high water content, above 10 wt%, dissolution and conversion was largely inhibited.

Structural investigation of regenerated cellulose using solid-state NMR spectroscopy

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Cellulose is the most abundant polymer in nature (Klemm, Heublein, Fink, & Bohn, 2005). It was isolated in 1838 by the French chemist Anselme Payen (Payen, 1838) but was used long before that in everything from papyrus to building material. It can be found in flowers, trees and even animals and is a very important natural resource for many countries. With the ability to regenerate cellulose using dissolution and coagulation new products with improved properties could be developed.

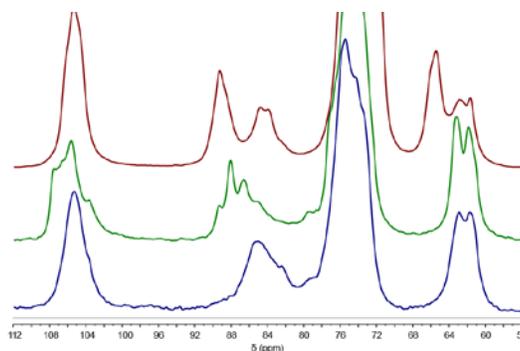


Figure 1. Solid-state NMR spectra showing mainly crystalline cellulose I (red), II (green) and amorphous cellulose (blue).

With the use of solid-state NMR spectroscopy, a lot of information can be acquired, when studying cellulose. A large benefit of NMR is that two nuclei with different electron environment can be distinguished in the NMR spectrum. By doing the measurements in solid form, i.e. using solid-state NMR, it is possible to distinguish between different kinds of crystalline forms. ^{13}C CP/MAS spectra of three different samples of cellulose can be seen in Figure 1. A sample containing mainly cellulose I is shown in red, mainly regenerated cellulose II in green and a sample containing mainly amorphous cellulose is shown in blue.

Additional information can be apprehended from the spectra by looking closer to the different regions. For processing of solid-state NMR spectra, overlapping signals could be separated by applying spectral deconvolution. The C-4 signals between 92 and 80 ppm are often quite resolved and are widely considered to hold most information (see Figure 2).

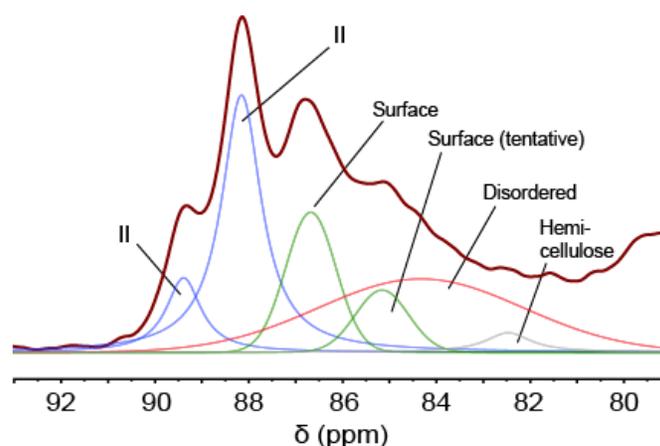


Figure 2 Deconvolution of C-4 region of a cellulose II sample. Signals originating from crystalline II can be seen in blue, surface signals can be seen in green and a non-crystalline signal can be seen in red.

For regenerated cellulose II, the C-4 spectral region, between 92 and 80 ppm, can be deconvoluted into six peaks. Two peaks, at 89.3 and 88.1 ppm respectively were elucidated to be from crystalline cellulose II [1]. A narrow peak at 86.6 ppm was assigned to origin from the crystalline surface and a broad one at 84.2 ppm was assigned to cellulose in disordered regions [2]. Zuckerstätter et al. tentatively assigned the narrow peak at 85.1 ppm, not previously seen by other groups, to origin from cellulose at crystalline surfaces [3]. In addition, they also assigned the peak at 82.5 ppm to origin from short cellulose chains or xylans.

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Investigations of the coagulation of cellulose solutions

Artur Hedlund

Swerea IVF, Mölndal

To understand coagulation of cellulose solutions, is becoming increasingly important as more and more resources and efforts are invested to achieve high quality cellulose fibers through new and more efficient processes. The aim of this study is to understand the foundations of causality between coagulation conditions and product properties in wet spinning of cellulose fibers. To do so a set of methods have been identified and developed that targets the key issues of the process. These key issues are net chemical exchange with the coagulation liquid, coagulation rate, coagulation values, gel structure and changes in viscosity during transition from solution to gel. The goal is to achieve as generally applicable set of methods as possible, so that any new solvents can be investigated and analyzed by the same procedures and logic. For the development of such a set of methods an example solvent system comprising a mixture of co-solvent and EmimAc will be utilized. Initial work is focused on investigating the exchanges by diffusion of solvent and non-solvent between the fiber and the coagulation liquid as well as coagulation values. The outset, hypothesis and identified key parameters and questions based on the literature will be presented along with early work and results.

Future regeneration of cellulose based fibers for textile purposes

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In the city of Karlstad viscose has been produced during more than 60 years and viscose research has been carried out at Karlstad University nearly 15 years. Thus, the academic research carried out at the university and the viscose production at Svenska Rayon in Vålberg, Karlstad has for a long time been very important for both organizations. However, viscose has environmental drawbacks and new dissolution chemistry is needed to be able to produce environmentally friendly cellulose based fibers that can replace cotton and polyester fibers in the textile products that we will use and wear in the future.

Karlstad University is now in a transition phase where we are reducing the research and education with focus on paper and board while we increase the research and education with focus on cellulose chemistry with respect to cellulose based textile fibers. We are therefore now extending our lab from a viscose lab to a cellulose based fiber lab including fiber spinning equipment in pilot scale. The cooperation with the Swedish School of Textiles in Borås, where they are responsible for fiber testing and manufacturing of fabric for extended testing as garment and other industrial products, is a strong benefit for the new activities.

The dissolution of fibers will primarily be done in alkaline aquatic systems at low temperature according to the pioneering work carried out by Kihlman et al 2011. The studies will be done on both low DP and high DP cellulose molecules and consequently both standard and strong textile fiber products will be included. The paper will give an overview of our current and future activities in the cellulose dissolution and textile fiber spinning area.

Ageing and hornification of cellulose in cotton textiles during long time use

Anna Palme

The goal of the Mistra Future Fashion Program is to create a systemic change of the Swedish fashion industry. One part of this is to investigate different routes to recycling of textiles. The project presented here relates to recycling of cotton textiles. Currently, most textile waste is either incinerated or landfilled, instead of being used as a resource. For the used textiles to be recycled back into the production cycle, it is important to understand the changes induced in the cotton morphology and the cellulose supramolecular structure during laundering and use.

In the present study, we have investigated ageing and hornification phenomena in cotton cellulose. Analyses were made on hospital cotton sheets at different stages on their journey from new material to waste. The focus of the analyses was to understand both physical and chemical changes occurring in cellulose during the use phase.

Cellulose carbamate from a new process

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DomInnova, Domsjö Fabriker AB

Background Today's regenerated cellulose production is dominated by the viscose process. The major draw-backs with the process are the highly toxic reagent, carbondisulfide, as well as a quite long residence time to get the spinning dope. However, no real alternative has been available. Lenzing has launched the Lyocell process where the cellulose is dissolved, without any chemical modifications, but those volumes are rather small compared to the total volume of regenerated cellulose. Furthermore, some issues regarding fibre quality has to be solved.

Another process that has been described in patents and articles is the carbamate process, where cellulose is reacted with urea to form a cellulose carbamate. This cellulose carbamate can be dissolved in a cold alkaline solution and spun to a fiber, either as cellulose carbamate fiber or to a regenerated cellulose fiber via warm alkali treatment. However, this process has needed co-solvents as ammonia or organic solvents in order to distribute the urea evenly in the cellulose and that process have been troublesome in the recovery of solvents. In a new attempt, the carbamate process is tested by simply mixing wet or dried cellulose with molten Urea in a special device, excellent in mixing capability.

Results Several parameters were altered and the result shows that cellulose carbamate can be made without any auxiliary compounds present and without pre-activation of the cellulose and that the carbamate could be dissolved into a clear solution in cold alkali.

Cellulose-xylan blends in viscose fibers

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Until now, the bio-polymer xylan could not be added to man-made cellulosic fibres successfully due to its degradation during the process or its lack of sorption on the fiber surface.

In this study, a new process modification has been developed to blend xylan and cellulose during the production of viscose fibers. A high molecular weight xylan was applied during a late stage of the viscose production process (Schild et al. 2012). The xylan was thus not objected to any degradation conditions during alkalization. A xylan content of up to about 10% on viscose fibers was achieved. About 95% of the added xylan was transferred to the final fiber indicating a high xylan yield and a low contamination of the spinning bath. Fiber properties like strength showed a comparable level to the reference fibers while the water retention value was clearly raised due to the higher content of hemicelluloses. The hemicellulose distribution over the fiber cross section was investigated by enzymatic peeling. Even though a segregation of the different polysaccharides was observed, the goal of a good blending of CCE-xylan into cellulosic fibers with new interesting features was achieved.

The hemicelluloses derived from a cold caustic extraction stage and showed a degree of polymerization of 150 to 200. The pure press lye was used directly. Therefore, the xylan was dissolved in NaOH and not subjected to any further processing except for a membrane filtration for the production of fibers with higher xylan contents. With this process modification a value-added use of CCE-xylan was achieved and a new type of xylan enriched viscose fiber was developed

Literature

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Conversion of regenerated cellulose woven textiles to carbon fibre pre-forms

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The last few decades have seen an increase in the use of carbon fibre based composite materials. A desire to reduce financial and environmental costs of their production supports research into new renewable and sustainable carbon fibre precursors. Cellulose is a truly renewable resource, being the main polymeric constituent of plants. Its use as a precursor for carbon fibres is well-known. The carbon fibres produced from cellulose have possibility for certain high volume applications where the very highest moduli are not required. Cellulose fibres can be woven into different geometries e.g. plain, satin weaves. The conversion of the cellulose geometries to carbon fibre pre-forms can allow the production of complex geometries without the need for manual contact and can simplify their production.

The production of the carbon fibre pre-forms with different geometries requires the knowledge of the conversion conditions and the properties of the carbon fibres obtained. A systematic study on the conversion of regenerated cellulose and a plain weave of fibres to a carbon pre-form allow making a

comparison on the impact of the geometry of cellulose on properties of the carbon fibre pre-forms. Optimisation of the stabilisation conditions of regenerated cellulose was crucial for producing uniform carbon fibres with minimal shrinkage and loss in weight. Shrinkage of the fibre length was around 35%, while the loss of the fibre weight was maintained around 90%. Both of these values were found to be typical for carbon fibre production from cellulose. The regenerated cellulose showed an onset of the graphitisation process after carbonisation at a temperature of 1500 °C. The carbon fibres produced exhibited increase uniformity with an increase in temperature after carbonisation. The uniformity in the graphitisation degree slightly decreased above a temperature of 2000 °C. The carbon fibre pre-form obtained from the plain woven cellulose exhibited a similar characteristic after the carbonisation process. The intensity of the G band increased with an increase of carbonisation temperature of the woven cellulose causing a decrease in the value of the ID/IG ratio from 1.03 for carbonisation at 2000 °C to 0.17 for carbonisation at 3085 °C. This decrease suggested an increase of the structural order and the presence of graphitic structures in the material. Additionally, the carbon fibre textile remained reasonably flexible enabling the formation of other more complex geometries. Further work is required to characterise its mechanical behaviour.

Structure and property design of polysaccharide-based nanoparticles

Holger Wondraczek

A general concept for the preparation of functional polymeric nanoparticles from solutions of tailor made polysaccharide derivatives was developed. For this purpose, different polysaccharides including cellulose, xylan and dextran were chemically modified under homogenous reaction conditions. The broad structural diversity in the molecular structures of the particle-forming polysaccharides is the prerequisite for the functional versatility of the final nanoassemblies. It is possible to obtain the functional particles with a size of 80 to 500 nm by procedures like a simple solvent exchange, as exemplarily demonstrated for polysaccharides decorated with pharmacologically active, reactive and sensor substituents. The particles obtained are suitable for different applications in the biomedical field. For example, hydrophobic drugs can be mobilized and delivered in aqueous environment and the physiological relevant parameters (e.g. pH value) can be monitored in biological entities like living cells.

Enzymatic vs. chemical phosphorylation of nanocellulose fibers

Mojca Božič

Cellulose phosphorylation is a well-known strategy in producing materials with promising properties applicable in orthopaedic, biomedical, textile, fuel cell, bio-chemical separation and others applications. Employing enzymes for the regioselective formation of cellulose phosphate esters seem to be very promising alternative to chemical heterogeneous phosphorylation as enzymes makes syntheses more efficient with the additional benefit of involving mild processing conditions and preserving the primary integrity of the substrate. In this study, enzymatic phosphorylated cellulose nanofibers (CNF) are engineered by covalently grafting phosphate on cellulose C-6 positioned hydroxyl groups, being confirmed by ^{13}C CP/MAS NMR and ^{31}P MAS NMR studies. Hexokinase enzyme was used to mediate the phosphorylation of glucopyranose unit of cellulose using an ATP as the phosphate donor and Mg^{2+} as cofactor. The efficacy of phosphorylation was determined by using ATR-FTIR and XPS spectroscopy's. Thermal properties of phosphorylated CNFs were investigated by DSC and TGA measurements, showing excellent flame-resistance properties, and thus offering a potential to be used as biobased flame-retardant material. Furthermore, phosphorylation significantly enhanced adsorption capacity of Fe^{3+} ions making them interesting for fabrication of biobased filters and membranes. Finally, the biomimetic growth of Ca-P crystals (hydroxyapatite) in simulated body fluid was characterized by SEM and showing further practicability for biomedical materials.

Preparation methods and characterisation of nanostructured cellulose

Vikele L., Sable I., Treimanis A., Laka M.

Due to their abundance, high strength and stiffness, low weight and biodegradability, nanostructured cellulose materials serve as promising candidates for biocomposite production. Such new high value materials are the subject of continuing research and are commercially interesting in terms of new products from pulp and paper industry and the agricultural sector. In this study we describe three different preparation methods of nanostructured cellulose: thermocatalytic method, method by applying of ionic liquids and traditional acid hydrolysis as comparison.

Thermocatalytic method provides the possibility to produce cellulose nanoparticles with tailored dimensions, different aspect ratio and shape. In this way, it is possible to obtain nanoparticles which extend the optimal properties as constituent of the paper coatings. In compliance with the thermocatalytic method (Latvian Patent), the polysaccharide materials are impregnated with small quantities of weak acid (HCl) solution and thermally treated at the elevated temperature. Then the partially destructed materials are dispersed in water medium in a ball mill 1;14 This process is close to the "green chemistry" methods as it utilizes very small quantities of acid which can be washed out or left within the fibres (Laka et. al. 2000, 2007).

Discovering and applying of ionic liquids (IL) in cellulose dissolution and processing have been started in recent years. It has been reported (Swatlowski et al. 2002) about good dissolution of cellulose in alkyl substituted imidazolium IL's. Our method is based on report (Zakaria et al. 2011) about using IL as catalyst to transform microcrystalline cellulose (MCC) to cellulose nanocrystals. In our case MCC was mixed with 1-butyl-3-metylimidazolium chloride (bmimCl) in 100°C for 3h, reaction was quenched by adding hot deionized water to the mixture. Sonication was used in regenerating process of cellulose particles. Suspension was washed with deionized water and centrifugation was used to isolate cellulose nanocrystal particles.

Acid hydrolysis was carried out using 64% H₂SO₄ at an initial concentration of 0.08 g/ml. The mixture was hydrolyzed by stirring at 45°C for 15 min. Hydrolysis was stopped by adding 500 ml cold water. After hydrolysis resulting suspension was centrifuged and then placed inside the dialyses membrane tube and dialyzed in cold water for 2 weeks.

Characterisation of the nanostructured cellulose dimensions was carried out by a Malvern "ZetaNanosizer", morphology by atomic force microscopy (AFM) and transmission electron microscopy (TEM), crystallinity by x-ray diffraction (XRD) and FTIR.

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Posters 4th of December 2013

Increased accessibility and reactivity of wood and non-wood paper grade pulps using enzymatic and chemical pre-treatment

Monica Ek

Cellulose is the most abundant biorenewable material, constitutes an important polymer since it is used as raw material for several products, e.g. paper and board but also cellulose-based products which have many important applications in the pharmaceutical, textile, food and paint industries. A raw material with high cellulose content and low content of hemicelluloses, residual lignin, extractives and minerals is required for the production of these products, e.g. cotton and dissolving grade pulp are used. However, the high cost production of dissolving grade pulps has aroused the possibility of upgrading paper grade pulps into dissolving pulps by selective removal of hemicelluloses and subsequent activation of the pulps.

This study reports the feasibility to produce dissolving grade pulps from different wood and non-wood paper grade pulps employing enzymatic and chemical pre-treatments.

A monocomponent endoglucanase and a xylanase followed by alkaline extraction were tested in order to increase the accessibility and reactivity of the cellulose pulp and decrease the hemicellulose content, respectively. An optimization of these treatments in terms of enzyme dosage, incubation time and a possible combination of them was investigated.

The treatment effects on reactivity according to Fock's method, viscosity, hemicellulose content and molecular weight distribution, using size exclusion chromatography, were analyzed. The characterization of cellulose structure after the enzymatic and chemical treatments was investigated by ¹³C-CP/MAS NMR and Raman Microspectroscopy. The effect of the different treatments on the fiber surface treated pulp samples was studied by Scanning Electron Microscopy. Some product properties will also be reported. The results were compared to those of commercial bleached dissolving pulp.

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Nanocellulose reinforced adhesives for wood composites

Zeki Candan, Oktay Gonultas, Turgay Akbulut

Urea formaldehyde, melamine formaldehyde, and phenol formaldehyde resins are commonly used in manufacture of wood composite panels such as plywood, particleboard, fiberboard, and oriented strandboard. Nanoscience and nanotechnology can play an important role for forest products industry. Cellulose is one of the most abundant natural biopolymers in the world. Nanocellulose has an important potential to be used in a variety of applications because of its enhanced properties. Thus nanocellulose has an increasing attention from researchers. Nanocellulose could be used to reinforce the adhesives which use in manufacture of wood composites. Investigating physical/mechanical properties of nanocellulose reinforced thermosetting adhesives and wood composite panels made from the adhesives was objected in this work. For this aim, previous studies have been scanned and reviewed in this work. In addition, opportunities of using nanocellulose in wood composite panels industry have been discussed.

Study of sulphite process to obtain dissolving pulp and other valorisation options from spent liquor

Alberto Coz

The biorefinery concept is gathering strength in the industrial sector and many pulp and paper factories are trying to convert the lignocellulosic materials into bioethanol and other bioproducts. In this sense, a new research Project named BRIGIT, FP7-KBBE-2012-6-311935 (www.brigit-project.eu) is being carried out. The main objective of the European Project is develop a cost-competitive and environmentally friendly continuous process to produce fire-resistant biopolymers for goods and passenger transport, from the valorisation of waste-derived lignocellulosic sugar feedstock liquor of wood sulphite pulping process.

The first task of the project is the optimisation of the sugar content in the sulphite digestion process by means of the study of different raw materials. Kinetic parameters have been obtained in this stage. In addition, dissolving pulp quality parameters and all of the valorisation options have been studied giving the main operation variables of the process.

Hemp fibers: Enzymatic effect of microbial processing on fibre bundle structure

A. Thygesen, M. Liu, A.S. Meyer, and G. Daniel

The effects of microbial pretreatment on hemp fibres were evaluated after microbial retting using the white rot fungi *Ceriporiopsis subvermispora* and *Phlebia radiata* Cel 26 and water retting. Based on chemical composition, *P. radiata* Cel 26 showed the highest selectivity for pectin and lignin degradation and lowest cellulose loss (14%) resulting in the highest cellulose content (78.4%) for the treated hemp fibres. The pectin and lignin removal after treatment with *P. radiata* Cel 26 were of the order 82% and 50%, respectively. Aligned epoxy-matrix composites were made from hemp fibres defibrated with the microbial retting to evaluate the effects on their ultrastructure. SEM microscopy of the composites showed low porosity on the fibre surfaces after defibration with *P. radiata* Cel 26 and *C. subvermispora* indicating good epoxy polymer impregnation. In contrast, fibres treated by water retting and the raw hemp fibres were badly impregnated due to porosity caused by surface impurities such as epidermis and other pectin rich plant cells. The pectin and lignin mainly located in the outer part of the fibres were assumed to be extracted and degraded by pectinase and peroxidase enzymes produced by the fungi.

Nature inspired bio-adhesives

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Development of high performing bio-adhesives is of high interest and challenge. Potential solution for such a challenge is based on DOPA-functionalized resilin and Nano Crystalline Cellulose (NCC). Resilin is an insect's protein (Figure 1.A) and considered as being the most elastic material in nature. Its unique mechanical properties combine high elasticity of 97%, exceeding all available synthetic rubbers¹. Cellulose, the most abundant and renewable biopolymer on earth, contains highly crystalline regions. These regions can be processed into Nano-scale crystals that have a tensile strength similar to super strong materials such as aramid fibers². DOPA-proteins are considered as being the strongest non-covalent adhesives on earth. Mussels use these proteins for adherence to organic and inorganic materials under water (Figure 1.B)³. Inspired by the remarkable elasticity of resilin, the strength of NCC and the adhesion strength of DOPA-proteins, we fused a cellulose binding domain (CBD) to the resilin and also modified it to create DOPA-resilin. Hence, we paved the way to create novel DOPA-resilin-CBD/NCC Nano-composite adhesives. Preliminary results showed good adhesion of the DOPA-resilin to both inorganic and organic surfaces (figure 1.C). Recently, we were also successful in integrating NCC and resilin-CBD with Epoxy resins resulting in novel Bio-nanocomposite adhesive. The mechanical and physical properties of the composite adhesive are under investigation.

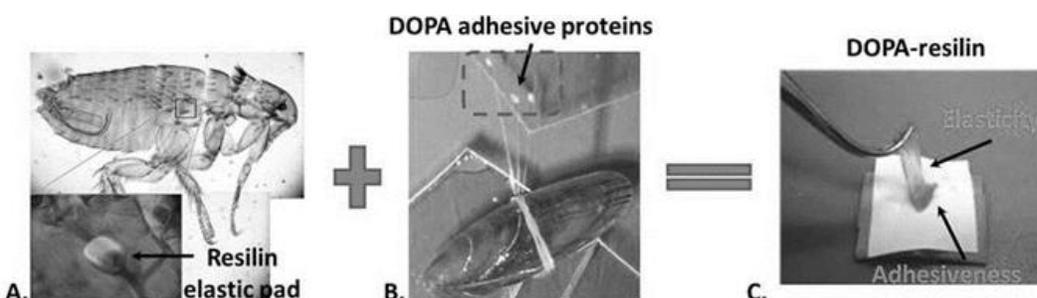


Figure 1. A resilin elastic pad enables flea's extraordinary mobility and jumping as high as 400 times its height (A). DOPA containing proteins in mussel's threads enable strong adhesion to surfaces and the support of the mussels own weight (B). Novel DOPA-resilin combines both adhesion and elastic properties. The white surface is a cellulose sheet (C).

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Green enzymatic acylation of nano cellulose fibers in the presence and absence of scCO₂

Vera Vivod

Cellulose acetates (and hydrophobic cellulose) are of great importance because of e.g increased thermo-processability, improved compatibility with hydrophobic polymers, increased ability of selective absorption and removal of low levels organic chemicals (and proteins) etc. In this respect, the acylation (i.e. substitution of OH group to acetyls) of cellulose nanofibers (CNFs) with acetic anhydride as acyl donor was studied using Amano Lipase A from *Aspergillus niger* in organic solvent (DMSO) with or without the addition of phosphate buffer and scCO₂ as advanced non-aqueous solvent in order to enable good CNFs dispersability, acetic anhydride dissolution as well as affords adequate enzyme activity. According to ATR-FTIR spectroscopy analysis, the highest ester contents were obtained in combination with scCO₂, which can be attributed to the increased diffusion rates and ability to swell cellulose. The substitution reaction and chemical structures of CNF esters was confirmed and identified by solid-state CP/MAS ¹³C-NMR spectroscopy, which indicated that acylation occurred predominantly at the C-6 carbon of the polysaccharide ring. SEM images showed smoother surface with enhanced density and more uniform structure after acylation reaction. Thermal properties, evaluated by DSC and TG analysis, showed decreased thermal stability after acylation, most probably due to the disintegration of intramolecular interactions such as hydrogen bonds.

Nano Crystalline Cellulose/Nano Particles (NCC/NPs); Light Tunable Reinforced Plastic Sheets

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New processes and systems are constantly being innovated in order to meet the demand for higher performances polymeric materials, and furthermore to meet today's environmental and energy requirements. A single polymer or a combination of polymers may achieve a certain properties enhancement; however major improvements may be achieved via nano-particles reinforcements of polymers.

Nano Crystalline Cellulose (NCC) is an exciting new bio-material made from cellulose. It can be produced from cell walls of plants but also from huge waste streams such as that of paper meals and municipal sewage system sludge. These nano-crystals are 200-300 nm in length and 20 nm in diameter, and nearly as strong as Kevlar. NCC has intriguing properties and many potential applications. It may be present as

liquid crystal solution in water and self-assemble to macro scale ordered films having a thickness at the nano-scale.

In this work we aim to take advantage of the NCC properties and reinforce plastic sheets such as polyethylene (PE- non-degradable) and poly-lactic acid (PLA- degradable) by coating them with ordered NCC layer. Furthermore, we aim to integrate nano-particles such as SiO₂ and ZrO₂ in order to tune the material's optical properties.

Novel nano-reinforced composite materials, with improved mechanical properties compared to regular plastic sheets as well as controlled optical properties, were developed. The young modulus of the plastic sheets and their toughness increased due to the NCC coating. Moreover, blocking of UV and IR spectra was achieved by the incorporation of NPs inside the NCC coating. These new materials will be applicable in fields such as greenhouses covers and food packaging, and will present greener solutions than currently used plastic sheets.

NCC from lignocellulosic biomass: applications and future prospects

Valentina Coccia

Nano-crystalline cellulose (NCC) is a cellulose derived nano-material that received great academic and industrial interest over the last few years. NCC is promising as new class of bio-based reinforcing material for the preparation of nano-structured composites due to impressive mechanical properties (i.e. large tension modulus) associated with low density and high aspect ratio. Advantages in the use of NCC are not only related to its useful, unsurpassed, physical and chemical properties, but also to their renewability, low cost, sustainability, abundance, biodegradability, and high biocompatibility. Furthermore, thanks to its dimensions in the nanometer scale, many other potential properties might be discovered. This contribution discusses the preparation, the morphological features, and the physical properties of NCC, as well as the incorporation in nano-composites and some of their applications. Challenges and opportunities of NCC-biomass-based materials for the future will be also presented.

Renewable lignocellulosic biomass for the synthesis of cellulose derivatives

Elena Vismara

High grade cellulose of 48% crystallinity index has been extracted from the renewable marine biomass waste *Posidonia oceanica* through an environmentally benign and chlorine-free process, which uses H₂O₂ and organic peracids as oxidants.

The new high-grade cellulose of waste origin appeared quite similar to the high-grade cellulose extracted from more noble starting materials like wood and cotton linters. The transformation of α -cellulose recovered from *P. oceanica* into valuable derivatives enhanced the benefits in using a waste biomass a source of cellulose.

Fully acetylated cellulose acetate (CA) was prepared by conventional acetylation method and easily transformed into a transparent film. Glycidyl methacrylate cellulose derivative (GMA-C) with a molar substitution (MS) of 0.72 was produced by quenching Fenton's reagent (H₂O₂/FeSO₄) generated cellulose radicals with GMA. GMA grafting endowed high-grade cellulose from *P. oceanica* with adsorption capability. In fact, GMA-C was able to remove β -naphthol from water with an efficiency of 47%, as measured by UV-Vis spectroscopy. The hydrolysis of the glycidyl grafting groups to glycerol groups allowed to obtain a modified GMA-C, which was active in removing p-nitrophenol from water with an efficiency of 92%, as measured by UV-Vis spectroscopy. Therefore, α -cellulose and GMA-Cs from *P. oceanica* waste can be considered as new materials of potential industrial and environmental interest.

Mechanical behaviour of wood fibre reinforced concrete matrix

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Natural fibres are renewable and abundant, and provide a low cost resource for reinforcing concrete matrices. The use of wheat stalks fibres as traditional reinforcement solution is known since 18th century in Portugal, for the production of artisanal brickworks. At the present time some work has been done by others researchers in characterization of wood fibres, wood fiber-cement matrix and micromechanics.

The scope of this researcher is to ascertain the possibility of wood fibre reinforced concrete being an alternative solution in structural design, by the use of a more eco-friendly material. Generally in fibre reinforced cementitious composites the most used fibres are from steel, carbon, propylene, etc, which have a high ecological foot print. This project has the following main tasks: conceive a mix design rational method; evaluate most relevant mechanical material properties; assess the structural behaviour; and develop numerical tools.

The concrete mix design and material properties will be done applying current methods and standard tests, and the project aims to evaluate the influence of the fibre type, size, dispersion, quantity in the concrete's fresh state. The mechanical behaviour will be assessed by compressive, tensile, flexural and shear tests.

Finally, it will be developed numerical tools in order to derive the material constitutive laws based upon the experimental results. In the case of indirect flexural tensile tests, the material laws will be obtained through an inverse analysis procedure. The laws rendered by the simulation of latter tests will be compared with the one derived with the direct tensile test. At the end of this project is expected to develop a wood fibre reinforced concrete with a competitive cost and to define constitutive laws for the design of structural elements.

Cellulosic Fibers: Effect of Processing on Fiber Bundle Strength

Anders Thygesen, Bo Madsen, Hans Lilholt

A range of differently processed cellulosic fibers from flax and hemp plants were investigated to study the relation between processing of cellulosic fibers and fiber bundle strength. The studied processing methods are applied for yarn production and include retting, scutching, carding, and cottonization. There was a monotonically decreasing relationship between the strength and the number of processing steps, which was well fitted by an exponential regression line. The reduction factor was determined to be 0.27, indicating that the fiber bundle strength was on average reduced by 27% per processing step at the applied conditions. No large changes in cellulose content and crystallinity were observed, so the reduction in strength must be explained by other changes in the fiber ultrastructure. Altogether, the study presents a quantitative basis for reduction in strength of cellulosic fibers due to processing.