NORDIC POLYMER DAYS 2017

STOCKHOLM JUNE 19 - 21

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ABSTRACTS

GENERAL INFORMATION

Venue

The conference will take place at KTH Royal Institute of Technology. Keynote lectures will be held in lecture hall Q1, Osquldas väg 4. Parallel sessions will be held in lecture room Q31, Q33, and Q34.

Registration and registration desk

The registration desk is located in the entrance hall outside lecture room Q1, Osquldas väg 4. The desk is open for registration on Monday at 08:30 – 09:00 and 11:30 – 13:00, and Tuesday at 08:30 – 09:00.

Message board

There will be a message board next to the registration desk where all incoming messages will be posted.

Scientific topics

Presentations on all areas of polymer science and engineering are welcome, but the conference will devote special emphasis on the synthesis, physical and chemical properties, modeling and applications of:

- Biomedical materials
- Nanostructures and composites
- Biomass and biobased materials
- Energy related materials

Posters

Posters will be displayed in the atrium area outside lecture rooms Q31, Q33, and Q34. There is time allocated for poster exhibition on Monday afternoon at 17:00 but all posters will be on display during the whole conference. During the poster mingle on Monday afternoon, drinks and refreshments will be served (included in the conference fee. All posters should be mounted as soon as possible on Monday and removed on Wednesday morning.

Exhibition

We are happy to host 7 companies for the exhibition during the conference. All exhibitors will be on display outside lecture rooms Q1, Q31, Q33, and Q34.

Lunch

Three lunches are included in the conference fee. Lunch is served at Restaurant Q located next to lecture hall Q1. Lunch coupons are available in the envelope you receive when you register at the registration desk upon arrival.

Coffee / Tea

Coffee and tea will be served in the entrance hall outside lecture room Q1.

Computer access

All conference delegates will have access to the wireless network operating throughout KTH campus. You will find a password in the envelope you receive when you register at the registration desk upon arrival. For university employees, the wifi network Eduram is available all over campus.

Conference dinner

The conference dinner will be held at Spårvagnshallarna on Tuesday at 7 pm. Spårvagnshallarna is located on Birger Jarlsgatan 57 A in center city Stockholm, approximately 15 minutes' walk from KTH. A map and travel directions are available at: http://www.sparvagnshallarna.com/

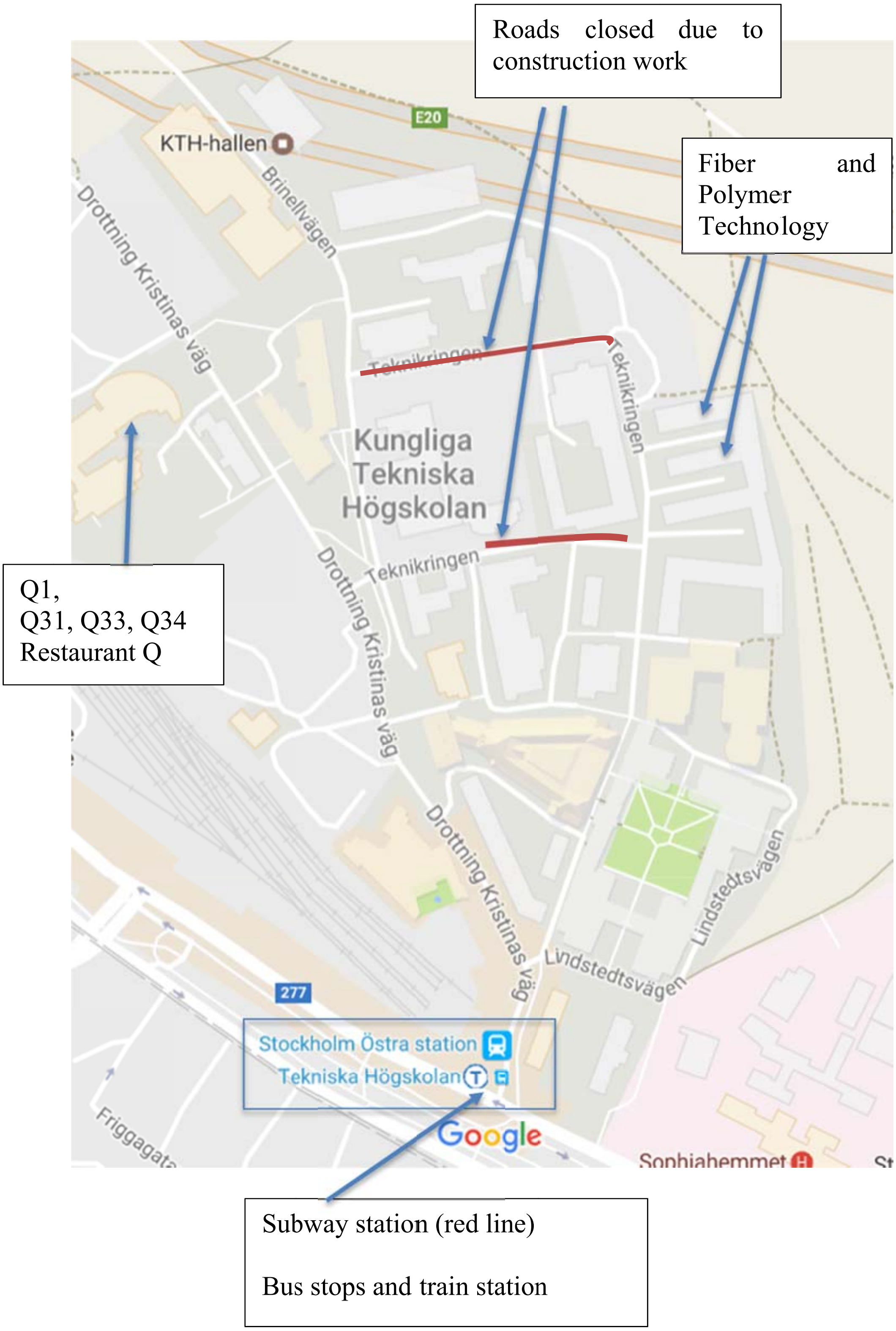
The closest subway station is Rådmansgatan (green line). Spårvagnshallarna is located 200 m walk from the exit Tegnérgatan.

For those who prepaid and registered to attend the dinner, the ticket will be available in the envelope you receive when you register at the registration

Biomacromolecules award

The ACS publication Biomacromolecules will kindly sponsor an award, given to the best PhD student presentation during Nordic Polymer Days 2017. The winner will be announced at the closing ceremony on Wednesday, June 21.

MAP



Roads closed due to construction work

Fiber and Polymer Technology

Q1,
Q31, Q33, Q34
Restaurant Q

Subway station (red line)

Bus stops and train station

COURSE ON 'THERMAL ANALYSIS OF POLYMERS'

Time: June 19

Place: Lecture room Q31

Time: 9 - 12

Lecturer: Professor Ulf W. Gedde (gedde@kth.se)
Fiber and Polymer Technology, KTH Royal Institute of Technology

The course is free of charge for the participants of the conference. The course will provide 4.0 credits and includes lectures and home assignments.
Course code: FKF3370

Synopsis:

Thermal analysis is a whole family of different analytical methods. They are based on a common principle that some physical property (e.g. enthalpy, volume or mass) is measured while the sample is undergoing a controlled temperature program. Modern thermal analysis uses very small sample amounts typically a few mg. The efficiency of the thermal analytical methods makes them often the primary choices to solve a problem. They provide an initial overview of your problem and may inspire you to design further more specialized measurements. This before-lunch-course provides the basic knowledge about the most commonly used methods and quite a number of application cases relevant to a range of different polymeric material types. You will receive the pdf of the lectures together with a 50-60 pages text written by me. The final part of the text presents a number of problems, which you are supposed to solve. I hope that you will ask questions during the lectures. Bring questions relevant to your research to the lecture. Heartily welcome to join us.

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CONFERENCE PROGRAM

Monday 19/6					
Time					
8:30-9:00	Registration: Osquldas väg 4 Participants of thermal analysis course				
9:00 – 12:00	Thermal Analysis course, room: Q31				
11:30 – 13:00	Registration: Osquldas väg 4 Lunch: Restaurant Q				
13:00 – 13:15	Conference Opening, room: Q1				
13:15 – 13:45	Chairperson: S. Hvilsted Keynote Lecture: Bjørn Torger Stokke, High precision monitoring of swelling of responsive hydrogels, room Q1				
13:45 – 14:15	Keynote Lecture: Monika Österberg, Cellulose nanofibrils in biomedical materials – Importance of understanding the interfacial interacions, room Q1				
Time	Session: Teaching and Learning Chairperson: K. Odelius Room: Q31	Time	Session: Biomass and biobased materials Chairperson: R. Moriana Room: Q33	Time	Session: Synthesis and Characterization Chairperson: C.-E. Wilén Room: Q34
14:30 – 14:40	Karin Odelius	14:30 – 14:50	Harri Setälä	14:30 – 14:50	Massimiliano Mauri
14:40 – 15:05	Pirjo Pietikäinen	14:50 – 15:10	David Sandqvist	14:50 – 15:10	Riccardo Borgani
15:05 – 15:30	Emma Strömberg	15:10 – 15:30	Joakim Engström	15:10 – 15:30	Karolina Gaska
15:30 – 16:00	Coffee break, room: Q-building				
Time	Session: Biomedical Materials Chairperson: T. Fuoco Room: Q31	Time	Session: Biomass and biobased materials Chairperson: M. Tengdelius Room: Q33	Time	Session: Biomass and biobased materials Chairperson: M. Österberg Room: Q34
16:00 – 16:20	Anders E. Daugaard	16:00 – 16:20	Andrea C. Ruthes	16:00 – 16:20	Steven Spoljaric
16:20 – 16:40	Monika Golda-Cepa	16:20 – 16:40	Emelie Norström	16:20 – 16:40	Antonio Capezza
16:40 – 17:00	Tina Borke	16:40 – 17:00	Rosana Moriana	16:40 – 17:00	Qiong Wu
17:00 – 19:00	Poster session, room: Q-building				

Tuesday, 20/6					
Time					
9:00 – 9:30	Chairperson: A.-C. Albertsson Keynote Lecture: Karin Odelius, Design of Functional Biobased Materials Through Green Chemistry Approaches, room Q1				
9:30 – 10:00	Keynote Lecture: Carl-Eric Wilen, Innovative Halogen free Flame Retardants for Plastics, room Q1				
10:00 – 10:30	Coffee break, room: Q-building				
Time	Session: UV-curable thermosets Chairperson: M. Johansson Room: Q31	Time	Session: Synthesis and responsive polymers Chairperson: A. Zelikin Room: Q33	Time	Session: Modelling and Advanced Characterization Chairperson: F. Nilsson Room: Q34
10:30 – 10:50	Marco Sangermano	10:30 – 10:50	Sami Hietala	10:30 – 10:50	David B. Haviland
10:50 – 11:10	Massimo Messori	10:50 – 11:10	Luis Valencia	10:50 – 11:10	Dirk W. Schubert
11:10 – 11:30	Erno Karjalainen	11:10 – 11:30	Fiona L. Hatton	11:10 – 11:30	Per-Anders Thorén
11:30 – 11:50	Marcus Jawerth	11:30 – 11:50	Fabian Pooch	11:30 – 11:50	Ali Moyassari
11:50 – 13:00	Lunch: Restaurang Q				
13:00 – 13:30	Chairperson: U. Gedde Keynote Lecture: Christian Müller, Polyethylene Blends, a Material Concept for HVDC Power Cable Insulation, room Q1				
13:30 – 14:00	Keynote Lecture: Malin Åkermo, Fibre composites in vehicle applications – opportunities and challenges, room Q1				
Time	Session: Synthesis and characterization Chairperson: B. Stokke Room: Q31	Time	Session: Biomass and biobased materials Chairperson: U. Edlund Room: Q33	Time	Session: Biomedical Materials Chairperson: M. Malkoch Room: Q34
14:10 – 14:30	Søren Hvilsted	14:10 – 14:30	Akram Zamani	14:10 – 14:30	Tiziana Fuoco
14:30 – 14:50	Anja Lund	14:30 – 14:50	Tiia-Maria Tenhunen	14:30 – 14:50	Joonas Siirilä
14:50 – 15:10	Daniel Hult	14:50 – 15:10	Martin Sterner	14:50 – 15:10	Viktor Granskog
15:10 – 15:40	Coffee break, room: Q-building				
Time	Session: Energy Related Materials Chairperson: C. Müller Room: Q31	Time	Session: Biomass and biobased materials Chairperson: E. Strömberg Room: Q33	Time	Session: Synthesis and characterization Chairperson: P. Pietikäinen Room: Q34
15:40 – 16:00	Ellen Moons	15:40 – 16:00	Antonia Svärd	15:40 – 16:00	Lilian Forsgren
16:00 – 16:20	Niklas Ihrner	16:00 – 16:20	Karin Adolfsson	16:00 – 16:20	Andrea Träger
16:20 – 16:40	-	16:20 – 16:40	Nejla Erdal	16:20 – 16:40	-
19:00 -	Conference dinner at Spårvagnshallarna				

Wednesday, 21/6					
Time	Session: Polymer Stability and Degradation Chairperson: M. Hedenqvist Room: Q31	Time	Session: Biomass and biobased materials Chairperson: L. Fogelström Room: Q33	Time	Session: Biomass and biobased materials Chairperson: E. Malmström Room: Q34
9:00 – 9:20	Klas Esbo	9:00 – 9:20	Mattias Tengdelius	9:00 – 9:20	Christofer Lendel
9:20 – 9:40	Alberto Vega	9:20 – 9:40	Samer Namer	9:20 – 9:40	Salla Välimäki
9:40 – 10:00	Xinfeng Wei	9:40 – 10:00	Maja Finnveden	9:40 – 10:00	Tobias Ingverud
10:00 – 10:30	Coffee break, room: Q-building				
Time	Session: Fibrous systems Chairperson: R. Olsson Room: Q31	Time	Session: Polymer processing Chairperson: M. Åkermo Room: Q33	Time	Session: Waste water treatment Chairperson: M. Golda-Cepa Room: Q34
10:30 – 10:50	Mostafa Jabbari	10:30 – 10:50	Blanca Maria Lekube	10:30 – 10:50	Tetyana M. Budnyak
10:50 – 11:10	Nina Forsman	10:50 – 11:10	Abhijit Venkatesh	10:50 – 11:10	Geng Hua
11:20 – 11:50	Chairperson: M. Hakkarainen and M. Johansson Keynote Lecture: Alexander N. Zelikin, Polymers fight viruses: design, in vitro, in vivo, room Q1				
11:50 -	Closing Ceremony, Q1 Best PhD presentation award sponsored by Biomacromolecules: Ann-Christine Albertsson				
	Lunch: Restaurang Q				

ABSTRACTS

KEYNOTE SPEAKERS

in alphabetical order

Polyethylene Blends, a Material Concept for HVDC Power Cable Insulation

Christian Müller

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High-voltage direct-current (HVDC) cables are a critical component of tomorrow's power grids that seamlessly integrate hydro, wind and solar power. The insulation of state-of-the-art extruded HVDC cables is composed of low-density polyethylene (LDPE), which must be crosslinked to provide adequate creep resistance. The electrical performance of the crosslinked cable insulation is limited by its residual electrical conductivity. In this talk the use of polyethylene blends is explored. The addition of high-density polyethylene (HDPE) is demonstrated to be a versatile tool that permits to improve both the thermo-mechanical and electrical properties of the cable insulation material. Additive-like amounts of HDPE are sufficient to impart creep resistance even above the melting temperature of LDPE, which may ultimately alleviate the need for crosslinking. Further, a considerable reduction in electrical conductivity by about one order of magnitude can be achieved, which opens up an intriguing avenue towards thermoplastic HVDC cable insulation.

Design of Functional Biobased Materials Through Green Chemistry Approaches

Karin Odelius

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Designing methodology and polymerization routes to enable a gradual shift from the overwhelming use of fossil resources to biobased resources for plastic production is ongoing. Strong examples of such plastics are on the commercial market and in use, and their market shares are growing – although maybe at what could be considered by some at a too slow pace. These new materials are both interesting as direct replacements of their oil-based counterparts and as plastics that offer new function. Although, as these biobased plastics, bioplastics, are being marketed concerns connected to their overall environmental impact are being raised. Our way of thinking is that to reach sustainable plastics for tomorrows market, the principals of green chemistry need to be applied already when performing basic research and should continue to advance all the way to the market and after-use-handling. This ideally means that the building-blocks are either non-food based, available in large quantities with a reasonable price or that they can be created through waste treatment. That the synthesis methods for monomers, oligomers and polymers are as facile as possible, that benign catalysts and chemicals are used, that solvents and other auxiliaries are avoided, that energy consumption is always a consideration and that we from the start consider the end-of-life handling of the materials. In this presentation some examples of the ongoing work in the design of functional biobased materials through green chemistry approaches will be presented and discussed.

This financial support of this project comes from The Swedish Research Council, VR (grant ID: 621201356 25).

High precision monitoring of swelling of responsive hydrogels

Bjørn Torger Stokke

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Hydrogels adapts to changes in environmental conditions and particular molecules by adjusting their swelling volume. In addition to being dependent on molecular composition and connectivity of the network part, the interplay with the solvent, the overall hydrogel swelling properties are also depending on overall size and geometry. Hydrogel swelling are an inherent property principally displayed by all hydrogels, but the extent, dynamics and underlying molecular mechanics may differ. The main theoretical foundation relating various contributions to the overall swelling properties have been outlined. Despite of this and the importance of swelling both within basic understanding as well as applications, there is limited focus on developing instrument dedicated to reliable, high performance determination of this property. This is at variance with instruments available for determination of other properties of hydrogels, e.g., structure and mechanical properties. Thus, researchers have resorted to adoption of procedures based on general laboratory infrastructure, often in combination with adoption of not straightforward measurement principles and specimen features compatible with the particular strategy. Thus, hydrogel swelling have been reported based on gravimetry, optical imaging, MEMS resonator mass sensor, dynamic light scattering, diffraction from embedded colloid crystals, diffraction from hydrogel grating, interferometric principles and others. The various strategies are reported with inherent differences in resolution, temporal sampling capacities and applicability with respect to overall size. In the presentation, we will highlight application of a fiber-optic interferometric platform for precise monitoring of changes in hydrogel swelling response. A resolution of 2 nanometer is achieved in changes of the optical length within hemispherical ~60 μm radius hydrogels. Examples of application of this monitoring technique will be shown for specific molecular responsive gels to glucose,[1] oligonucleotide based recognition[2,3] as well as examples where hydrophobic[4] and electrostatic interactions[5,6] are dominating. Thus, the high resolution swelling monitoring offer enhanced sensitivity towards the analyte concentration for the molecular responsive hydrogels, and e.g., discrimination between ionic and polyampholyte swelling response as function of ionic strength for some of the other specimens. Such results illustrate how high precision in monitoring of swelling of hydrogels can offer more detailed information as compared to technique with more inherent uncertainties.

References

1 Tierney, S. *et al.* Biosensors & Bioelectronics **2009**, *24*, 2034.
2 Tierney, S. *et al.* Biomacromolecules **2009**, *10*, 1619.
3 Gao, M. *et al.* Soft Matter **2011**, *7*, 1741.
4 Gao, M. *et al.* Soft Matter **2013**, *9*, 5178.
5 Gao, M. *et al.* European Polymer Journal **2014**, *53*, 65.
6 Prot, V. *et al.* Soft Matter **2013**, *9*, 5815.

Innovative Halogen Free Flame Retardants for Plastics

Carl-Eric Wilén

Head of laboratory
Laboratory of Polymer Technology, Center of Excellence for Functional Materials at Biological Interfaces, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo, Finland
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Halogenated flame retardants have long been reported to effectively interfere with the combustion cycle of polymeric materials primarily through a free-radical scavenging mechanism in the vapor phase. Although halogenated flame retardants still form one of the most widely applied flame retardant class in combination with antimony oxide for different polymeric materials their persistency in the environment, troublesome recyclability, corrosiveness, large smoke generation during a fire situation and legislative actions in combination with increasing safety awareness of consumers have in recent years significantly decreased their popularity and market growth prospects. Preferentially, new flame retardant formulations should have very low environmental imprint and be free of halides, ammonium salts, heavy metals and borates.

Our main research objective has been to address the existing gaps towards eco-friendly and high performance flame retardant technology by the design, synthesis and application of innovative radical generators such alkoxyamines, azoalkanes and disulfides that are effective at much lower concentrations than conventional flame retardants in various polymers.

More recently, we have synthesised a wide variety of molecules containing S-N, S-N-S or N-S-N moieties, and their flame retardant properties either alone or as synergists with conventional flame retardants in various polymers ranging from PP, LDPE, PS, epoxy and wood composites have been investigated. The sulfenamide based flame retardants offer easy of synthesis, control of its thermal stability and most importantly, flexibility of design and tunability of properties. Polymers or oligomers bearing the SN-functionality have also been synthesized showing excellent flame retardant action in various polymer types. The choice of most suitable sulfenamide structure varies depending on the polymer type. It is anticipated that sulfenamides will open the door to an exciting new chapter in the use of halogen free radical generators. As a consequence of this, work to explore the full possibilities of these versatile sulfenamide additives as flame retardants for a number of polymer types are currently ongoing in our group.

Polymers fight viruses: design, in vitro, in vivo

Alexander N. Zelikin

Department of Chemistry and iNano Interdisciplinary Nanoscience Centre
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Viral pathogens continue to presents an enormous healthcare and socio-economic burdens. Some viral pathogens are highly contagious and have high associated mortality rate, others do not cause terminal diseases but are debilitating. Success of medicinal chemistry over the past decades was highly admirable but even now, the overall majority of pathogenic viruses have no approved treatment. Another tremendous challenge is that there is no approved broad-spectrum antiviral agent. Finally, antiviral drugs are short-acting and require frequent administration.

Our approach to counter viral pathogens is based on polymers and specifically – macromolecular prodrugs. Towards to the overall goal, we make polymers that serve as optimized drug carriers and/or have inherent antiviral activity. Conjugation of drugs to polymers we develop through cunning, stimuli-responsive linkers such as to achieve fast drug release upon the prodrug cell entry. Conjugation of prodrugs to albumin confers long body and blood residence time to the prodrugs.

During this presentation, I will outline the criteria of design for successful antiviral macromolecular prodrugs, illustrate that these agents counter infectivity of Zika and Ebola viruses, HIV, and almost every other viral pathogen we worked with, and critically evaluate if these agents will ever enter clinic.

Selected publications

1. Albumin-polymer-drug conjugates: long circulating, high payload drug delivery vehicles", *ACS Macro Lett.* **2016**, *5*, 1089-1094
2. HIV anti-latency treatment mediated by macromolecular prodrugs of histone deacetylase inhibitor, panobinostat", *Chem. Sci.***2016**, *7*, 2353-2358
3. "Polyanionic macromolecular prodrugs of ribavirin : antiviral agents with a broad spectrum of activity", *Adv. Healthcare Mater.,* **2016**, *5*, 534-540.
4. "Self Immolative Linkers Literally Bridge Disulfide Chemistry and the Realms of Thiol-Free Drugs", *Adv. Healthcare Mater.* **2015**, *4*, 1887-1890
5. Macromolecular prodrug of ribavirin : towards a treatment for co-infection with HCV and HIV", *Chem. Sci.* **2015**, *6*, 264-269.
6. "Disulfide reshuffling triggers the release of a thiol-free anti-HIV agent to make up fast-acting, potent macromolecular prodrugs", *Chem. Commun.* **2014,** *50*, 14498-14500

Fibre composites in vehicle applications – opportunities and challenges

Malin Åkermo

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The vehicle industry is currently under large development facing challenges considering demands on lower emissions at the same time as the customer base is not yet prepared paying for improved fuel economy. Except for electrification and development of new energy efficient/low emission motors, focus in on reducing structural weight since this directly result in lower energy consumption during usage. This presentation focuses on increased usage of structural composite materials as one route to weight reduction for the vehicle industry and the challenges this development is facing.

In the presentation it is shown that the cost of a composite vehicle components produced in large series is dominated by material costs and tooling costs, at least if the component is large and have moderate to high complexity [1]. While the latter can be reduced by changing the component design, material costs are more difficult to approach. Future composite vehicle components will therefore consist of several different composite material configurations that, at lowest price, provides the functionalities required.

The presentation will also show how alternative, more environmentally friendly material systems like self-reinforced thermoplastic composites can be used as alternative low density material system for less structural components. Using a combination of different manufacturing processes and keeping control of the processing parameters is important to ensure that the reinforcing morphology remains intact after processing [2].

To the end, when introducing a novel material system into large series production it must be adapted for easy forming into desired component geometry. The produceability of a material system is set by the combination of fibre architecture and surrounding polymer matrix. However, reading the data sheet from the material supplier, there are no characteristic data addressing this aspect. Examples on how material characteristics of the raw material influences the formability of a material system is discussed toward the end of the presentation [3].

References

1. Mårtensson, P. Zenkert, D., Åkermo, M, ”Structural partition of a composite body structure: - effects on cost or performance efficiency”, Polymer Composites, Vol 34(17), pp 1444-1453
2. Jerpdal, L. Åkermo, M., Influence of fibre shrinkage and stretching on the mechanical properties of self-reinforced poly(ethylene terephthalate) composite, Journal of Reinforced Plastics and Composites September 2014 33: 1644-1655.
3. Hallander, P. Sjölander. J., Åkermo. M., “Forming induced wrinkling of composite laminates with mixed ply material properties; an experimental study, Composites Part A, 78 (2015) 234–245

Cellulose nanofibrils in biomedical materials – Importance of understanding the interfacial interactions

Monika Österberg

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Cellulose nanofibrils, CNF, is an interesting material for various biomedical applications. It is xeno free, has been found not to be cytotoxic and it can be enzymatically degraded when needed. It is furthermore strong and highly hydrated. However, to utilize efficiently the properties of CNF it is important to understand and control its interactions with cells and tissue. Herein we describe two possible applications of CNF, for cell culture and for treatment of articular cartilage damage, focusing on how measuring direct forces using the atomic force microscope and the colloidal probe technique can enhance our understanding of the systems.

In the first project, our aim is to understand what interactions between living cells and extracellular matrix (ECM) components are crucial for successful cell culture. For this purpose we use direct force measurements between living cells and various ECM materials. This research is part of a general strive for finding better in vitro models for drug testing. It is known that stem cells respond to the physical and chemical properties of culturing matrices, but so far little is known about the underlying mechanisms and its outcomes in stem cell behavior. We have measured the forces between various cell culturing materials; CNF, laminin, and collagen and between the materials and either dead or living cells to distinguish between specific interactions and interactions due to e.g. surface charge. The studied cells were human pluripotent stem cells and human hepatocarcinoma cells. The measured interactions correlated well with observations during cell culturing.

In the second project, our aim is to demonstrate a simple, and solvent-free method to develop a highly lubricating but strong CNF material by attaching hyaluronic acid to CNF. A detailed analysis of the tribological properties of the CNF films with and without hyaluronic acid is also presented. We measured surface and friction forces at micro/nanoscale between model hard surfaces (glass microspheres) and the CNF thin films using an atomic force microscope and the colloid probe technique. The effect of hyaluronic acid attachment, pH and the ionic strength of the aqueous medium on the forces is described. Excellent lubrication was observed for CNF films with HA attached in conditions where the HA layer was highly hydrated. These results pave the way for the development of new nanocellulose-based materials with good lubrication properties that could be used in biomedical applications.

ORAL CONTRIBUTIONS

in alphabetical order of presenting author

Enhanced properties in nanocomposites by carbon dots from cellulose

Karin Adolfsson and Minna Hakkarainen
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Carbon spheres were derived from cellulose[1] and waste paper[2] through an efficient microwave-assisted hydrothermal treatment. Graphene oxide quantum dots (GOQDs) were then obtained in a subsequent oxidation of the carbon spheres with nitric acid.[3] The dots were highly oxidized and possessed interesting optical properties. The effect of incorporation of the dots in aliphatic polyesters, polycaprolactone (PCL)[4] and polylactide (PLA),[5] was further studied.

GOQDs were shown to induce mineralization on the surface of PCL nanocomposites. Calcium phosphate (CaP) deposits were formed on the nanocomposites and no mineralization was induced on neat PCL. Increasing the concentration of GOQDs gave rise to larger and fewer CaP on the surface of PCL.

In the PLA nanocomposites, barrier and mechanical properties were evaluated after incorporation of GOQDs. The addition of GOQDs induced additional nuclei in comparison to neat PLA. The elongation at break was especially improved in comparison to neat PLA and PLA with commercial 2D graphene oxide. The addition of GOQDs also successfully increased the barrier against oxygen.

In these studies, GOQDs it was shown that GOQDs from renewable material through an easy route with microwave irradiation are valuable property enhancers in aliphatic polyesters.

References

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3. K. H. Adolfsson, S. Hassanzadeh, M. Hakkarainen, **2015**. RSC Advances, 5(34), 26550-26558.
4. S. Hassanzadeh, K. H. Adolfsson, D. Wu, M. Hakkarainen, **2016**. Biomacromolecules, 17(1), 256–261.
5. H. Xu, K. H. Adolfsson, L. Xie, S. Hassanzadeh, T. Pettersson, M. Hakkarainen, **2016**. ACS Sustainable Chem. Eng., *4* (10), 5618–5631.

Local charge injection and extraction on nanocomposite insulators

R. Borgani[1], P.-A. Thorén[1], D. Forchheimer[1], and D. B. Haviland[1]*
Love K. H. Pallon[2], Mikael S. Hedenqvist[2], and Ulf W. Gedde[2]
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We image the surface potential on a nanocomposite insulation material under different bias conditions with Intermodulation Electrostatic Force Microscopy[1] (ImEFM). We show experimental results[2] that support a proposed mechanism for the increased insulating capabilities of the material.

The high resolution scans in Fig. 1a show strong contrast between the aluminum oxide nanoparticles and the surrounding low density polyethylene (LDPE) matrix, and even reveal a nanoparticle buried in the LDPE. In contrast to standard Kelvin Probe Force Microscopy (KPFM), ImEFM is performed in an open-loop fashion. This enables the use of a DC bias between the tip and the surface as a free parameter, to effectively perform the scan under different gating conditions. While the surface potential difference between the nanoparticles and the LDPE increases with a positive bias (Figure 1b), it vanishes under negative bias conditions (Figure 1c). We interpret these results in terms of charge injection and extraction by the AFM tip, and infer the presence of localized energy states in the area surrounding the nanoparticles with the help of a simple band structure model of the sample.

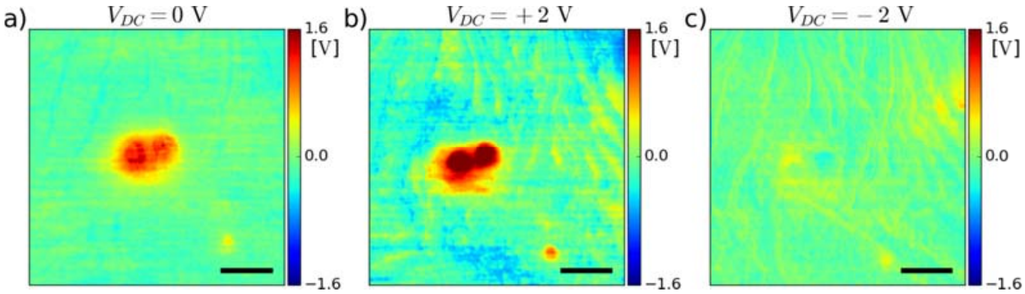

Figure 1: ImEFM study of the Al_2O_3 nanoparticles embedded in LDPE. Surface potential V_{SP} under different DC bias conditions. The black scale bar is 100 nm. Figure adapted from [2].

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Hyaluronan-graft copolymers with cleavable arms: Methods to quantify polymer-from-polymer release

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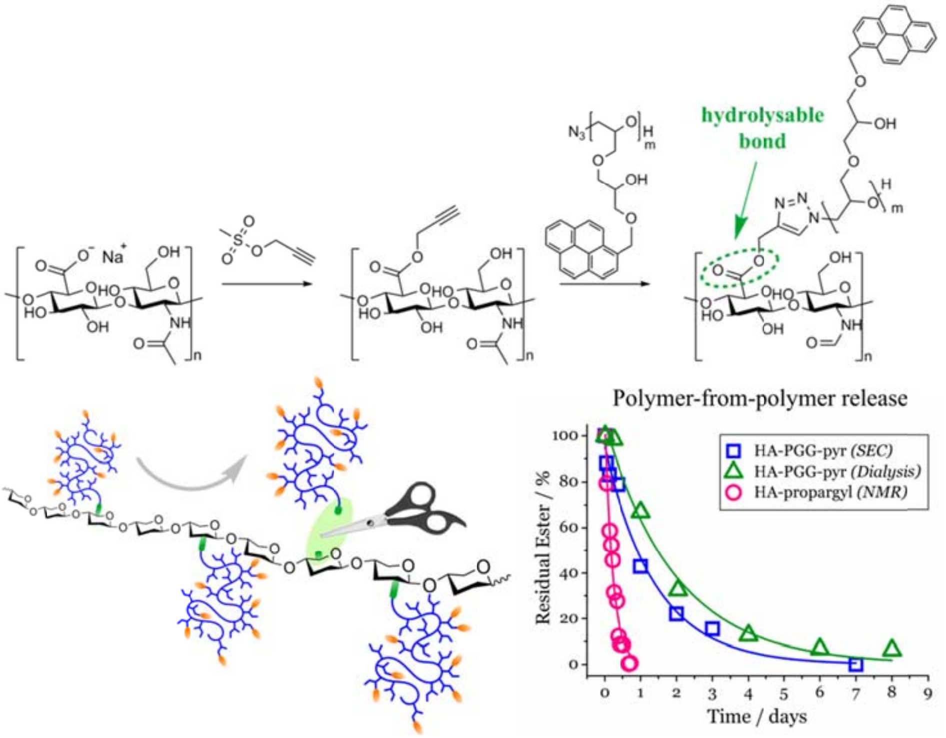
Multihydroxy-functional graft copolymers of hyaluronic acid (HA) and poly(glyceryl glycerol) (PGG) were prepared by a two-step procedure involving esterification of HA with propargyl linkers and subsequent click reaction with azido-PGG. The water-soluble copolymers are intended for sustained ophthalmic drug delivery. The PGG grafts can carry a multitude of drugs, probes and targeting ligands[1] and they are slowly released from the HA backbone by hydrolysis of the ester bond.

Here we present the synthesis of HA-PGG graft copolymers and methods to quantify the release of side chains from the copolymer backbone. Determining the release kinetics of PGG-grafts from HA-PGG is essential to predict the action time of the release platform. Therefore we evaluate commonly used *in vitro* release setups for the study of soluble polymeric systems. The separation of macromolecules with very similar chemical structures (plethora of hydroxyl groups) and solubility behaviour is considerably more difficult than separation of small drugs. Hence establishing and verifying procedures for the quantification of polymer-from-polymer release is of fundamental interest, but rarely covered in the literature.



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Synthesis of chitosan-silica composites and its application as adsorbents of toxic compounds from aqueous solutions

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Plenty of approaches have been studied for the creation of ecofriendly, low-cost and effective adsorbents for extraction of toxic heavy metals. To improve the adsorption properties of mineral adsorbents it is expedient to immobilize the appropriate substances with well-pronounced ion-exchanging and complexing properties onto their surfaces. Application for these purposes natural biopolymers, such as a nitrogen-containing polysaccharide chitosan, is of a great interest. In that case, properties of inorganic sorbents could be upgraded by valuable characteristics of organic polymer. In particular, chitosan has good biocompatibility, high adhesion to the surface, a wide range of pH stability, expressed chelating properties. Silica is characterized by advanced surface stability in the acidic medium, acceptable kinetics, thermal stability, and resistance to microbial attack. All these facts confirm that nanocomposites mineral-chitosan can be used as effective adsorbents, enterosorbents, *etc*.

Hybrid materials were prepared using various synthetic methods: adsorption and covalent binding of polymer on the carrier surface, partial crosslinking of amino groups of adsorbed polymer, forming of inorganic matrix in polymer solution (sol-gel method). Anchorage of chitosan on the minerals surface was confirmed by IR spectroscopy. Concentration of immobilized chitosan was estimated using thermogravimetric analysis. Specific surface area of the obtained nanocomposites was estimated.

It was found that the biocomposites based on chitosan and silica are effective as adsorbents with respect to highly toxic contaminants such as heavy metals, synthetic dyes and herbicides from aqueous solutions. Thus, hybrid biocomposites chitosan-silica was found to be effective towards oxoanions V(V) and Mo(VI) (1.6 and 1.5 mmol/g, respectively), sulfonated azo dyes: Orange II and Acid Orange 8 (0.20 mmol/g), Orange G (0.12 mmol/g), Acid Red 88 (0.48 mmol/g) and Acid Red 1 (0.09 mmol/g). The study of adsorption of herbicides has shown that composite chitosan-silica could adsorb up to 0.31 and 0.35 mmol/g of 4-chlorophenoxyacetic and 2,4-dichlorophenoxyacetic acid, respectively. The experimental equilibrium data were analyzed by the Langmuir and Freundlich equations. The effect of temperature on pollutants uptake and adsorption rate were studied. The thermodynamics parameters such as ΔG°, ΔH° and ΔS° for adsorption of studied ions and dyes were calculated from the equilibria at different temperatures. Kinetic adsorption characteristics also were studied for the obtained composites.

The research was funded by the Visegrad 4 Eastern Partnership Program of the International Visegrad Fund under the contract for financing Visegrad/V4EaP Scholarship No 51400001 and the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement No° PIRSES-GA-2013-612484.

Novel absorbent materials obtained from plant proteins

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Polymers with high water uptake properties have had a significant role in the expansion of the daily-care product industry. Polyacrylic acids (PAAc) and polyamides (PA) are the preferred raw polymeric materials for addressing applications where important absorbent features in ionic solutions are needed. In 2014, ca. 2 million tons of such polymers were produced, of which most is used in the diapers and cellulose pads industry1. However, these petroleum-based materials are unsustainable and lack in degradability. As a consequence, the global daily-care industry is generating a direct impact in the environment when producing these materials. Previous work has shown that 100% wheat gluten (WG) protein foams have the ability to absorb water in a similar range as synthetic absorbent polymers2. The main downside, however, of such foams is the observed compression-reversible capillarity effect; during mechanical compression the material releases the water that has been absorbed. Another type of structure, e.g. hydrogels synthetized from different protein sources, were shown to have similar water uptake properties, with no water release. In consequence, natural polymers like proteins obtained from biological resources may function as a substitute for petroleum-based absorbent materials.

The main objective of this project is to study the thermal and chemical processes that can be applied to proteins in order to promote water absorption and retention of the liquid within the structure. In addition, the research involving protein-based absorbent materials shows a potential since they have been studied infrequently compared to polysaccharides-related research. The protein concentrates that are being used are co-streams from the agricultural and food industries. Heat-treated and functionalized wheat gluten (WG) has shown an absorption capacity of 7 g/g in 0.15 M NaCl solution after 5 minutes. Similar procedures applied to potato proteins resulted in 10 g/g of absorption in saline solution within the first 2 minutes. Swelling capacity is evaluated in ionic solutions since such systems determine the strength of the material to ionic conditions, typically encountered in daily-care applications. The increase in hydrophilic functional groups together with the homogenization of the proteins before being chemically treated will be the focus for improving the chemical response of the material. As a consequence, an increase in the water uptake of these protein-based materials is expected.

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Activity of enzymes immobilized on OSTE surfaces as a function of surface functionality

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Successful immobilization of enzymes on surfaces requires an exact match between the surface chemistry and the specific enzyme. This would normally be identified through time consuming screening of conventional resins in multiple reactions using individual immobilization strategies. Here we present a strategy that largely expands the number of possible surface functionalities that can be tested for enzyme immobilization in a single, generic platform. This platform combines several methods in one modular system to permit faster and more efficient screening, which we believe will result in a higher chance of discovery of beneficial surface/enzyme interactions.

We have prepared a thiol-functional microplate through fast photochemical curing of an off-stoichiometric thiol-ene (OSTE) mixture. Surface functionalization by thiol-ene chemistry (TEC) with allyl, vinyl or acrylate compounds resulted in the formation of a functional monolayer in each well. Alternatively, polymer surface grafts were introduced through surface chain transfer free radical polymerization (SCT-FRP) of acrylic or methacrylic monomers. Both TEC and SCT-FRP led to tailored surface modifications with control over surface properties. For instance, water contact angles of functionalized surfaces ranging from 21 to 118° demonstrated high control over hydrophilicity and hydrophobicity. Subsequently, the functionalized surfaces served as support for immobilization of horseradish peroxidase (HRP) as a model enzyme.

This process of OSTE fabrication followed by controlled surface modification showed high potential to determine suitable surface – enzyme combinations for the development of biocatalytic materials with improved activity.

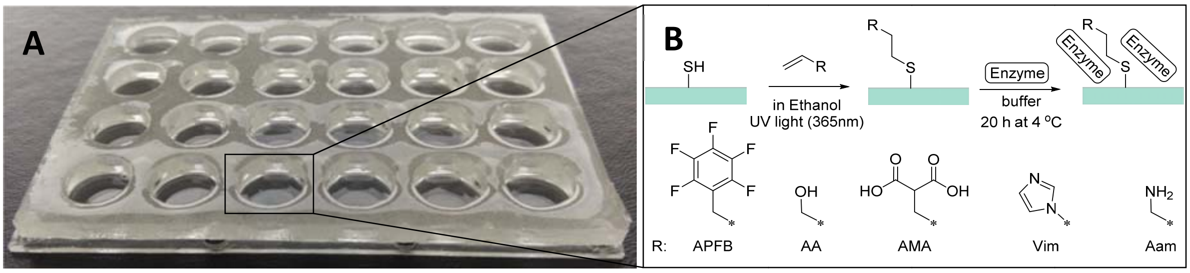

Figure 1. A: OSTE based microwell plate, B: functionalization of surface thiols via TEC followed by enzyme immobilization

Soft and rigid latex nanoparticles for improvement of interfacial adhesion and flexible cellulose nanofibrils (CNF) composite applications

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Cellulose is an interesting natural polymer due to its renewability, large abundance and mechanical properties.[1] It has been shown that by adsorbing block copolymers onto its surface, cellulose nanofibrils (CNF) can be compatibilized with hydrophobic matrices in composites applications.[2] Our group has previously implemented amphiphilic latex nanoparticles synthesized by RAFT-mediated surfactant free emulsion polymerization [3, 4] with polymerization-induced self-assembly (PISA) [4, 5], subsequently adsorbed to cellulose surfaces.[6] In this study we have extended the work to produce different types of latex particles of a hydrophilic, cationic charged block and hydrophobic blocks of either poly(methyl methacrylate) (PMMA) or poly(*n*-butyl methacrylate) (PBMA), where the degree of polymerization (DP_n) of the hydrophobic blocks have been varied [7]. PMMA and PBMA were chosen as high and low T_g polymer, respectively, to investigate the influence of the T_g of the core. Increasing the DP_n of the hydrophobic block (from 176 to 1410) increased the latex particle diameter (from 35 to 140 nm). The effects of adsorption of the latexes were studied in composite applications, CNF aqueous dispersions and onto cellulose model surfaces in a QCM-D.

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Cellulose derived reduced nano graphene oxide as a property enhancer in PCL nanocomposites

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Previously we utilized cellulose as raw material for production of graphene oxide quantum dots (GOQD) with a mild hydrothermal microwave treatment via carbon nanospheres as an intermediate product[1,2]. An interesting property of these GOQD nanoparticles is that they can be partly reduced to graphene like materials by removing oxygen functionalities to recover a more uniform conjugated structure. Here, we developed a green microwave process to produce nanosized reduced graphene oxide (nano-rGO) with the inclusion of a green, naturally abundant reducing agent. The hydrothermal microwave process carries advantages such as the use of water as a solvent, no toxic or explosive reducing agents involved that are generally employed to reduce graphene oxide[3, 4] and effective heating through microwave irradiation. In addition to developing the synthetic route to nano-rGO, the produced nano-rGO was characterized and tested as property enhancer in PCL composites. An evident decrease in oxygen functionalities after the microwave process was found with FTIR and XPS and an increased thermal stability was shown by TGA. Nano-rGO had good cell viability and functioned as property enhancer in PCL. Composites of nano-rGO and PCL were formed with extrusion and compression molding to allow for proper mixing and to create homogeneous films. After processing the bioactivity, in the form of mineralization test and the rheological properties were assessed. Mineralization, as shown by calcium phosphate growing on the surface of the films, could be detected on the surface of the PCL films after addition of nano-rGO, in accordance with previous results shown for PCL/GOQD composites.[5] The rheological properties such as storage modulus and loss modulus were improved with increasing loading of nano-rGO further suggesting advantages for e.g. biomedical applications.

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Polymeric materials in corrosive environments

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The Polymer Group at Swerea KIMAB (former Swedish Corrosion Institute) has more than 30 years of experience of the use of polymeric materials in process equipment. Our work aims at characterizing and understanding the corrosion resistance properties of different polymeric materials and how they affect the potential use of these materials. The work, which is carried out in close cooperation with the industry, include studies on materials, such as PVC, fluoroplastics, polyethylene and polypropylene plastics, fibre-reinforced plastics (FRP), etc. The corrosive environments include pickling acids, chlorine, sulphuric acid, pulp and paper chemicals, flue gas, petrochemicals, disinfection agents, and others. Experience from our previous work has shown that valuable knowledge about the corrosion properties and the durability of plastics and rubber in different applications under practical conditions may be achieved by corrosion analysis of samples which have been taken from various process equipment that have failed, have been replaced or are still in service. Another important area is welding in process equipment after exposure to chemicals during service. This is a frequently encountered problem among end users of plastic process equipment where there are no general guidelines to rely on.

In short, this presentation aims to highlight the polymeric materials importance for corrosive environments and thereby clarify, with examples, the most important failures as well as give an outlook for the future challenges and demands.

Lipase catalyzed synthesis of a series of bifunctional cationically polymerizable monomers

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Monomers that undergo rapid photopolymerizations are of interest due to their uses in applications such as photocurable coatings, adhesives, and printing inks.[1,2] Vinyl ethers have a strongly electron-donating oxygen and consequently they can be homopolymerized fast using cationic initiators.

Utilizing mild lipase catalysis bifunctional vinyl ether terminated ester monomers havebeen synthesized from hydroxyl vinyl ether and various carboxylic acids. The use ofcarboxylic acids as one of the components permits the use of a vast variety of accessiblerenewable starting compounds with interesting functionalities. Additionally, lipasesdisplay chemo, regio and enantio selectivity, which can be used to add value if morecomplex monomers are desired.

The reaction conditions for the acylation of hydroxy vinyl ether with 10-undecenoic acidwas studied and demonstrated that the enzyme catalyzed synthesis route allow a vast variation in solvent and temperature that can be adapted to fit the choice of carboxylic acid as reactant.

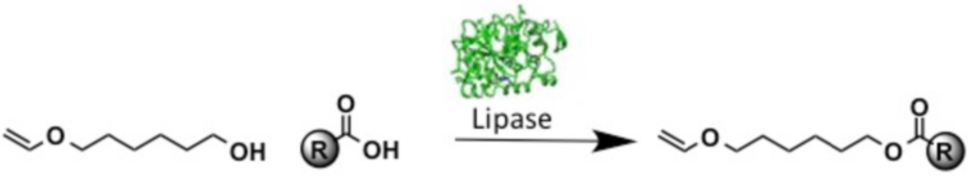

Figure 1. Synthesis of bifunctional momers utilizing lipase catalysis

Bifunctional vinyl ether terminated ester monomers were synthesized from hydroxyl vinyl ether and either 10-undecenoic acid with an external double bond or 11-mercaptoundecanoic acid with thiol functionallaty. The behaviour of the monomers in photoinitiated cationic and free-radical polymerization was investigated to determine whether the two types of functional groups would exhibit cooperative or differentiated reactivity during polymerization.

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Surface grafting of CNC – characterization and dispersion rheology

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Recognizing the great importance of cellulosic fibres in the pulp and paper industry, there are also other potentially interesting applications of this material. Inherent advantages of cellulose are for instance the renewability, its biodegradability and the possibilities for interesting modifications. With the use of different treatments, cellulosic fibres or similar substances can be transformed into cellulose nanonfibrils (CNF) or cellulose nanocrystals (CNC). Both CNF and CNC are expected to exhibit good stiffness and strength properties which has resulted in an interest in these as reinforcing elements in polymer matrix nanocomposites. This presentation will focus on CNC which was obtained from microcrystalline cellulose via a treatment with sulphuric acid.

Incorporation of CNC into a hydrophobic polymer matrix is quite often associated with dispersion problems in the form of an unwanted aggregation of the nanoparticles and an insufficient adhesion between the hydrophilic nanocellulose and the polymer. A surface treatment of the cellulosic elements is a potentially possible route for reducing such difficulties. In addition, processing or compounding of the blend CNC/polymer benefits from an understanding of the rheological properties of the individual components, especially if the CNC is available in the form of an aqueous dispersion. Thus, the effect of the surface treatment on the rheological properties of CNC dispersions is of interest and relevance. It can also be argued that rheological measurements in themselves constitute in a sense a characterization of the dispersed system.

In this study, CNC was modified by grafting ring-opened azetidinium salts on the sulphate groups on the CNC surface, leading to an increased hydrophobicity. The changes in surface characteristics due to this treatment have been assessed using several techniques such as NMR, FTIR and ς-potential measurements. An interesting finding was that the onset temperature of the thermal degradation of the CNC was, due to the surface modification, increased from about 150 °C to approximately 250 °C according to TGA measurements. A focus of this study has been the rheological properties of aqueous CNC dispersions and their dependence on the applied surface grafting. The CNC concentration was kept quite low (0.65 and 1.3 weight-%) and the viscosity (as a function of the shear rate) as well as the dynamic-mechanical viscoelastic behaviour in shear were evaluated. The grafting of the azetidinium salts on the CNC had a pronounced effect on the rheological behaviour of the dispersions. The viscosity increased, the shear-thinning character changed and the dynamic moduli clearly increased in magnitude due to the surface treatment. This can be interpreted in terms of a network formation, since also the gel point of the dispersions was significantly lowered in case of the grafted systems. This behaviour is suggested be attributed to hydrophobic interactions between the grafted entities.

Functional textiles using natural non-toxic materials

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Textiles today are often made of non-renewable synthetic fibers, which raise sustainability issues. Even though more and more sustainable fabrics are entering the market, the functional clothing industry is still using mainly synthetic materials.[1] Furthermore, the surface treatments to enhance properties like for example water resistance are far from sustainable. We have developed a simple and green method based on layer-by-layer deposition of alternatingly cationic poly-L-lysine compound and anionic colloidal wax particles (Figure 1a) that can introduce hydrophobicity to natural cotton or linen fabrics. The layer build-up and morphology of the layer were studied using microgravimetry (QCM-D) and atomic force microscopy, respectively and the effect of pH on adsorption was evaluated. The surface coverage was determined using x-ray photoelectron spectroscopy. The water contact angle depended on the roughness of the substrate, being the lowest on smooth model surfaces and the highest on rough fabrics. The combination of multiscale roughness, open film structure, and low surface energy of wax colloids, resulted in superhydrophobicity on cotton surface already after two bilayers.[2] Although the textiles could resist water for over three hours (Figure 1b), there was no major decrease in their moisture transport ability, allowing the textiles to breathe. The coating was deposited onto small pieces of fabrics by dipping, and onto larger pieces with brushing and spraying, methods industrially used to coat textiles. This green and simple approach has the potential to be used in a large variety of textile applications, and enhance the use of environmentally friendly material in the textile industry.

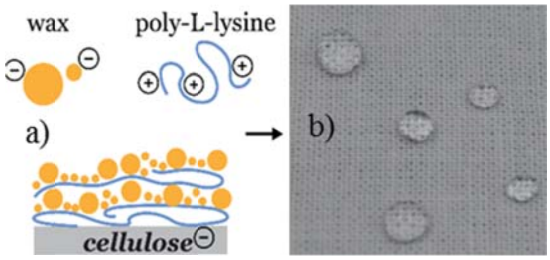

Figure 1. a) Schematic picture of the coating. b) Water droplets after 3h on textiles coated according to our method. Note that on unmodified samples, the water completely penetrates the fabric in less than 5 seconds and no contact angle can be measured.

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Aliphatic poly(ester)s with thiol pendant groups: synthesis, post-polymerization modification and applications

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The degradable aliphatic polyester family has gained interest for applicability in biomedical and pharmaceutical fields. These polymers are often used for manufacturing resorbable devices, from tissue engineering scaffolds to drug release systems. One drawback of the aliphatic polyesters is the lack of functional groups along the polymeric chains. The presence of functionalities could allow the tuning of the physical and chemical properties as well as to improve hydrophilicity and biocompatibility.[1]

We have addressed this issue by designing and synthesizing a lactide-type monomer featuring a latent thiol group, the TrtS-LA. Due to its versatility, thiol chemistry plays an important role in polymer synthesis and post-polymerization modification.[2]

The TrtS-LA revealed to be a useful building block for the preparation of functionalized aliphatic polyesters. The monomer has been copolymerized with commercially available monomers and we have, by using different catalytic systems, achieved good control over the chain growth.[3,4]

The potential applications of such polyesters in biomedical field have been evaluated. The latent thiol groups along the polymeric chains were modified into pyridyl disulphide functionalities and the polymer was subsequently used to fabricate editable porous scaffolds. As a proof of concept, to demonstrate the applicability of this material as scaffolds for tissue engineering with enhanced biological response, a cysteine-terminated RGD peptide was covalently attached to the porous scaffolds by a disulphide-exchange reaction in aqueous solution.[3]

Furthermore, we have prepared redox-responsive PEG-PLA based nanoparticles by reaction of pyridyl disulphide functionalized polyesters with a telechelic PEG having thiol groups at both ends. In water solution, they assembled in flower-like particles, with size in the range 167 – 300 nm, thus suitable for drug delivery. The redox responsiveness to glutathione was also ascertained, thus, the prepared nanoparticles could be used as drug carrier with controlled and targeted release.[4]

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Properties of low density polyethylene- graphene nanoplatelets nanocomposites

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The aim of this research is to elucidate the influence of processing conditions on rheological, electrical, thermal, and gas barrier properties of low density polyethylene-GnP nanocomposites. Samples were prepared by means so called dry-coating method [1], then melt extrusion and compression molding. The influence of graphene nanopowders size and content was also considered.

It is shown that the extrusion process imposes a strong anisotropy in material's morphology. The graphene nanoplatelets become aligned along the extrusion direction. Similar findings were earlier reported in the work of Gaska et al [2]. Compressed samples show similar morphology with filler alignment along polymer flow, however filler is more agglomerated with a poor distribution (see Fig 1 b).

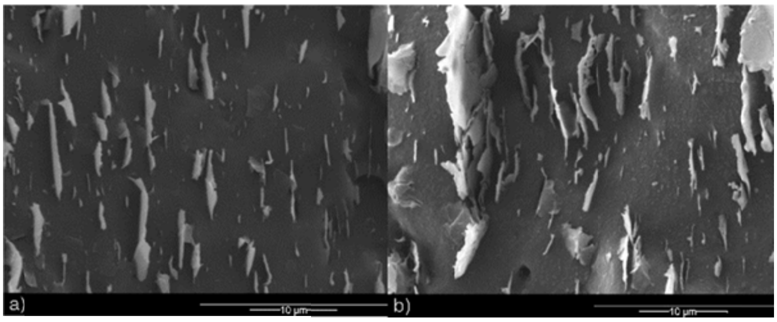

Fig 1. Morphology of a) extruded sample b) compressed sample with 5wt% of GnP

The performed tests of gas permeability showed a drastic decrease of this property with increasing filler content. The linear and nonlinear oscillatory shear measurements of LDPE-GnP nanocomposites were carried out to elucidate the impact of GnP loading as well as to study the morphology and the formation of internal network within the manufactured composites [3]. Evidence of the influence of dispersion properties was found in linear viscoelastic dynamic frequency sweeps, while the percolation of the nanocomposites was detected in nonlinearities found in dynamic strain sweeps. A strong anisotropy of the thermal conductivity is also achieved for extruded samples whereas more isotropic behavior has been shown for compressed samples. GnP filled LDPE composites show interesting electrical properties as non-linear field depended behavior. Significantly lower conductivity as compared to pure LDPE is observed in them at low electric field, while higher conductivity is measured at higher electric field.

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Multifunctional PLGA/parylene C coating for implant materials: an integral approach for biointerface optimization

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The challenges of metal implant engineering are to introduce specific properties which result in optimization of the metal-implant tissue interface. Among various approaches, one of the most explored is coating metal implants with a thin polymer layer which can be additionally provided with functions essential for a long-term implantation success, namely: anti-corrosive, biocompatibility, anti-infection and therapeutic. The aim of the study was to develop multifunctional polymer coating based on drug+PLGA/parylene C with four essential functions (Fig.1).

Parylene C micrometric coatings provided a superior increase in corrosion resistance (1×10^9 Ω cm^2) when compared with uncoated SS 316L (1×10^4 Ω cm^2). Surface modification of parylene C with oxygen plasma caused changes in its chemical composition by the generation of functional groups such as –COOH, –OH as well as nanotopography. Fluorescent staining of focal contacts of osteoblasts cells together with SEM observations revealed improved biocompatibility of the modified parylene C. The area of focal contacts (FC) was quantified for oxygen plasma treated samples and compared to unmodified parylene C, where the FC level was minor or below the detection limit. Generated nanotopography, effectively limited the surface area available for bacteria. The studies of drug+PLGA/parylene C systems revealed that the drug molecules remain unchanged upon interaction with the PLGA matrix and the drugs distributions were homogenous. The obtained release profiles are suitable for prolonged elution up to 21 days for both of the investigated systems (ibuprofen- and gentamicin-loaded) [1].

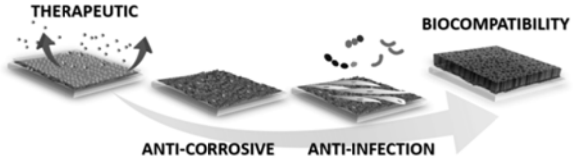

Fig.1 The overview of the conducted research strategy on PLGA/parylene C coating introducing four key functions essential for implant long-term success.

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Bone adhesive based on thiol-ene coupling

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Bone fractures remind us abruptly of our fragile nature and induce a major burden for both patients and society. In the coming years, an increased fracture incidence is foreseen due to an older population, violence, road accidents and sport injuries[1]. The combined load from surgeries, hospital stay and lost working days for the patient motivate a major interest to improve surgical methodologies. A revolutionary step towards optimal fracture fixation, long desired by orthopaedic surgeons, would be to use an adhesive as complementary fixator in multi-fragmented fractures or in non-load bearing reduction of fractures, holding bone pieces in place during healing. Despite intensive research over the last decades, where various approaches have been evaluated, the struggle with either poor adhesion, low biocompatibility or an inadequate fixation methodology have delayed the expansion of the area further than the present use of bone cements[2].

One promising adhesive-based fracture fixation method is the Fiber Reinforced Adhesive Patch (FRAP)[3]. FRAP is applied as a plate over the fracture without entering the cross-section of the bone, thus diminishing the interference with the healing of the fracture compared with inserting the adhesive into the fracture. The FRAP technology can enable a quick and mild fixation of various fractures that today are considered difficult due to sensitive locations; near joints or when drilling is not a possible option. FRAP exploits the mild and efficient Thiol-Ene Coupling (TEC) crosslinking chemistry[4]. The robust stepwise polymerization reaction through TEC leads to gelation at high conversions, which can induce a tough and highly connected network with minimized leakage of low molecular weight compounds.

Here, we present a FRAP composition with exceptional bond strength towards wet bone. To tackle the difficulty in adhering to wet surfaces and then remain stable in the wet environment, the adhesive system consists of components that are designed for different purposes and used in combination to create a synergistic effect on the bond strength. The influence of adhesion-enhancing groups, the molecular architecture and linking strategy were evaluated in order to optimize the FRAP composition and create a high-performance TEC adhesive system for bone repair.

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Synthesis of epoxy-functional diblock copolymer nano-objects via polymerisation-induced self-assembly

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The synthesis of various epoxy-functional diblock copolymer nanoparticles has been investigated *via* polymerisation-induced self-assembly using a reversible addition-fragmentation chain transfer aqueous emulsion polymerisation formulation.[1] A poly(glycerol monomethacrylate) (PGMA) chain transfer agent was chain-extended using glycidyl methacrylate (GlyMA) at 50 °C (Fig. 1A). The solution pH was maintained at pH 7 to preserve the epoxy functionality of the hydrophobic PGlyMA block. Fast rates of polymerisation and high final monomer conversions (>99%) could be obtained under these relatively mild conditions when targeting 10-35% solids. Varying the mean degrees of polymerisation (DP) of the PGMA stabiliser block and the PGlyMA core-forming block resulted in well-defined nano-objects with either spherical or worm-like morphologies (see Fig. 1B and 1C). The average worm width (19 nm) corresponded to the average sphere diameter (16 nm), and worm lengths were in the range 0.1-2 µm, determined by TEM. Analysis of the diblock copolymer nanoparticles by GPC revealed low dispersities (<1.3) with lower core forming block lengths (DP GlyMA <100).

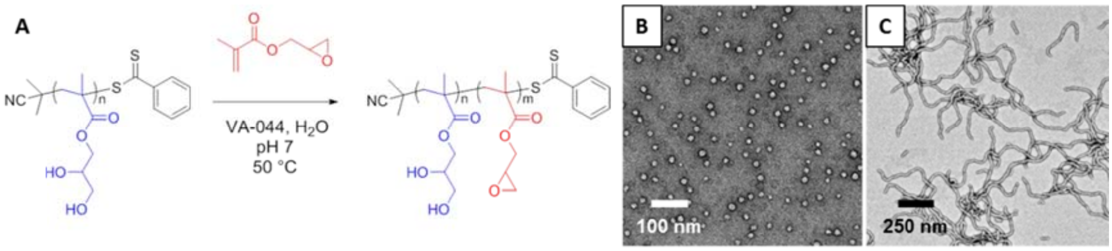

Figure 1 A) Synthetic route to prepare PGMA-PGlyMA latex particles and TEM images of B) PGMA45-PGlyMA35 spherical particles and C) PGMA26-PGlyMA50 worm-like micelles.

Cationic nanogels could be prepared from these epoxy-functional precursor nano-objects via diamine cross-linking in aqueous solution. Addition of DMF, a good solvent for both blocks, caused molecular dissolution of the linear precursor nanoparticles, whereas diamine cross-linked nanoparticles became swollen but retained their morphology, as judged by DLS and TEM. These reactive epoxy-functional nanoparticles have been evaluated for their suitability as Pickering emulsifiers for the preparation of oil-in-water macro- and nanoemulsions. In principle, the reactive epoxy groups can be utilised to produce colloidosomes *via* crosslinking between adjacent nanoparticles adsorbed at the oil/water interface.

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Measuring the viscoelastic response of polymer surfaces at the nanometer scale

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Dynamic Atomic Force Microscopy allows for understanding not only the elastic character of the tip-surface interaction, but also its viscous nature. We use a special multi-frequency excitation and detection scheme to extract two dynamic force quadrature curves: $F_I(A)$ revealing the conservative (in phase with motion) and $F_Q(A)$ showing the dissipative (in phase with velocity) forces, as a functions of oscillation amplitude A. Our measurements are well-explained by a model that treats the cantilever and surface as a two-body dynamical system with an interaction that depends on their separation. Adhesive forces give rise to large surface motion on soft materials, with dissipation resulting from the viscous character of the material and interface. with this technique we extract local (nanometer-scale) relaxation times on heterogeneous polymer surfaces [1].

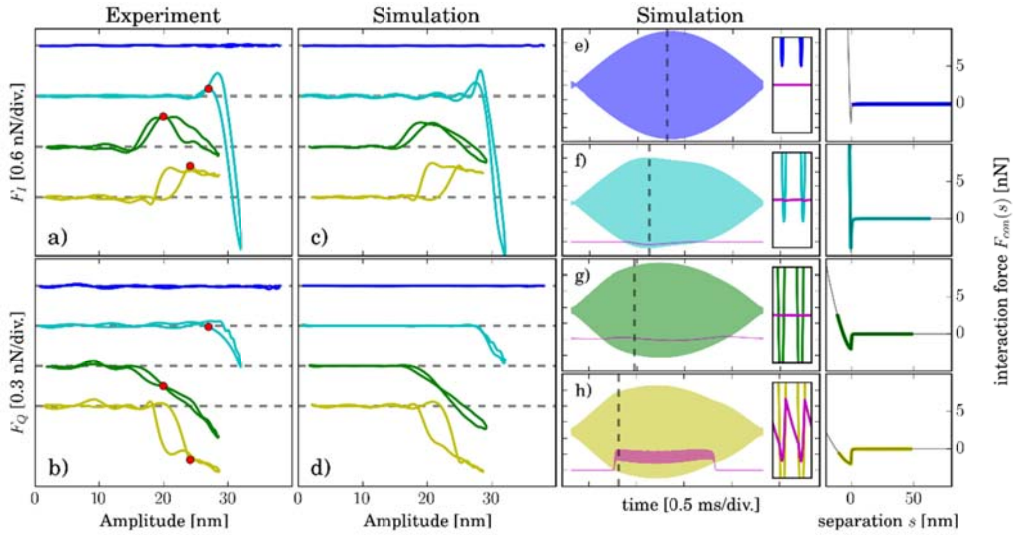

Fig. 1: Dynamic force quadratures F_I and F_Q as a function of oscillation amplitude. Experiments compare well with numerical simulations of the moving surface model. Simulated time dependence of the cantilever motion and surface motion are shown together, as well as the region of the conservative interaction experienced by the tip during the modulation of oscillation amplitude.

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Thermosensitive (UCST-LCST) triblock copolymers

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Poly(N-acryloylglycinamide) (PNAGA) is a non-ionic polymer that shows Upper Critical Solution Temperature (UCST) type of phase transition behaviour in water and saline solutions.1 On the other hand, Poly(N-isopropyl acrylamide) (PNIPAM) has Lower Critical Solution Temperature (LCST) type of transition in aqueous medium. In order to combine these behaviour, polyethylene oxide macro-RAFT agent was used first to polymerize either N-acryloylglycinamide (NAGA) or N-isopropyl acrylamide (NIPAM) to diblock copolymers.2 These diblock copolymers exhibited typical thermoresponsive character of PNAGA and PNIPAM in aqueous solutions leading to formation of nanoscale aggregates either at low or high temperature. Chain extension of these polymers with either NAGA or NIPAM lead to double thermosensitive triblock copolymers that show both UCST and LCST type of transition. The effect of the length and order of the blocks (PEO-b-PNAGA-b-PNIPAM or PEO-b-PNIPAM-b-PNAGA) on the thermoswitchable polymer aggregates were studied.

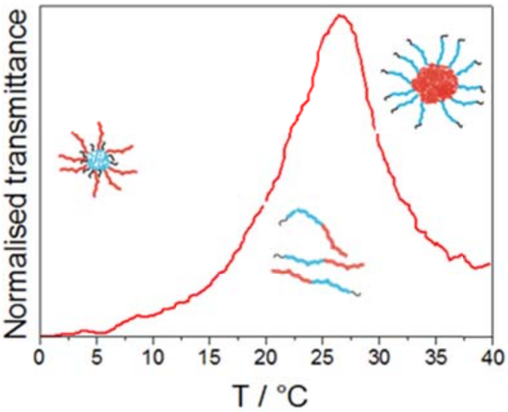

Figure1.Thermoswitchable aggregates of PEO-PNAGA-PNIPAM.

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Biosourced heavy metal-ion waste water adsorbent — Design, synthesis and characterization of a hydrogel

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Waste water pollution is an increasing environment concern and has been so for the past decades, especially in countries where pollution-generating industries are located.[1] Among which, heavy metal-containing waste water is a large difficulty, as the metal ions accumulate in the human body and the subsequent harm that arises.

Adsorption of heavy metal ions through filtering is an efficient and widely applied strategy. Biosourced adsorbents for heavy metal waste water have been developed with examples including crosslinked chitosan and cellulose.[2] In this study, we designed a new crosslinked polyester based adsorbent with the naturally occurring and hence biobased δ-gluconolactone as the starting material. Aminolysis of the lactone was performed to ring-open the cyclic lactone which resulted in a poly-ol building block. Due to the well-defined structure of the poly-ol, some well-tuned and controlled networks were synthesized using ethylenediaminetetraacetic (EDTA) dianhydride as the crosslinker. A great benefit of the system is the use of EDTA, which is known as a strong and efficient metal chelating reagent and within our system this moiety is evenly and densely distributed throughout the network.[3]

The metal ion adsorption ability of the network was determined via titration, thermal gravimetric analysis and isothermal kinetics. An outstanding chelating ability was showing with the maximum adsorption capacity of Cu(II) of ~ 121 $mg{\cdot}g^{-1}$, which out-performed most of the existing biosourced adsorbents. The corresponding strength of the swelling adsorbent hydrogel was also examined under different pH conditions, where a responsive gel structure was shown.

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Fluoride-promoted polymerizations using imidazolide-activated monomers towards poly(esters and carbonates)

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Based on the growing demand for facile and more sustainable synthetic methods towards functional biomedical materials, we present a new approach for the synthesis of polyester dendrimers and linear polycarbonates, capitalizing on 1,1'-carbonyldiimidazole (CDI). Cesium fluoride (CsF) is shown to be an essential catalyst for these reactions to reach high conversions, and *in situ* generated imidazole indicate no inhibition of the catalytic activity through competitive H-bonding. This approach was successfully applied to synthesize a sixth generation bis-MPA polyester dendrimer with a molecular weight of 22.080 g mol^{-1} and 192 peripheral hydroxyl groups. [1] Dendrimers were obtained on a large scale with high yields using simple purification steps and under more sustainable reaction conditions [2]. To further expand the scope of CsF for alcohol-induced displacement of imidazolide-activated monomers, a new synthetic approach with emphasis on operational practicality was sought to produce linear polycarbonates. The overall two-step strategy capitalizes on the synthesis and step-growth polymerization of bis-carbonylimidazolide and diol monomers of 1,3- or higher configurations. The methodology serves to complement ring-opening polymerization (ROP) [3] and allows fabrication of a wider range of previously inaccessible functional polycarbonate-based materials with structurally diverse backbones. The bis-carbonylimidazolide monomers can be synthesized as bench-stable white solids, easily obtained on 50-100 g scales from their parent diols using cheap commercial CDI as activating reagent. The polymerization works well in both solution and bulk, does not require any stoichiometric additives or complex setups and produces only imidazole as a relatively low-toxicity by-product. The synthesis enabled the production of a unique library of polycarbonates covering rigid, flexible and reactive polycarbonate backbones, with glass transition temperatures, covering -45 up to 169°C.

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Surface-initiated atom transfer radical polymerization from electrospun mats: An alternative to Nafion

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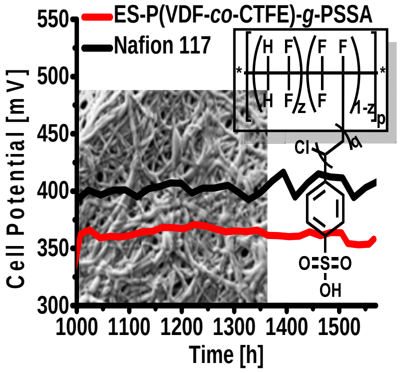
Materials for proton exchange membranes often referred to as polymer electrolyte membranes (PEMs) have been intensively researched for more than half a century. PEMs especially aiming for low temperature fuel cell applications as alternative to mobile or stationary energy conversion devices due to its high efficiency and low emission are of immense interest. Nafion®, the DuPont membranes based on perfluorinated polyether with sulfonic acid groups that are employed in many fuel cells is often considered the market leader. Nafion, however, suffers several drawbacks since it requires high degree of humidification and has low mechanical strength and conductivity at temperatures above 90°C, furthermore it is expensive; thus alternatives with improved properties and performance are still in great demand.

We here present our novel PEMs for fuel cell applications that are synthesized by surface-initiated (SI) atom transfer radical polymerization (ATRP). Poly(vinylidene fluoride-*co*-chlorotrifluoro-ethylene) (P(VDF-*co*-CTFE) is electrospun into a 50 µm thick mat, which is then employed as multifunctional initiator for copper-mediated SI ATRP of 4-styrene sulfonic acid sodium salt. Fine-tuning of the ATRP conditions allows adjustment of the membrane's ion exchange capacity by varying the loading of the grafted ionomer. The structure and composition of the membranes are investigated by spectroscopic means and thermogravimetric analysis, respectively. The membrane morphology is probed by scanning electron microscopy. A membrane with proton conductivity as high as 100 mS cm^{-1} is obtained. A long-term durability study in direct methanol fuel cells is conducted for over 1500 h demonstrating the viability of this novel facile approach. Thus our alternative is simple to produce and have fuel cell performance similar to Nafion.



Long-term durability tests for direct methanol fuel cells: Membrane electrode assemblies with Nafion 117 and electrospun P(VDF-*co*-CTFE)-*g*-PSSA. Current density: 18.6 mA cm^{-2}.

Structural battery electrolytes via reaction induced Ppase-separation: high storage modulus and high ionic conductivity

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Structural batteries has evolved as one possible route to enhance the system performance of Lithium ion (Li-ion) batteries in vehicle applications addressing future demands on more efficient systems.[1,2] The structural battery should have sufficient mechanical performance to allow it to be an integrated part in a device or a vehicle and thus not only contribute with energy storage but also be a part of the structure.[3] Earlier research has shown that carbon fibres can be used as electrodes in Lithium ion (Li-ion) batteries, they have excellent mechanical properties and are electrically conductive moreover they readily intercalate Li-ion's.[4,5] To fully utilize the loadbearing potential of carbon fibres they need to be combined with a suitable matrix (electrolyte), which exhibits both Li-ion conduction and load-transferring. This study focuses on the preparation and characterization of a structural battery electrolyte (SBE) that can be used as a matrix in a structural battery using carbon fibres as electrodes.

A series of phase separated SBE films with varying degree of crosslink-density and liquid electrolyte concentration has been produced. By utilizing Hansen solubility parameters, a system where the monomers and liquid electrolyte are miscible prior to curing was found. During the UV-light initiated polymerization the miscibility of the system changes, the liquid electrolyte is no longer miscible with the growing polymer which induces a phase-separation, creating a two-phased SBE. The crosslinked polymer provides the film with stiffness, while the liquid electrolyte is responsible for transporting Li-ion's. At ambient temperature the ionic conductivity can reach 2,1 x 10^{-4} S cm^{-1} with a corresponding storage modulus of 530 MPa. As a final step, a SBE-carbon fibre lamina half-cell is prepared and cycled against lithium metal for 10 cycles.

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Hydrogels of cellulose nanofibrils and thermoresponsive cationic block copolymers

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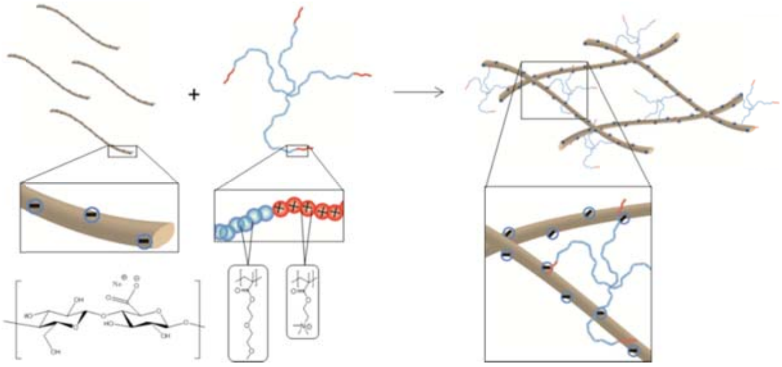

Figure 1 Schematic representation of electrostatic crosslinking of TEMPO oxidized CNF and cationic star block copolymer

Atom transfer radical polymerization (ATRP) has been utilized to synthesize triblock and star-block copolymers of poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA) and quaternized poly(2-(dimethylamino)ethyl methacrylate) (qPDMAEMA). The block copolymers, that all contained a minimum of two cationically charged blocks, were sequentially used for ionic crosslinking to a dilute dispersion of anionic TEMPO-oxidated cellulose nanofibrils (CNF, 0.3 wt%), forming free-standing hydrogels through electrostatic crosslinking, with a storage modulus up to 2.9 kPa. The ability of the block copolymers to adsorb to CNF was confirmed by quartz crystal microbalance with dissipation monitoring (QCM-D) and FT-IR, and the thermoresponsive properties of the hydrogels were investigated by rheological stress and frequency sweep, and gravimetric measurements. [1]

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A new solvent for polyamides and its application in preparation of all-polyamide composite coated fabrics

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Polyamides (PAs) are one of the most important engineering polymers; however, the difficulty in dissolving them hinders their applications. Formic acid (FA) is the most common solvent for PAs which has detrimental effects on the environment and also has industrial limitations.

In this contribution, we proposed a new solvent system for PAs by replacing a portion of FA with urea and calcium chloride (FAUCa). Urea imparts the hydrogen bonding and calcium ion from calcium chloride, as a Lewis acid, was added to the system to compensate the pH decrease because of adding urea. The results showed that the proposed solvent (FAUCa) could readily dissolve PAs and less degradation during dissolution happens. The film prepared by FAUCa has superior properties than the film prepared from FA solution. The solution was applied on a polyamide fabric to make all-polyamide composite coated fabric which then was characterized.

As the FAUCa solution had a lower viscosity than the one prepared from the neat FA solvent, less solvent is required to prepare the same amount of coating material on the fabric which decreases the use of the solvent. In conclusion, using the FAUCa solvent has two merits:

1. replacement of 40% of FA with less harmful and environmentally-friendly chemicals,
2. enabling the preparation of higher concentration solutions, which means less use of solvent.

Lignoboost Kraft lignin in thiol-ene thermoset resins: fractionation, modification, and curing

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Utilizing lignin as a resource for new high value applications puts high demands on the processing of this renewable, aromatic, raw material. Tools to extract technical lignins feasible for different applications are being developed and one such method is the Lignoboost process for Kraft lignin recovery[1]. Further refining by "green" solvent fractionation to obtain more well defined fractions with a significantly more narrow dispersity ($Đ_N$) has been established[2]. One of these is the ethanol soluble fraction which has a molecular weight of about 2000 g/mol and a $Đ_N$ of about 1.9.

Chemical modifications of lignin provide further tools to tailor the properties for different applications. In previous work a model recipe for selective allylation of phenol hydroxyls under benign conditions was developed[3].

Based on the model recipe, selective allylation has been employed on the ethanol soluble fraction of Lignoboost Kraft lignin and used as a thiol-ene thermoset resin constituent. The lignin fractionation and modification was thoroughly characterized using SEC as well as various NMR techniques. The crosslinking of the thiol-ene resin was confirmed by FT-IR and material properties were examined by DSC measurements.

In a presentation the solvent fractionation procedure will be mentioned and argument for the use of selective allylation of the ethanol fraction will be detailed. Furthermore the thiol-ene resin system will be discussed.

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Post-polymerization modification of printable polycation materials

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The effect of post-polymerization modification on the thermal and mechanical properties of crosslinked polycation materials is still a largely unexplored topic. This kind of an approach would be highly useful in inkjet printing, since there would be a need to optimize the printing conditions only for one ink. The printed polymers could then be diversified to many different types of materials using simple reactions to achieve post-polymerizaton modification.

In this study, a family of different polycation materials has been synthesized by modification of cross-linked copolymer films prepared by UV polymerization of commercially available monomers. Afterwards, the materials have been modified by altering their protonation state of the amine groups in the monomers or by covalent attachment of alkyl groups to the amines by quaternization reactions. The effect of counterion on the protonated or quaternized films was also studied.

With this methodology, it is possible to vary the properties of the films from soft and flexible to hard and brittle – all starting from the same original film. A variation of approximately 150 °C in the glass transition temperature could be achieved by modifying the preformed film. Also, the films could be turned from hydrophobic to hydrophilic and back. The thermal decomposition behavior of the films also changed significantly with the modification reactions.

The approach of manipulating the material properties by simple post-polymerization modification will be highly useful in additive manufacturing (3D-printing). It was demonstrated that the materials could be processed by inkjet printing to regular shapes and the printed materials could be modified by similar reactions than the traditionally polymerized films.

The methodology allows the manufacture of very different materials from the same original composition. The properties of the product can be then tuned by the modification reactions after the final shape has been achieved. The method removes the need of optimizing the printing conditions separately for each type of material. The approach will significantly increase the amount of materials available for printing by making it possible to print materials that are not directly printable because of e.g. high viscosity or insolubility.

The influence of reprocessing on the properties of bioplastic materials

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The plastic sector has an important role to play in sustainability to reduce the huge amount of waste produced every year. Biodegradable materials have introduced themselves in many market segments as a real alternative to conventional plastics and since long-lasting bioplastic products are being developed, the study of other disposal options rather than composting such as recycling is required.

Therefore, the aim of this work was to investigate to what extent selected bioplastics can be mechanically recycled without significant loss of their properties. With that purpose, the recycling of film grades of polylactic acid (PLA), polybutyrate adipate terephthalate (PBAT) and a starch based blend (S-blend) was simulated by means of multiple compounding process and the changes on the mechanical properties of the films as well as the thermal, rheological and morphological properties of the blends were analysed. PLA 2003D was obtained from Natureworks LLC (USA), Ecoflex F C1200 from BASF GmbH (Germany) and Mater-Bi EF05S from Novamont GmbH (Italy). The behaviour of these bioplastics was compared to that of a conventional low density polyethylene (LDPE) FA7220 grade for film applications, obtained from Borealis AG (Austria).

We found that viscosity of PLA and PBAT (Figure 1) show a significant reduction with increasing number of processing steps, probably due to chain length reduction of the polyesters. However mechanical properties are not significantly affected due to reprocessing. The viscosity of the S-blend increases slightly; however it shows the highest reduction of mechanical properties, especially after the first reprocessing cycle. In the case of LDPE, mechanical and rheological properties stay constant over the complete recycling simulation. In conclusion we found that reprocessing has some influences on the properties of the bioplastics, although these influences are limited, which would allow their reuse for various applications. However future investigations should focus on the possibility of upcycling bioplastics via reprocessing route and additivation, i.e. using these materials in applications similar as virgin polymers due to their then uninfluenced properties.

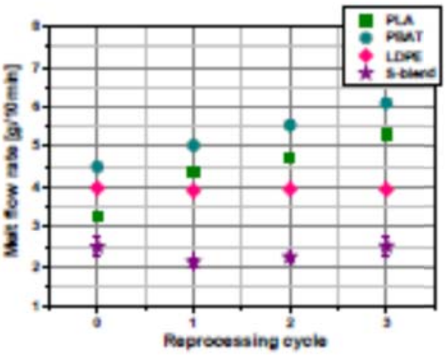

Figure 1: melt flow rate vs reprocessing cycle

Flow-assisted assembly of nanostructured protein microfibers

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Proteins are Nature's own high-performance materials providing both extraordinary mechanical properties (e.g. muscles, silks) and sophisticated functionality (e.g. adhesion, biological signaling). These materials have served as inspiration for man-made structures for long time but the challenge to produce synthetic materials with comparable properties from biobased resources remains. The key to achieve this is to gain control over the assembly of hierarchical structures from the biomolecular building blocks. Protein nanofibrils have emerged as a promising foundation for the synthesis of novel bio-based materials for a variety of applications. Such nanofibrils are formed through self-assembly and have mechanical properties comparable to silk. Here we demonstrate that micrometer sized protein fibers can be created from protein nanofibrils using a simple microfluidics setup without the addition of plasticizers or crosslinkers. Furthermore, we are able to connect the nanoscale morphology of the fibrils with the mechanical properties of the obtained fiber and we find that the strongest fiber is obtained with a sufficient balance between ordered nanostructure and fibril entanglement. The results reveal essential parameters associated with the formation of protein fibers and provide new insights about the assembly processes of hierarchical protein materials.

Reference

Kamada *et al.* (2017) Flow-assisted assembly of nanostructured protein microfibers. *Proc. Natl. Acad. Sci. USA,* 114: 1232–1237.

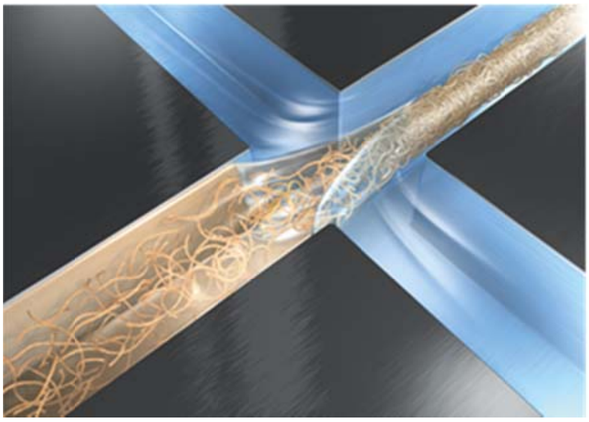

Illustration of the assembly of protein nanofibrils by micro-fluidics.
(DESY/Eberhard Reimann)

Melt spun PVDF fibres towards textile electronics

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We present a variety of melt spun textile electronics fibres fabricated from poly(vinylidene fluoride) (PVDF). Depending on the processing parameters and textile architectures the fibres can function as piezoelectric sensors, thermally activated actuators or piezoelectric energy harvesting fabrics.

Piezoelectric yarns can be fabricated through melt-spinning of PVDF into fibres with a core/sheath configuration. The core is a composite of 10% carbon black in polyethylene, and serves as the inner electrode. A single yarn can generate an output of several volts at less than 1% strain, and functions as a sensor e.g. for footsteps integrated into a sock, as well as for heartbeats when placed close to the chest. The presence of polar β phase crystals, and thereby the piezoelectric effect of PVDF, can be further enhanced by adding minute amounts of carbon nanotubes.

Further, we have fabricated woven straps where the piezoelectric yarn is combined with a variety of electrically conducting yarns constituting the outer electrode. This textile was used as a shoulder strap attached to a laptop case, and permits to scavenge energy during walking using a standard energy harvesting circuit.

The thermal stability and high mechanical properties of PVDF also makes it appropriate for use as a thermally activated actuator, where the actuating effect is due to the reversible fibre-direction negative thermal expansion of highly oriented tie molecules. This effect was studied both experimentally and by computational modelling.

Click-chemistry crosslinking of an ethylene-glycidyl methacrylate copolymer

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Polyethylene constitute the most widely used family of commodity polymers. For electrical and medical applications, were a particularly clean material is required, low density polyethylene (LDPE) typically is the material of choice because it can be polymerized at high pressures without the need for catalysts. LDPE however must be crosslinked in order to ensure dimensional stability at high temperatures and to prevent stress cracking,[1] and to improve the resistance towards chemicals.[2] Peroxide crosslinking is the most common process, but results in unwanted by-products that must be removed,[3] which is typically achieved by degassing for an extended period of time at elevated temperature; however, degassing of thick XLPE architectures is both time and energy consuming.[4] Moreover, peroxide products and their decomposition by-products pose a considerable health hazard. These problems related to peroxide crosslinking drive the research toward alternative crosslinking concepts for polyethylene. One attractive alternative is crosslinking with the help of epoxy functional groups.[5-7] In order to convert epoxy resins into solid, infusible thermoset networks it is necessary to use crosslinking agents. Nucleophilic substitutions on small tensioned rings like epoxides are a well-known class of click-chemistry reactions that involve one step and release no byproducts. Epoxy-opening click chemistry reactions occur in one-pot, generating no or minimal and inoffensive by-products.

In this work we studied the use of different crosslinking agents in combination with a polyethylene-glycidyl methacrylate copolymer (PE-stat-GMA), demonstrating that efficient network formation without the formation of undesirable by-products is possible.

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Photo-curable resins modified with in situ generated silver nanoparticles for stereolithography

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Three-dimensional printing (3DP) has drawn tremendous attention from both academia and industry with its potential applications in various fields. The integration of nanotechnology into 3DP offers new opportunities for the manufacturing of 3D engineered materials exhibiting optimized properties and multifunctionality. In fact, the incorporation of nanomaterials, such as metal and oxide nanoparticles, into 3DP can result in improved functional and structural properties of the manufactured device [2-3]. 3D printing of nanocomposites usually concerns the mixing of ex situ synthetized nanoparticles in a commercially available acrylated monomer, followed by the proper printing process. Nevertheless, in all the cases, the addition of nanofillers strongly affects the printing process: solution viscosity, light penetration depth and nanoparticles dispersion and stability [4-5].

In this work, a novel approach for the preparation of 3D nanocomposites by means of stereolithography (SLA) is proposed: the simultaneous photo-reduction of metal precursors (silver acetate) with the photo-polymerization of the acrylated monomer mixture to form a nanocomposite using the SLA technology, is presented and discussed. The focused ultraviolet laser beam of the printer is used to locally photo-induce the reduction of silver cations, generating silver nanoparticles (AgNPs), and at the same time photo-polymerize the acrylated monomers, by means of the homolytic photo-cleavage of the photoinitiator [6].

The SLA printing process is used to produce 3D-printed specimens, tested for thermo-mechanical characterization (dynamic-mechanical and tensile analysis). Structure of AgNPs and microstructure of Ag nanocomposites are analysed respectively using X-ray diffraction and transmission electron microscopy. The antimicrobial and cytotoxicity tests are also performed to verify the presence of these functional properties due to AgNPs.

The result of this study shall provide a new way of developing a product for biomedical use as well as providing further rapid prototyping option to research and development.

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Morphology control in polymer blend thin films for solar cells

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Morphology control has been one major key to the recent improvements in energy conversion efficiency of polymer-based bulk heterojunction solar cells. The distribution of the electron-donor polymer and the fullerene-based electron-acceptor material, PCBM, has strong effect on the charge generation and transport processes in the solar cell. The nanostructure in the solution-cast thin film is influenced by the polymer-fullerene-solvent interactions, the molecules' tendency to self-organise, and the kinetics of the film formation. During spincoating, characterized by rapid solvent evaporation, the kinetics of nucleation and of liquid-liquid phase separation compete. The formation of vertical concentration gradients has been reported for several blend systems. Characterization of the composition and molecular orientation at the interfaces is a major challenge, because very few techniques exhibit both the chemical contrast and the lateral or depth resolution required to unveil the nanostructure of these bulk heterojunctions.

We have used a combination of Atomic Force Microscopy (AFM), dynamic Secondary Ion Mass Spectrometry (d-SIMS), Near-Edge Absorption Fine Structure (NEXAFS) spectroscopy and Scanning Transmission X-ray Microscopy (STXM), to probe the surface and bulk composition of polymer:fullerene blends. To rationalize the lateral and vertical phase separation, we use Flory-Huggins interaction parameters, surface energies, and solvent properties. The organisation of molecules gives us new insights on morphology-performance relations in polymer-based solar cells.

From forest residues to green packaging

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The extraction of biomass from forests to produce paper, furniture and energy generates large amounts of forest residues (branches, tops, bark and un-merchantable wood). These logging residues are often subjected to controlled burning or are left in large piles, causing a negative environmental impact and risks of pests and fire[1]. The use of forest biomass residues to produce environmentally friendly materials constitutes an attractive waste management solution from a biorefinery perspective, contributing to a sustainable future economy. Residual biomass has many significant advantages over fossil resources, such as renewability, sustainability, biodegradability, low cost, lower impact on global warming and non-dangerous emissions during processing, storage and disposal[2]. Nevertheless, interest in using forest residues for polymeric material applications is relatively recent. In this study, the potential of three different logging residues (woody chips, branches and pine needles from softwood) were assessed to be used as raw materials to isolate cellulose nanocrystals (CNCs) for designing sustainable composites for packaging applications. The forest residues were critically evaluated in terms of structure, chemical composition and thermal properties[3]. Woody chips showed the highest carbohydrate content but a lower proportion of hemicelluloses/pectins than branches and pine needles. The higher cellulose content of woody chips rendered a more crystalline and thermal stable biomass. However, the cellulose from pine needles was more crystalline than the cellulose in the branches and woody chips. Therefore, specific cellulosic fibres with different structure and morphology were possible to extract from the different forest residues. All the extracted fibres provided a suitable raw cellulosic material for the isolation of CNCs, reaching higher yields than those found from microcrystalline Norway spruce cellulose. The physico-chemical properties of this residual biomass during conversion from macro- to nano-dimensions were studied together with their capacity of using the resulting CNCs as reinforcements in nanocomposites[4]. The high aspect ratio and crystallinity along with the good thermal stability of the isolated CNCs from logging residues correlated well with their chemical composition, showing great possibilities to be used as reinforcing agents in composites and target specific properties. The reinforcing capability of forest residue CNCs in polysaccharides-based biocomposites was also studied with different matrixes (arabinoxylan and pectin)[5,6], showing good thermo-mechanical performances, high oxygen-barrier properties and therefore a great potential to be used in packaging applications.

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First-principle simulations of electronic structure in semicrystalline polyethylene

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In order to increase our fundamental knowledge about high-voltage cable insulation materials, realistic polyethylene (PE) structures, generated with a novel molecular modeling strategy, have been analyzed using first principle electronic structure simulations. The PE structures were constructed by first generating atomistic PE configurations with an off-lattice Monte Carlo method and then equilibrating the structures at the desired temperature and pressure using molecular dynamics simulations. Semicrystalline, fully crystalline and fully amorphous PE, in some cases including crosslinks and short-chain branches, were analyzed. The modeled PE had a structure in agreement with established experimental data. Linear-scaling density functional theory (LS-DFT) was used to examine the electronic structure (e.g. spatial distribution of molecular orbitals, band gaps and mobility edges) on all the materials, whereas conventional DFT was used to validate the LS-DFT results on small systems. When hybrid functionals were used, the simulated band gaps were close to the experimental values. The localization of valence and conduction band states was demonstrated. The localized states in the conduction band were primarily found in the free volume (result of gauche conformations) present in the amorphous regions. For branched and crosslinked structures, the localized electronic states closest to the valence band edge were positioned at branches and crosslinks, respectively. At 0 K, the activation energy for transport was lower for holes than electrons. However, at room temperature, the effective activation energy was very low (~0.1 eV) for both holes and electrons, which indicates that the mobility will be relatively high even below the mobility edges and suggests that charge carriers can be hot carriers above the mobility edges in the presence of a high electrical field.

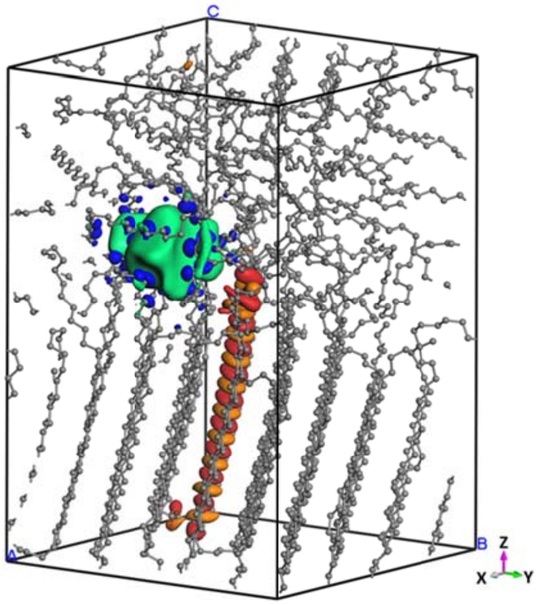

Figure 1. Simulated semicrystalline PE after MD equilibration. HOMO/LUMO orbitals are illustrated with red-orange/blue-green colors.

One-pot enzyme-catalyzed synthesis of dual-functional polyester macromers towards surface active hydrophobic films

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Introduction

Today biomass such as bark from the forest industry is regarded as a low value waste and is mainly used as heat production. It has earlier been shown that birch bark contains an interesting epoxide functional building blocks e.g. *cis*-9, 10-epoxy-18-hydroxyoctadecanoic acid (EFA) [1, 2]. EFA can be extracted from birch bark by alkaline hydrolysis and can further be used for thermoset applications [2]. In addition, it has earlier been shown that EFA can undergo enzyme catalyzed esterification reactions to create a homopolymer keeping the epoxy group still intact [3]. Such procedure creates an opportunity to introduce interesting functionalities such as thiols to EFA and keeping the epoxy group intact

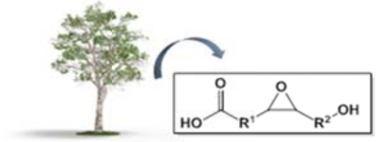

Figure 1: Epoxy fatty acid found in outer birch bark, $R_1 = 7$ and $R_2 = 8$.

Results

In the present study a thiol-epoxy functional polyester resin was synthesized from partly bio-based monomers via enzyme catalysis. Furthermore, the epoxide functional was selectively reacted by cationic polymerization forming a thiol-functional crosslinked film. The resin had reasonable curing rates. In addition it was possible to modify the surface of the film by reacting the thiol group with a desired molecule.

Figure 2: The synthesized thiol-epoxy functional polyester resin and curing to a functional network

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Hemicellulose as a green binder for wood adhesives

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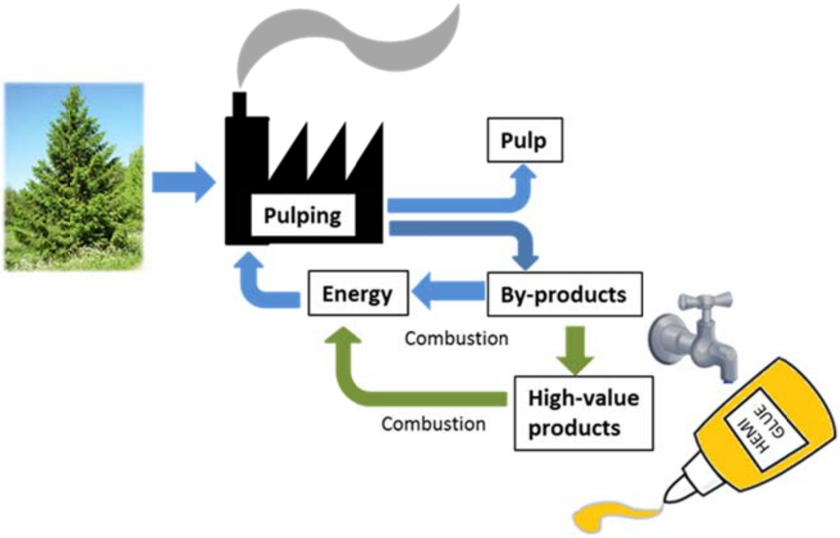
Wood adhesives of today perform very well and are inexpensive. However, most of them are prepared from fossil resources that are both limited and non-renewable. Some of these adhesives contain hazardous chemicals e.g. formaldehyde that have a negative impact on the environment and human health. With the increasing environmental concern it is necessary to decrease the use of fossil resources by using environment-friendly and biobased alternatives instead. To enable a transition for wood adhesives, the biobased alternative has to possess properties comparable to the adhesives used today. The adhesive must have sufficient bond strength, water resistance and heat resistance. Proteins, lignins and tannins are some examples of biobased polymers that have been investigated for wood-adhesive applications. However, it has proven difficult to find a biobased alternative that fulfill all requirements and can compete in terms of cost. Inspired by the idea to use the tree's own building blocks and by surprisingly good results from our previous studies on other types of polysaccharides, we are investigating wood hemicelluloses. In the pulp industry, hemicellulose is usually removed and combusted for steam production. According to the biorefinery concept, high value applications such as industrial chemicals or materials are more desirable. Water dispersions of hemicelluloses have been prepared and evaluated as adhesives. However, hemicellulose cannot be used as a wood adhesive by itself, due to its limited bonding performance, especially regarding the water resistance. To enhance the bonding performance, the addition of different additives and the variation of different preparation- and application methods have been evaluated. Several of the hemicellulose dispersions in our study demonstrate surprisingly good properties in terms of bond strength, water resistance and heat resistance and can compete with commercially available wood adhesives.



Pedagogical aspects of teaching: Continuous assessment of learning at Aalto CHEM

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Teaching and especially learning are in focus when it comes to development of university education. Assessment clearly guides students' learning. One way to guide learning towards deeper learning is to apply so called continuous assessment in form of learning assignments that are due throughout the course instead of conventional practice of having an exam in the end of the course. Continuous assessment can help students to define the levels of understanding required and it enhances high-level engagement in guiding students form memorizing and describing towards explaining, relating and applying.

The value of continuous assessment is the enhancing of deep learning when students are actively involved during the whole course, which is also appreciated in the students' feedback. Another benefit is that learning is divided into smaller parts and it takes place evenly during the whole course instead of concentrating on the assessment period. Furthermore, this way of assessment provides the teacher feedback of students' learning throughout the course and the difficult issues can be reviewed if needed.

Challenges in continuous assessment deal with creating meaningful exercises, keeping the workload of the teachers reasonable and ensuring coherency in assessment if various teachers are involved. Individual tasks and feedback is the optimal case but the available teaching resources have to be ensured. Essays were observed to be suitable for courses with limited number of students to ensure constructive feedback whereas automatically corrected quizzes were better for larger courses.

In this presentation, three case studies are introduced which describe the application of continuous assessment. The aim was to find out how to engage students to work continuously during the course to result in deep learning and how to manage the workload of both teachers and students to support high quality in learning. Based on our observations we think that continuous assessment helps the students to direct their activities in deeper learning. In addition, we think that continuous assessment gives us tools to guide the students to constructively align their learning by providing them an active role in their learning process.

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Self-organization of Poly(2-isopropyl-2-oxazoline)-block-Poly(lactide)

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Poly(2-isopropyl-2-oxazoline)-block-poly(lactide) (PiPOx-b-PLA) block copolymers (BCPs) are interesting from fundamental and biomedical viewpoints.
In solid state, organization of the BCPs is driven by crystallization of at least one of the blocks. The observed thermal transitions depend on the molecular weights of the constituting blocks and the stereo-chemistry of PLA. PiPOx and PLA influence each other's ability to crystallize resulting in varying morphologies after isothermal crystallization.

Aqueous self-assembly of PiPOx-b-PLA is driven by the hydrophobicity of PLA. Micelles with either amorphous PDLLA or semi-crystalline PLLA core and PiPOx corona were studied by scattering techniques. PiPOx is a thermo-responsive LCST-type polymer which can crystallize in heated, phase-separated aqueous solutions. This irreversible transition is unique to PiPOx and an additional handle to engineer polymeric nanoparticles.

In order to clearly relate the properties of PiPOx and PLA in the block copolymers to their parent homopolymers the synthesis is based on conjugation by click-chemistry. This allows us to study all homopolymers, their blends and BCPs.

Hemicelluloses from wheat bran: Valuable biopolymers for the design of multifunctional materials and additives

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Wheat bran is a major by-product of cereal production that still has limited use for advanced nutritional and material applications. Arabinoxylans (AXs) are the most abundant hemicellulose in cereals, consisting of a backbone of (1→4)-linked β-D-Xylp units, substituted by α-L-Araf in O−2 and/or O-3 positions to different extents and intramolecular distributions, depending on the biological source and tissue. The L-Araf residues can be further substituted by phenolic acids (e.g. ferulic acid), which can dimerise creating a complex covalently crosslinked supramolecular architecture. The molecular heterogeneity of the native biopolymers and the crosslinked nature of such cereal tissues have great impact on the extractability of these hemicelluloses and on their macroscopic properties (e.g. rheological and mechanical properties).

A sequential process using subcritical water, membrane filtration and selective enzymatic treatments has been designed for the combined fractionation of functional high molar mass hemicelluloses (over 105 g mol−1) and oligosaccharides from wheat bran. This process not only offers increased total solid yield compared with conventional protocols based on alkaline extraction, but it also preserves the inherent functionalities of the phenolic groups that substitute the carbohydrate structures of the extracted hemicelluloses. The extractability of different wheat bran polysaccharide components is influenced by their molecular structures, which enables the isolation of hemicellulose fractions with specific structure by tuning the temperature, time and pH conditions of hydrothermal treatment. Feruloylated arabinoxylans (F-AX) with high molar mass and significant radical scavenging activity can be isolated from the subcritical water extract. Structurally different oligosaccharides, including mixed-linkage β-D-glucan oligosaccharides (BGOs) and arabinoxylo-oligosaccharides (AXOs) can be recovered from the eluent after membrane filtration. The crosslinked residue after subcritical water extraction was further treated with xylanolytic enzymes to release valuable feruloylated arabinoxylo-oligosaccharides (FAXOs). The oligo- and polysaccharide fractions isolated from this sequential process show great potential for use in food and biomedical applications as prebiotic or platform chemicals, and as polymeric matrices for carbohydrate-based materials with radical scavenging properties, respectively.

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Dyed cellulose nanofibril coating as paint

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Wood based cellulose is the largest cellulose source on earth, and it has been used in paper and board manufacturing over the last two millennia. Cellulose microfibrils can be liberated as micro- and nanofibrils from various plant fibers using mechanical-, chemical- or enzymatic treatment, or combinations thereof. The most typical mechanical methods include homogenization, microfluidization, microgrinding or cryocrushing. After fibrillation, the width of the micro/nanofibrils is typically between 5 to 20 nm and the length ranges in several micrometers. Micro/nanofibrils have inherent affinity to wood and also to various small scale particles such as color pigments. This property has been exploited to create a colored coating on wood surfaces using only nanocellulose as binder, to create an interior design element called "Rag Rug".

Cellulose nanofibrils have different affinity and surface chemistry depending on the fibre origin and processing method. Micro/nanofibrils can easily be dyed for visual effects. Films and structures made from nanofibrils in general have comparable tensile strength to that of aluminium, although the surface appearance is paper-like. In addition, the films and structures are also completely recyclable. Micro/nanofibril paint can be washed away from surfaces using water. The CNF based paint has a solids content between 10-15%, and the drying time is comparable to conventional water based paints.

Micro/nanofibril coating as paint may provide for interior decoration a new eco-friendly option for surface coating and treatment. Non-permanent markings that are easily removed using water spray and cloth e.g in construction, stencils, temporary protection during transport or dressing paint could apply the technology. The technology will be developed further to provide enhanced wear and water tolerance.

UV-Cured graphene-polymer nanocomposites
(Times New Roman, 14pt, bold, centered)

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The preparation of electrically conductive acrylic and epoxy resins containing reduced graphene oxide (rGOx) by photopolymerization is presented. The synthesis consists of a single-step procedure starting from a homogeneous dispersion of GOx into a UV-curable monomer, which undergoes reduction induced by the UV radiation during UV-curing of the photocurable formulation. The role played by the amount of photoinitiator added to the resin has been evaluated in relation to the in-situ reduction of GOx, that was monitored by X-rays photoelectron spectroscopy (XPS). Epoxy nanostructured coatings with enhanced viscoelastic and electrical conductive properties were achieved [1].

In radical photopolymerization results show that the UV-induced photopolymerization of acrylic resins containing GOx gives rise to conductive materials, thanks to the simultaneous reduction of GOx to rGOx and crosslinking of the resin [2,3].

On this basis UV-induced photopolymerization is proposed as a sustainable strategy for the production of conductive graphene/polymer composites or conductive inks. Printed samples of the nanocomposite material were obtained by inkjet direct printing through a commercial piezoelectric micro-fabrication device [4]. Printed samples of the nanocomposite material showed a decrease of resistivity with respect to the polymeric matrix.

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Effect of particle size and size distribution on the permeability of soft magnetic liquid silicone rubber

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In this work polymer bonded soft magnetic composites (PBSMC) of liquid silicone rubber and the nanocrystalline alloy Vitroperm 250F were investigated to reveal the quantitative effect of particle size and size distribution on the magnetic permeability of the composite. Originating from solid tape wound cores different size fractions of the magnetic filler were prepared by milling and sieving. The actual particle size was determined using a video microscope and image processing software. A simple model proposed by Schubert et al. was used to describe the magnetic permeability of toroidal PBSMC cores as function of the degree of filler requiring only one adjustable parameter k [1]. At a constant degree of filling a correlation was found between the size of the particles d and the parameter k. By mixing fractions of small and large particles suggestions were made for the mathematical form of a governing mean, taking into account the particle size distribution ni.

$$\langle d \rangle_{\lambda} = \left(\frac{\sum_i n_i \cdot d_i^{\lambda}}{\sum_i n_i} \right)^{1/\lambda}$$

The obtained mean shows self-consistent behaviour and holds for different mixtures. Therefore the simple one-parameter-model can be modified to predict the permeability of PBSMC from the particle size distribution and the degree of filling.

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Synthesis, properties and modification of novel allyl ether and amide substituted cellulosic fibres and membranes

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Several strategies were used to modify cellulose. For example, cellulose was first either TEMPO oxidized or hydroxypropylated or used as is. Cellulose or hydroxypropylated cellulose was modified in alkaline aqueous *tert*-butanol (tBuOH) using allyl glycidyl ether (AGE). Degree of substitutions for modified celluloses were varied typically in the range of DS_{allyl} 0.02-0.20. TEMPO oxidized cellulose was converted to allyl amide derivative.

The obtained alkylated cellulose samples can be dissolved in sodium zincate (6.5 wt% NaOH with 1.3 wt% ZnO) or in ionic liquid (IL) like [emim][OAc], 1-ethyl-3-methylimidazolium acetate for fibre spinning or membrane preparation processes. The results showed that the substitution clearly improves the solubility of modified celluloses in the NaOH/ZnO system up to 7-8 wt% compared to unmodified cellulose with 5.8 wt% solutions. The solubility in the IL was even up to 10-15 wt%.

The membranes were prepared first by casting a thin layer (250 µm) of 9 wt% cellulose IL solution onto a glass plate and then by regenerating to a membrane in aqueous coagulation bath.

The allyl group of cellulose derivatives as fibres or membranes can be used further for crosslinking and/or grafting reactions or also for so-called thiol-ene “click” chemistry to adjust the final properties of fibrous or membrane materials. For example, water-soluble hydroxypropylated (DS_{HP} 0.8) and allylated (DS_{allyl} 0.2) cellulose reacted very efficiently and fast in 5 min and quantitatively with the thiol group of amino acid cysteine in mild aqueous reaction conditions.

Synthesis of clickable, thermoresponsive PVCL-based microgel particles and conjugation via click chemistry

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Poly(N-vinylcaprolactam) is a thermoresponsive, biocompatible polymer and as such promising template for the biomedical field. [1,2]

Here, clickable PVCL-based hydrogel particles were made via precipitation polymerization in buffered water. Propargyl acrylate was used as comonomer to introduce alkyne moieties to the particles. The alkyne moieties where used in a click reaction *i.e* copper-catalyzed azide-alkyne cycloaddition, to decorate the particles.

PVCL particles were decorated with gold nanoparticles bearing azide containing ligands. The resulting particles were thermo- and light responsive. This represented an approach to use click chemistry to introduce new stimuli-responsiveness to the gel particles.

In another approach click chemistry was used to introduce new functionality to the particles for interactions with biomolecules. 4 different sugar-azides were attached to PVCL-based gel particles. Titration studies with sugar binding protein, concanavalin A, showed the sugar moieties being available for protein binding.

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‘Sponge-like’ cellulose-pulp foams

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Foams are an important, versatile and widely-utilised class of materials. Common or ‘traditional’ application include lightweight packaging, building and construction materials, consumer goods, damping materials and various forms insulation. In addition to these aforementioned uses/products, research interest towards functional applications, including oil/water separation, catalyst support, sensors and energy storage is steadily growing (1). Therefore, there is a great need for developing foams and foam-like structures (such as aerogels) from alternative and non-conventional materials; this has especially been encouraged through increased environmental consciousness. Thus, new classes of ‘green’ foams and aerogels are gradually being developed and optimised (2).

Lignocellulosic derivatives are one of the most popular alternative source materials in foam and aerogel preparation. In particular, nanocellulose derivatives have become a commonly-utilised reinforcing material and/or building block (matrix) in foam/aerogel preparation. This interest is encouraged by the extensive list of favourable properties; renewability, nano-dimensions and high aspect, web-like network structure, low percolation threshold, high stiffness and strength and a low coefficient of thermal expansion (3).

Previously (4), enzymatically-fibrillated cellulose pulp (EFP) was compounded with poly (vinyl alcohol) (PVA) and glutaraldehyde (GA) to yield spinning dopes for filament preparation. In addition to their originally-intended purpose, the spinning dopes were observed to form stable and rigid foam-like structures following exposure to vacuum and removal of water. Due to the covalent (permanent) nature of the glutaraldehyde crosslinks throughout the PVA network, water stability could also be imparted into the materials Herein, the preparation and characterisation of these foams is presented. Lightweight, low-density foams containing ≥ 50 %·wt EFP possessed high strength and rigidity, while also being stable in water. One additional feature was the ‘sponge-like’ behaviour of the foams, repeatedly being able to absorb and expel water.

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Direct alginate fractionation by cyclic algal extractions

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The fast growing brown algae *Saccharina latissima* is cultivated at the Swedish west coast [1], a specie rich in the viscous polyelectrolyte alginate. To facilitate better utilization of the harvest, we have developed a new process for alginate extraction in which the extraction solution is regenerated with ion exchange resins and cycled back to the biomass [2].

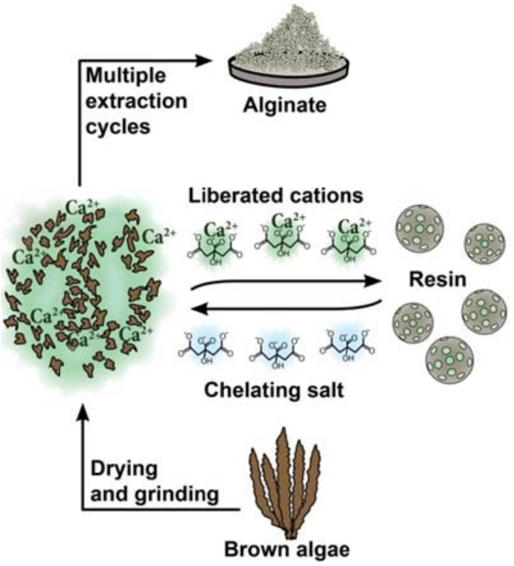

Fig. 2. Schematic route to alginate liberation from brown algae *Saccharina latissima.*.

The procedure was developed to be liquid conservative and alginate was stripped of continuously to circumvent the problem of a high viscosity build-up. A gradual destabilization of the alginate based cell wall was achieved by removal of structurally important polyvalent cations, mainly calcium (Fig. 1). A chelating salt operating at neutral pH was used for the cation liberation to enable several consecutive alginate extractions without product degradation [3].

The multistep extractions with a steady decrease of polyvalent cations lead to complex yield patterns (Fig. 2) indicating that alginate was fractionated based on its ion affinity. When analyzing the fractions along the course of the extraction this property selective fractionation was observed as a significant increase in guluronic acid content and molecular weight. To also display the concurrent non-alginate fractionation, the residues after completed extraction were analyzed for their carbohydrate compositions, revealing rich sources of mannitol, the β-glucan laminarin and cellulose completely free of lignin.

The direct alginate fractionation of algal biomass like that of *Saccharina latissima* would increase product control and simplify tailoring of alginate properties such as viscosity and calcium alginate gel strength.

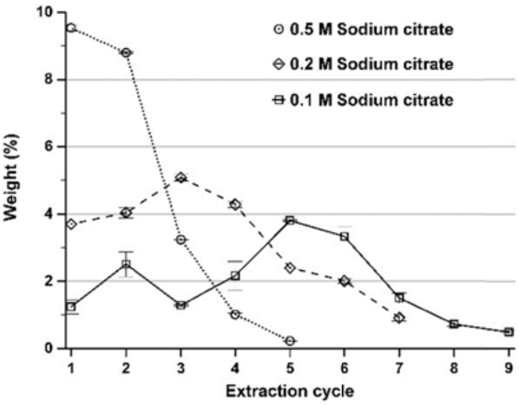

Fig. 3. Alginate yield from cyclic extractions assisted by different concentrations of chelating salt.

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Integration of sustainable development in education at KTH

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As part of a strategic initiative at KTH on enhancing focus on environment and sustainable development (ESD), a university-wide project on "Integration of ESD in the educational programs at KTH" was initiated in 2012. To assure the continuous work with integration of sustainability in all educational programs, the project has focused on two complementary strategies: evaluation of the programmes' efforts and providing tools and support for all Program directors and teaching staff to achieve the set goals. The evaluation process was conducted in several steps, from schools' self-assessment of the fulfillment of the learning outcomes on ESD stated in the Swedish Higher Education Ordinance, to set-up of action plans (by all schools) on how to develop and integrate the objectives on ESD in all educational programmes, and finally a follow-up of the programmes' progress within the area. To support the process, several tools and inspirational activities were conducted.

This presentation will focus on the process of integration of ESD in the educational programmes at KTH and the tools that were provided to support the Program directors and teaching staff during the process. Some examples on course activities will also be addressed.

Extraction of hemicelluloses from rapeseed straw for renewable plastic film

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A more efficient utilization of bio-based resources is needed to meet the sustainability demand of the future. One such biobased resource is rapeseed straw - an agricultural residue with little to no utilization except burning. The straw contains valuable biopolymers such as the hemicelluloses xylan and glucomannan. Hemicelluloses with high molecular weight were extracted from rapeseed straw by hydrothermal extraction and with the purpose to obtain a bio-based raw material for material production.

The extraction method was purposely designed to be industrially viable and extensive purification steps were avoided. The extraction of the hemicelluloses is a first step in a full scale biorefinery approach on rapeseed straw. The influence of extraction conditions, such as time, temperature and extraction medium, on the extracted hemicelluloses composition, molecular weight and mass flow was analyzed. Three kinds of extraction mediums were used to extract hemicelluloses, water, acid and alkali. Water and acidic extraction yielded an extract rich in glucomannan and some co-extracted lignin. The acidic extracted glucomannan was more degraded compared with the water extracted glucomannan. Extraction with water at high temperature resulted in xylan co-extracted with glucomannan in nearly equal quantities. Alkaline extraction medium yielded mostly an extract rich in xylan and co-extracted lignin. The straw was not fully delignified and the cellulose fibres were not liberated during the extraction process.

Extracted xylan and glucomannan were used to make renewable plastic films. The glucomannan films were very fragile. The xylan films on the other hand demonstrated remarkable strain-at-break values of 70 – 90% without any added plasticizer.

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Versatile renewable sobrerol-based polymers for material applications

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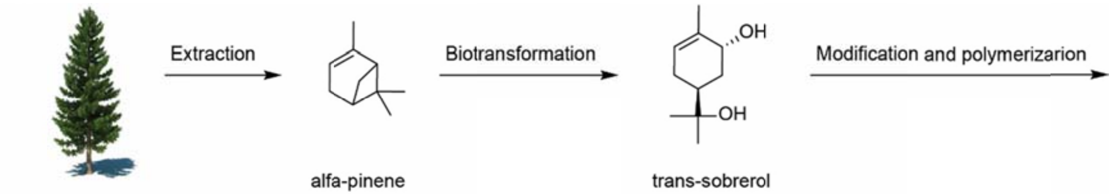
In order to reduce the need for fossil fuel chemicals, a lot of attention in modern chemical research goes in finding novel applications for renewable and biobased compounds from various sources. Using wood as the source primarily gives cellulose and lignin, for which many applications have been found in recent decades. One rather underutilized group of compounds from wooden sources, however, are terpenes.

Although several terpenes have found applications as, e.g., fragrances there are plenty more available with great potential in different fields. One such terpene is sobrerol, an unsaturated cyclic diol. Sobrerol has shown antimucotic properties[1] and prevents pulmonary hypertension[2] and development of breast cancer[3], but is yet to be used in material applications despite its versatile functional groups. As sobrerol is biotransformed from α pinene[4], the major compound of turpentine, it has great potential in future green materials.



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Influence of deep eutectic solvent composed of choline chloride and urea on wood based cellulose fibres

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Deep eutectic solvents (DESs) composed composed of choline chloride and urea has gained recently a lot of attention been and it has been successfully used in different cellulosic applications (Abbott et al. 2006, Sirviö et al. 2015, Suopajärvi et al. 2017, Park et al. 2013, Wang et al. 2015, Tenhunen et al. 2016, Xu et al. 2016). This mixture has been found suitable for e.g. facilitating the nanocellulose production and for textile fibre spinning directly from wood pulp (Sirviö et al. 2015, Tenhunen et al. 2016). Despite the suitability the mixtures of choline chloride and urea does not dissolve cellulose or alter the crystalline structure.

In this work, we clarify the influence of such solvent system on the structure and chemical composition of the wood based cellulose fibres before and after soaking fibres for 16 hours in DES at 100°C. We investigated changes in morphology (SEM, AFM) the dissolution of other wood fibre components (Carbohydrate analysis) or reactions with DES components (elemental composition) The detailed structural characterisation of the fibres was carried out using spectroscopic methods which include X-Ray Photoelectron Spectroscopy (XPS), solid state Nuclear Magnetic Resonance (^{13}CP/MAS NMR) and Raman Spectroscopy. Methylene blue adsorption was done in order to investigate changes in charge due to DES treatment. This work can be considered relevant in order to efficiently utilize DES solvent system for cellulosic materials.

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Imaging friction forces on stiff and soft materials with Intermodulation Friction Force Microscopy

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We present a technique [1] for measuring the velocity-dependence of frictional forces on a single asperity (an AFM tip) reaching velocities up to several cm/s. The method is based on the measurement and analysis of intermodulation products, or frequency mixing of multiple drive tones near a high Q torsional resonance, which arise from the nonlinear frictional force. The method gives the oscillation amplitude dependence of both conservative and dissipative dynamic force quadratures, revealing a transition between stick-slip and smooth sliding that is characteristic of friction at high speeds. We can explain the measurements on graphite with a modified Prandtl-Tomlinson model that accounts for the viscous and elastic nature of the asperity. On a soft PS-LDPE polymer blend sample the force quadrature curves look qualitatively similar to graphite, but the friction shows hysteresis. We explain the origins of the hysteresis with a simple model where the relaxation of the viscoelastic surface is taken into account. With its high force sensitivity for small sliding amplitude, our method enables rapid and detailed surface mapping of the full velocity-dependence of frictional forces to sub 10 nm spatial resolution.

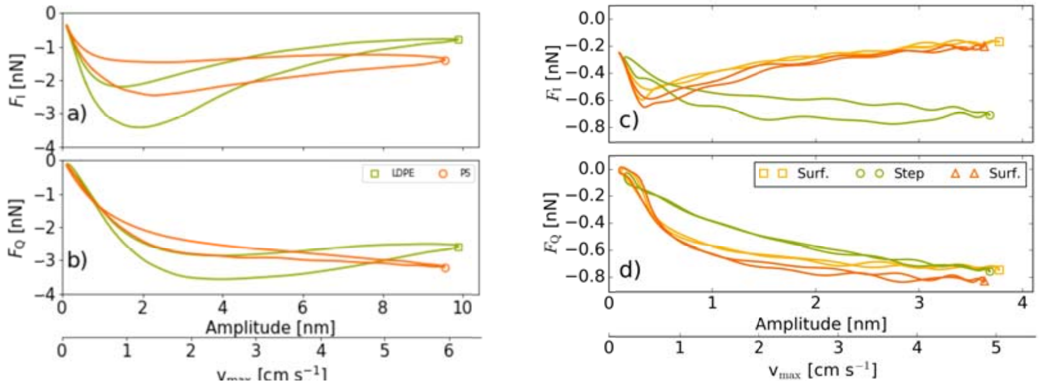

Figure: a) and b) show the force curves on the PS- and LDPE-areas of a PS-LDPE polymere blend. The presence of hysteresis on the soft polymeres suggests surface dynamics. c) and d) show the force quadrature curves on a graphite sample [1].

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Cellulose spheres grafted through ring opening polymerisation for use as probes for contact adhesion measurements

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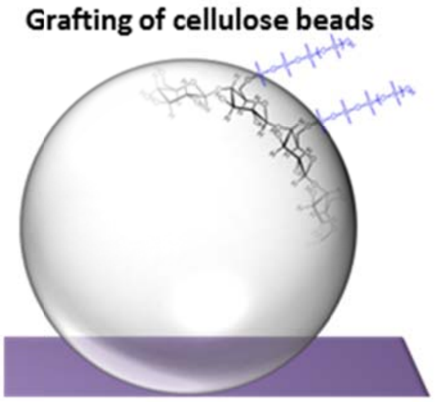
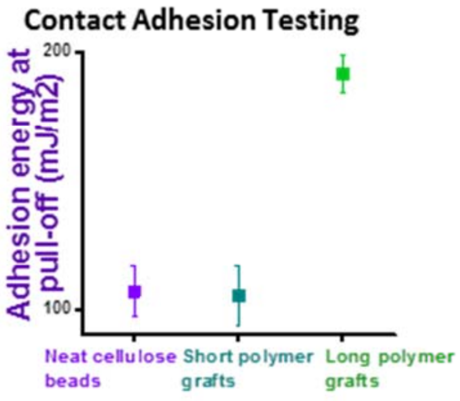
Cellulose has throughout many decades been utilized as a functional material for a multitude of applications. Many useful characteristics have been highlighted over the course of studying cellulose including high mechanical strength to material density, chemical resistance to many solvents, biocompatibility and the fact that it is an abundant and renewable resource. In our group, we have previously developed a method to produce nanometer smooth cellulose spheres with diameters in the range of 1 mm[1]. These spheres – with smoothness in the same range as spin coated cellulose surfaces but retaining bulk cellulose properties due to their size – are excellent probes for Contact Adhesion Testing (CAT) Measurements. In this study we have taken this concept one step further, by first devising a method to polymerize hexamethylcyclotrisiloxane from the surface of the cellulose breads through Ring Opening Polymerization and subsequently perform CAT measurements on the modified beads against a flat PDMS surface. The adhesion of the unmodified and grafted cellulose spheres was evaluated using the Johnson-Kendall-Roberts (JKR) theory. For short grafting lengths, both the JKR work of adhesion and the adhesion energy at the critical pull-off force (G_c) were very similar to unmodified cellulose beads. For longer grafting lengths, however, both the JKR work of adhesion and G_c were substantially increased. Given the multitude of options available to graft polymers from cellulose, this study shows the potential to use this type of cellulose spheres to study the interaction between different polymer surfaces in a very controlled manner.



Grafting of cellulose beads



Contact Adhesion Testing

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Developing dual responsive PNIPAM copolymers

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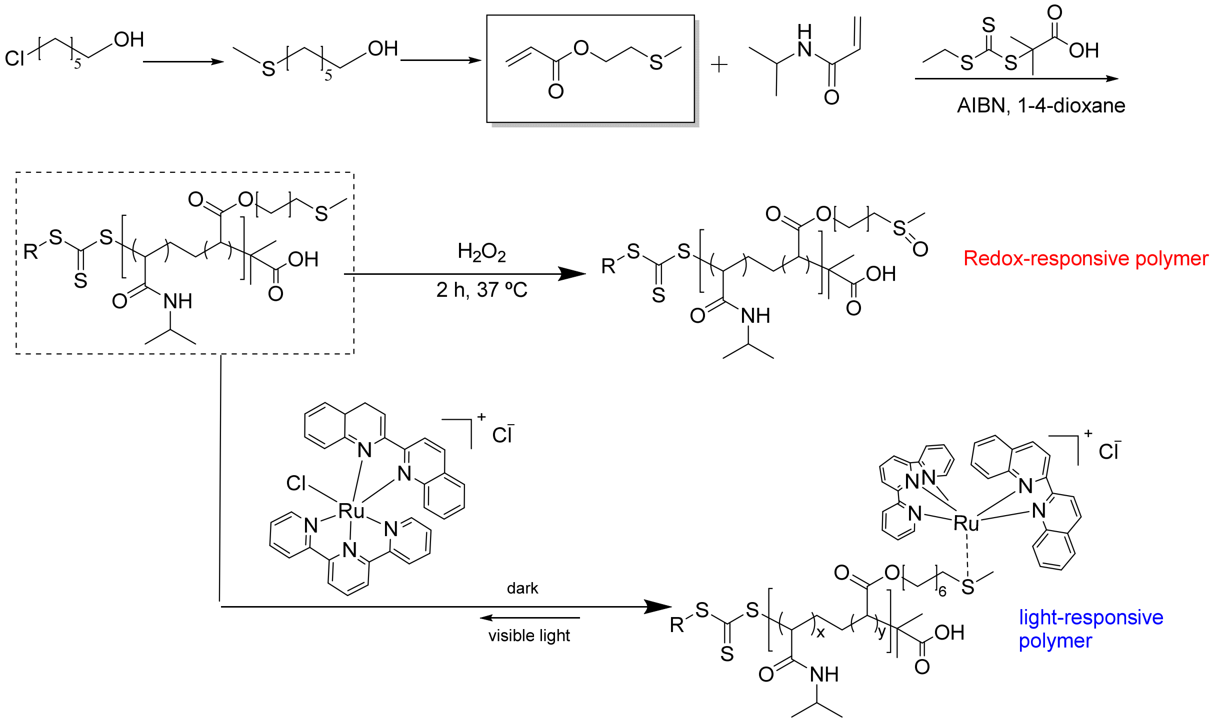
The current advancement in biomedical research have demanded the development of new smart polymers that respond in a specific manner to external stimuli, for applications such as controlled drug delivery, cell patterning, etc.
Special the research effort was focused on PNIPAM, which polymer has been considered an asset for biomedical applications due to its LCST at 32 Celsius. In this work, Thioether functionalities were randomly inserted onto the PNIPAM backbone via RAFT (co)polymerization, and which were proved to grant light and redox-responsiveness to PNIPAM, upon oxidation with hydrogen peroxide or coordination with photosensitive Ruthenium complexes.



The figure above schematized the methodology followed in this work. Our results demonstrate the capacity of PNIPAM to be coordinated by photocleavable Ruthenium complexes, and the capacity of tuning the LCST of PNIPAM upon oxidation reactions.

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Degradation mechanisms in PUR foam of district heating pipes after accelerated ageing

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Modern societies demand the use of non-fossil and sustainable energy resources. In this sense, district heating (DH) systems have been playing an important role in the last years. However, some questions still remains unanswered such as technical lifetime prediction, heat losses challenge or status assessment. These questions are the driving force of DH system development, especially for the DH pipe manufacturers.

Pre-insulated heating pipes include a HDPE jacket, rigid polyurethane (PUR) foam and steel service pipe, and are used to transport the heat from a central point out to the customers and then back again for reuse. These pipes must withstand axial mechanical loads and have good long-term thermal properties. Therefore, it is important to have reliable methods to evaluate the current status of a DH system at any time.

The main aim of the project is to determine the degradation mechanisms during natural and accelerated aging of DH pipes. In this project, the pipes have been aged using an accelerated thermal ageing and both mechanical and thermal properties were investigated. Mechanical property was evaluated using the SP plug method, which determined the remaining adhesion force between the PUR and the steel service pipe [1]. This method has also been designed for application in field for a quick status check. At the same time, the thermal property has also been measured in real-time using a transient plane source (TPS) technique instead of a steady-state method [2]. Characterization of the PUR material has been performed using a three-point flexural test, Fourier transform infra-red spectroscopy (FTIR) and gas chromatography-mass spectrometry (GC-MS) analysis [3].

Preliminary results suggest three different phases where the degradation of DH pipes is a combination of physical and chemical phenomena. In the early aging period, the changes in both mechanical and thermal properties are caused by physical effects. After that, an upturn is observed due to changes in the PUR chemical structure observed in the FTIR analysis. Finally, the chemical degradation takes over which is an effect of thermo-oxidation.
At the end a better model comprising all three phases for the entire degradation process is needed and will be proposed in order to determine the real technical lifetime of DH pipes.

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Extrusion of cellulose nanofibrils and amphiphilic copolymer based bio-composites

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The development of sustainable reinforcing material in plastics coupled with the novel developments in cellulose pulp processing have made cellulose nanofibrils (CNF) commercially available. These highly fibrillated cellulose pulps, with fibrillary dimensions in the nanoscale, have high aspect ratio and excellent potential to be used as reinforcements in thermoplastic composites. However, problems in the form of insufficient reinforcement dispersion, fibre-matrix incompatibility and poor fibre-matrix adhesion are commonly encountered during the melt processing of cellulose-thermoplastic composites and this leads to poor mechanical properties. In this work, composites of cellulose nanofibers and thermoplastic were prepared through a combination of water-assisted mixing, master-batch approach and extrusion. The CNF and poly(ethylene acrylic acid) (EAA), which formed the master-batch, were compounded with a polyolefin in a single-screw extruder to obtain the final composite. The mechanical properties of the obtained composites were compared to compression moulded samples of CNF- EAA and pulp-EAA samples

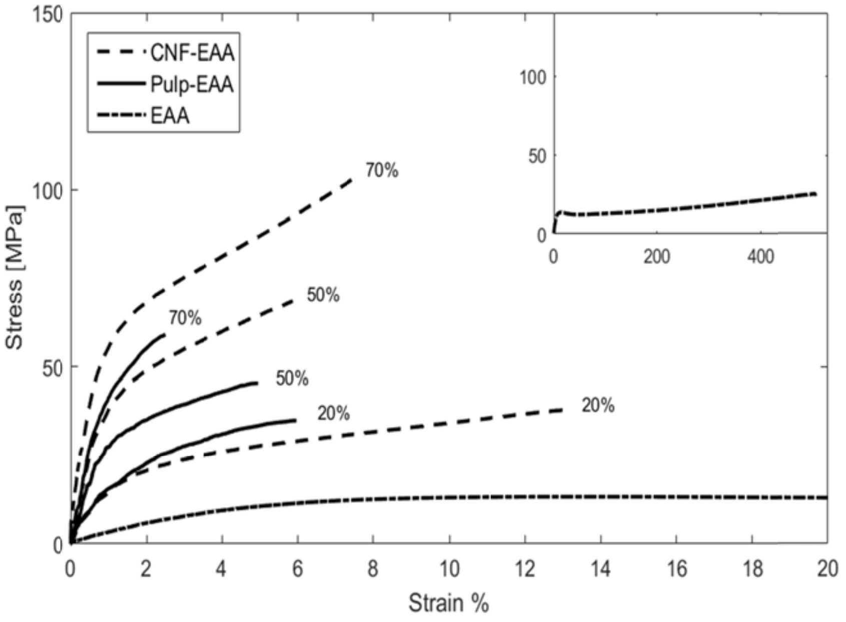

Figure 1: Mechanical properties of compression moulded samples of CNF-EAA and pulp-EAA composites w.r.t the matrix material (EAA).

Cationic heparin binders and sensors

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Heparin is a naturally occurring highly charged polyanion and well-known anticoagulant that is widely used in surgical practice. Anticoagulant effect of heparin is based on its ability to inactivate coagulation cascade, and consequently prevent fibrin and clot formation. To balance and neutralize heparin dosing, a heparin inhibitor is needed, and commonly, protamine sulphate is used for this purpose. However, protamine can cause serious, even fatal, side effects. In the neutralization process electrostatic interactions play a key role as the heparin-protamine complex is formed due to the attractive forces rising from heparin's negative and protamine's positive partial charge. In addition to neutralization methods, also sensing applications for determination of the heparin concentration are needed to define the desirable antidote dosing.[1]

Inspired by these two goals we have designed cationic substances for heparin binding and sensing. In our first project[2], we synthetized block copolymers, and studied the binding affinity dependence on the polymer architecture. We could see clear differences and define the most optimal polymer for the reversal of heparin activity. To develop the system further, we designed new cationic compounds, which in addition to heparin binding, would be able to indicate the heparin concentration. We observed that these host-guest complexes with suitable cavity for signalling molecule and rim functionalization for heparin binding could fulfil both of these aims. As with the polymeric heparin binders, also in this system a charge dependent binding affinity towards heparin was observed. Signalling properties, on the other hand, were mostly depending on the cavity structure of the host, as the signalling molecule needs to fit into the cavity but upon heparin addition the guest should be able to move freely out from the cavity. Overall, we have extensively studied the effect of molecular architecture on heparin binding affinity, and in addition, added ability to detect heparin levels.

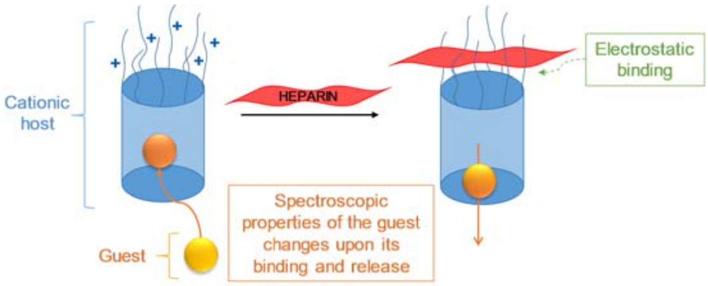

Figure 2: Schematic representation of the host-guest complex acting as heparin binder and sensor

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Long-term performance of polyamide-based multilayer (bio)diesel fuel lines aged under "in-vehicle" conditions

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The behaviour of a polyamide (PA)-based multilayer fuel pipe exposed to petroleum diesel (B0) and its mixture with 20 vol.% biodiesel (B20) was investigated. The pipes were aged under a "close to real" condition using a specially-designed ageing equipment with a program designed according to known customer driving modes and conditions. The plasticizer migrated from the PA6 innermost layer of the pipe to the fuel, and from the PA12 outer layer to the air surrounding the pipe. After 1000 h ageing, almost all plasticizer had left the pipe, and ca. 7 wt.% fuel was absorbed in the inner layer of the pipe. The EVOH barrier layer located in the middle of the pipe hindered the diffusion of the fuel from the inner surface to the outer part of the pipe. The oxidation of the PA6 innermost layer was promoted by the oxidation products of biodiesel. The diffusion limited oxidation of the PA6 layer led to the formation of a 30 μm highly oxidized zone at the inner surface of the pipe, resulting in discoloration and oxidative crosslinking of the polymer. The Young's modulus and tensile strength of the pipe increased with increasing exposure time, due to plasticizer loss and oxidative crosslinking. The toughness and extensibility of the pipe decreased significantly after prolonged ageing, the extensibility was only 7 % of that of the unaged pipe after 2230 h. The low extensibility was due to cracks developing at the highly oxidized brittle PA6 inner layer when the pipe was exposed to tensile stresses, which grew outwards and caused pipe fracture through a two-stage process.

Biofoams and composites based on wheat gluten proteins

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Wheat gluten (WG) is co-product from bioethanol industry, which is an interesting protein material (biopolymer) that could be considered as a possible replacement for petroleum-based plastics. In this work, we have investigated WG-based biofoams and biocomposites with new functionalities and improved mechanical properties. More specifically, non-flammable WG-based foams was developed via in-situ polymerization of silica nanoparticles into WG protein networks before foaming, these foams also showed very good thermal insulation properties. Secondly, the WG-based foams were made into antimicrobial by using Lanasol (an antimicrobial additive) from nature. The sorption properties of the biofoams are also of great interest. We also managed to synthesize flexible conductive WG foams by impregnating of carbon fillers (three types with different aspect ratios) to provide the conductivity. In particular, we found that the conductivity in some cases changes when the foam is mechanically compressed. Therefore, simultaneously measurements of compression test and electrical resistance was designed and performed. Possible applications include sensor that is triggered by the mechanical deformation, as well as packaging materials for electrostatic discharge protection (ESD) and electromagnetic interference (EMI) shields. In addition, a scaling up strategy through the assembling of smaller freeze-dried foams was investigated to provide a way of using freeze-drying even for larger objects. We also investigated the flexible biocomposites based on plasticised WG reinforced with a flax-fibre-weave, to demonstrate the mechanical properties could be tailored by the use of plasticiser and/or reinforcing fillers.

A new solvent-free method for production of pectin-based biofilms reinforced with fungal biomass

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Approximately half of the weight of the orange processed for juice extraction is converted into waste, containing both fruit peel and pulp, and composed of considerable amounts of poly-, di- and monosaccharides. Among the polysaccharides, pectin has a good potential to be used for the production of edible films for food packaging. Traditionally, pectin films are produced by casting technique where pectin is dissolved in water, solution is spread on a surface, and then the solvent is evaporated [1, 2]. Moreover, the free sugars present in the orange waste can be utilized for the cultivation of different microorganisms such as filamentous fungi [3].
In this study, a new solvent-free method was developed for production of pectin films. Accordingly, pectin from citrus peel (Sigma-Aldrich, USA) was mixed with glycerol, which was used as a plasticizer. The mixture was kept at 5 °C overnight to obtain a homogeneous paste-like material. The paste was then subjected to a compression molding process between two polystyrene sheets under a force of 30 kN at 120 °C, for 10 min to form a film. The obtained pectin film exhibited a tensile strength of 15.7 MPa, and elongation of break of 5.5%. The water vapor permeability for this film was 0.84 mg.mm/h.m^2.kPa. Pectin films produced by casting method have been reported to exhibit tensile strength values in the range of 10 to 50 MPa and elongation of break up to 3% [1, 2]. Enhancement of the pectin films characteristics was investigated by incorporation of fungal biomass. The edible fungal strain *Rhizopus oryzae* (CCUG 28958) was cultivated in the free sugar solution obtained from orange waste in a 26 L bubble column bioreactor. The obtained biomass contained 30% proteins and 20% lipids. The fungal biomass was freeze-dried and milled to a particle size smaller than 0.25 mm. Blends of glycerol (30%), fungal biomass, and pectin were prepared with various pectin-biomass ratios being tested (namely 60/10; 55/15; 50/20; 45/25; 40/30; and 35/35 g/g). Pectin-biomass films were generally more opaque than pectin films. At pectin-biomass ratio of 60/10, the obtained film exhibited almost the same tensile strength and more than 65% of the elongation at break compared to the pure pectin films. The water vapor transfer rate for this film was 0.5 mg.mm/h.m^2.kPa. At a ratio of 55/15 the pectin-biomass film still preserved more than 80% of the strength of the pure pectin film. Higher biomass ratios, however, decreased the strength of the obtained films. The results demonstrate the possibility of producing pectin films by compressing molding press technique without utilization of solvent. Fungal biomass incorporation in the films up to 15% of the blend enhanced the water vapor transition resistance while did not result in severe loss of the mechanical properties of the films.

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POSTERS

in alphabetical order of presenting author

Magnetic nanocomposite of chitosan/PVA: synthesis, characterization and application

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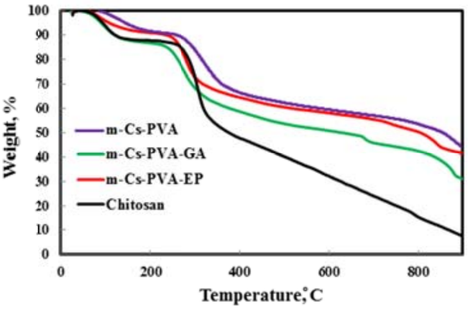
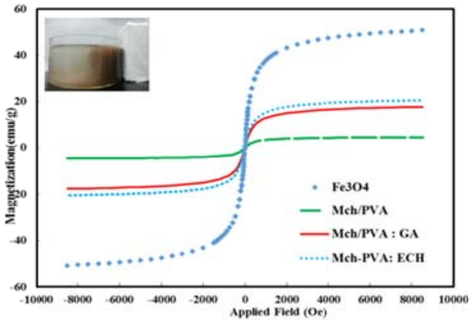
A series of magnetic chitosan-PVA nanocomposite (MCP) were prepared by using gelation method for removal of cationic (direct blue 71) and anionic (crystal violet and malachite green) dyes. Synthesised MCPs were characterized with vibrating sample magnetometer (VSM), field-emission scanning electron microscopy (FESEM), x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) (following figures, left; TGA, right; VSM).





In this research, effect of glutaraldehyde (GA) and epichlorohydrin (EPH) as two kinds of cross-link agent on the performance of the magnetic chitosan/PVA were investigated. Operational parameters such as temperature, pH, dyes initial concentration and amount MCP on the removal of dyes were studied as a function of contact time. The results show that the maximum adsorption capacity occurred on the surface of the MCP with glutaraldehyde (GA) for removal of DB71. The experimental data were analyzed by isotherm models and equilibrium results were fitted well with the Langmuir isotherm model and the maximum adsorption capacity of the MCP-GA was determined to be 1250 mg/g for DB71 (R^2=0. 9916), 714 mg/g for MG (R^2=0. 9939) and 263 mg/g CV (R^2=0. 9985). Adsorption data were analyzed with three kenitics models and pseudo second-order equation could best describe for adsorption of dyes. Finally, the thermodynamic parameters were determined.

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Effects of surface charge density on the phase separation and rheology of cellulose nanocrystal suspensions

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The self-organization of cellulose nanocrystals is lyotropic. At low concentrations, the suspension is isotropic, however at a critical concentration, phase separation occurs to give a biphasic suspension with a lower chiral nematic phase and an upper isotropic phase, and eventually the entire suspension becomes anisotropic. However, as the concentration increases, gelation sometimes interferes with self-assembly, particularly as attractive interparticle interactions become assertive (Mu and Gray 2014, Honorato-Rios et al. 2016). The self-assembly and gelation behavior of CNC suspensions are intertwined closely with the surface charge density of the particles, and additionally, the dispersive state impacts viscosity, with the shape/scale of shear viscosity profiles reflective of this state.

In this work, we present data on the self-assembly and rheology of a series of four suspensions characterized by identical particle sizes but varying surface charges in the range of 0.27 %S to 0.89 %S (surface charge is given in terms of elemental sulfur and directly translates to the number of charged sulfate half-ester groups grafted onto the surface of the particles during hydrolysis). Our results indicate substantial effects of surface charge on phase separation and rheology, with suspensions with lower surface charge beginning to self-assemble at concentrations 5–10× lower than the higher charge suspensions and exhibiting much higher shear viscosities. We largely interpret the phenomena in terms of effective particle volume. These results have implications for the commercialization of this material, where viscosity may be critical to processing and application.

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Qualitative characterization of nanoclay particle emissions from PP nanocomposites after thermal degradation

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The use of nanomaterials in polymeric materials is a rapidly expanding field, and the polymer nanocomposites are being introduced into various markets. But there is still little known about the fate of nanocomposites and nanoparticles during service life and end-of-life of the materials. To avoid possible environmental, health and safety problems, simulating different scenarios for nanoparticles release from the polymer matrix plays a key role in commercialization of these advanced materials. The polymer/nanoclay nanocomposites show superior material properties in comparison with the pure polymers, such as improved mechanical properties, heat resistance, flame retardancy and decreased gas permeability. Polypropylene (PP) nanocomposites have attracted a considerable interest due to the material's low cost, low density and extensive production volumes. In this study, in order to obtain reliable results regarding the release of nanoclays from PP nanocomposites, homogenous composite with predetermined content of nanoclay was produced and characterized to obtain information regarding content, dispersion and size of the nanoclays in the matrix. The PP nanocomposite was degraded under controlled conditions and the surface morphology as well as oxidation of the material was characterized with scanning electron microscopy (SEM) and infrared spectroscopy/microscopy during degradation. A prototype environmental chamber was designed in order to collect nano-sized particles in a controlled manner and subsequent characterization of the released or formed particles was performed with transmission electron microscopy (TEM) and the exposed nanocomposite was analysed with thermogravimetric analysis (TGA).

Keywords

Nanocomposite, Release, Degradation, Life cycle, Characterization

Low Molecular Weight Lignin as an Antioxidant Additive

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Since many years ago applying an antioxidant material to scavenge the free radicals has had an extremely important role in many products e.g., food, cosmetic, medicine and polymeric materials. Due to the increasing public awareness regarding the application of synthetic antioxidants, an attention has shifted towards the natural antioxidants. Naturally derived antioxidants i.e., flavonoids, lignin, etc., are currently considered as a promising avenue for future application. However, purification and especially fractionation of technical lignins is necessary in order to increase its antioxidant activity. In respect to the potential applications, low molecular weight lignin possessing high phenolic content is of interest as it can be used as an antioxidant in various systems. The main aim of this study was to investigate the properties of low Mw lignin, obtained by ultrafiltration of Lignoboost lignin in alkaline solution with 1kDa ceramic membrane. The detailed structural characterization of the initial lignin and fractionated low Mw lignin was performed by SEC, NMR analysis (2D-NMR and ^{31}P NMR) and by analytical pyrolysis (Py-GC/MS). Molecular weight of LignoBoost lignin and low Mw lignin were around 5500 Da and 500 Da respectively. Different types of interunit linkages and phenolic structures were analyzed by 2D NMR and Py-Gc/Ms. It was shown that, the low Mw lignin fraction consists of the fragments with shortened aliphatic chains, rich in phenolic and methoxy groups. The antioxidant activity of lignin samples was evaluated based on the results from ABTS$^{\bullet+}$, DPPH$^{\bullet}$ and ORAC assay as well as from the Oxipres test which evaluates inhibition properties of lignin in the oxidation of rich-in-lipids substrates. The results of the antioxidant tests demonstrated good potentials of the low molecular weight lignin fraction as a naturally originated antioxidant, in particular, for lipids containing systems. It was shown by the kinetic ORAC test that the inhibition effect of low molecular weight lignin on the substrate (fluorescein) oxidation was three times stronger in comparison with that for a reference antioxidant Trolox (a water-soluble derivative of vitamin E). Additionally, low Mw lignin fraction showed improved inhibition properties in the test with rich-in-lipids substrate (mayonnaise). The good antioxidant properties of the low molecular weight lignin fraction are in conformity with certain structural features established by Py-GC-MS analysis, e.g., lower condensation, higher portions of methoxylated phenyl-propane units (PPU) and PPU with shortened aliphatic side chains in comparison with the non-fractioned lignin.

Design of polymeric nanoparticles for drug delivery applications

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Polymeric nanoparticles (NPs) for drug delivery applications have great attention during last decades. Amphiphilic block copolymers, composed of core-shell nanostructures, are used to encapsulate small chemotherapeutic drugs in the hydrophobic core. The hydrophilic shell is utilized to protect the drug from physiological degradation, diminish capturing by mononuclear phagocyte system (MPS)[1, 2]. Recently, polymerization-induced self-assembly (PISA) is an important approach developed to synthesize amphiphilic polymeric NPs. A water-soluble polymer, synthesized by controlled radical polymerization, can initiate the polymerization of hydrophobic monomer in either polar or non-polar solvents. The chain extension with the hydrophobic block from the water-soluble polymer and the self-assembly of the resulting amphiphilic block copolymer chains lead to the formation of stabilized particles with well-defined and monodispersed molecular weight[3, 4]. Non-toxic amphiphilic latex nanoparticles were obtained in aqueous solution by PISA mediated-reversible addition fragmentation chain transfer (RAFT) technique. A macroRAFT based on hydrophilic polymer such as poly(oligo (ethylene glycol) methyl ether methacrylate) P(OEGMA) is chain extended by hydrophobic monomer to produce well-defined latex particles in nanoscale suitable for drug delivery purposes. The latex NPs are obtained by emulsion polymerization under RAFT control using redox initiator. Bio-functionalization of the latex nanoparticles by conjugating a target ligand was investigated for targeted drug delivery. The latex NPs were characterized by 1H-NMR, SEC, DLS, SEM and UV-vis spectrophotometry. The cell viability of the latex NPs was evaluated in MCF-7 and RAW 264.7 cell lines. The DLS results showed that the average hydrodynamic diameter of the formed latex was 50 nm with narrow distribution and that increasing solid content from 7 to 10 % resulted in increasing NPs diameter from 50 to 190 nm. The latex NPs don't induce major toxicity up to 1mg/ml NPs concentration after incubation 72 h with MCF-7 cell line.

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Catalyst Selectivity towards Dimethyl Itaconate in the Synthesis of Renewable Polyester Resins and the effect on Material Properties

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Itaconic acid (IA) is a fully bio-based monomer that is produced industrially through fermentation of carbohydrates using the fungi *Aspergillus terrus.*[1,2] With an increasing demand for renewable materials, IA and its derivatives such as dimethyl itaconate (DMI) are very interesting monomers. IA is a diacid which makes it possible to use in polyester synthesis and additionally it has a vinyl group. There are many studies on polyester synthesis from IA and DMI and the synthesized polyesters have been further crosslinked both thermally and with UV initiation into thermosets and coatings. [1,3]

The aim of this study was to provide insight in how the choice of catalyst affects the material properties of networks formed from DMI-based unsaturated polyesters (**Fig. 1**). Biocatalysis (*Candida antarctica* lipase B, CalB), acid catalysis (*p*-Toluenesulfonic acid, *p*TSA) and an organometallic compound (Titanium (IV) butoxide, $Ti(OBu)_4$) were used for the synthesis of unsaturated polyesters. The different catalysts showed different selectivity towards the conjugated and the non-conjugated side on DMI and this led to a varied distribution of the monomers in the polymeric chains. Polyester synthesized with CalB showed a significant selectivity towards the non-conjugated side and this led to that the double bonds were mainly found at the ends of the polyester chains. The $Ti(OBu)_4$ had a much lower selectivity which led to a more random distribution of unsaturations in the polymer chains. This difference has been seen to affect both the crosslinking and final material properties. Synthesis with *p*TSA was not successful because it caused side reactions.

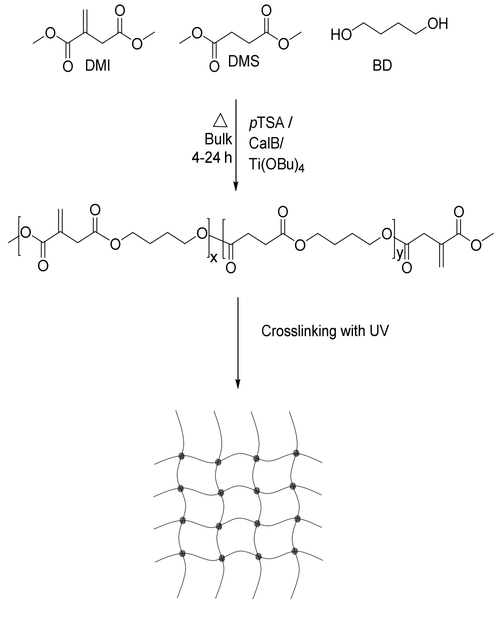

Figure 3. Unsaturated polyesters from DMI, dimethyl succinate (DMS) and 1,4-butanediol (BD) were synthesized and cross-linked with UV light and irgacure 651 (photo initiator).

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Peculiarities of hybrid lignin/silica composites synthesis

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In recent years, the functional polymeric compounds have been widely used to modify the silica surface, which allows one to obtain the corresponding organomineral composites for broad application prospects. In this case, lignin – cross-linked phenolic polymer – is of great interest according to its valuable properties and abundance as a by-product of pulp and paper industry.

Hybrid materials based on lignin and silica in different mass ratios were prepared by several synthetic approaches: via electrostatic attraction of modified lignin to aminosilica surface, by using sol-gel method in the acidic and basic media, crosslinking of functional groups of organic polymer and inorganic carrier with different agents, such as epichlorohydrin and formaldehyde. Lignin materials used in this study are kraft softwood lignins coming from the Lignoboost (LBL) and CleanFlowBlack (CFBL) processes. The molecular weights, determined by size exclusion chromatography were 5500 and 3000 Da, respectively and the number of phenolic OH groups, determined by ^{31}P nuclear magnetic resonance spectroscopy was 4.3 mmol/g and 5.5 mmol/g, respectively in these samples.

The peculiarities of different approaches to synthesis of lignin/silica hybrid materials were studied and the influence of synthetic conditions on physicochemical properties of obtained composites were investigated, by scanning electron microscopy, thermogravimetric analysis, and nitrogen adsorption/desorption.

It was found that changing of pH of system, variations with inorganic filler (carrier) mass content, type of crosslinking agent applied, time of preparation are greatly affect of physicochemical characteristics of obtained materials, such as specific surface area, porosity, morphology, and thermal characteristics. Such structural differences will affect the ability to sorb and release different active compounds, antibacterial properties of hybrid composites, *etc*.

Polymer-based nanocomposites for controlling the electrical arcs in electrical switching applications

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Polymer-based nanocomposites (PNCs) have been engineered and demonstrated for improving the arc interruption capability in low power electrical switching applications. PNCs, which are the combination of inorganic nanoparticles (NPs) and polymers, opened up new developments in materials science that includes their utilization for several electrical switching applications. Inorganic NPs are selected based on their physical and chemical properties which could make multifunctional PNCs in order to interrupt the electrical arcs effectively. In particular, we present on the PNCs fabricated by using ZnO NPs in a poly (methyl methacrylate) (PMMA) matrix via in-situ polymerization method, to avoid NPs agglomeration, leading to good spatial distribution of NPs in the polymer matrix. Thus, several samples with various wt% of NPs in PMMA matrix have been fabricated. These PNCs have been characterized in detail for the morphology of NPs, interaction between NPs and polymer matrix, and radiative absorption properties. In the next stage, PNCs are tested to determine their arc interruption performance and impact on the electrical arcs of current 1.6 kA generated using a specially designed test set-up. When PNCs interact with the electrical arcs, they generate ablation of chemical species towards core of the electrical arc, resulting in cooling-down the arc due to strong temperature and pressure gradient in the arc quenching domain. In conclusion, results demonstrate for the first time that these engineered PNCs are easily processed, reproducible, and can be used to improve the arc interruption process in electrical switching applications.

Keywords

Polymer-based nanocomposites, Nanoparticles, Electrical arcs, Circuit breakers, Ablation/Outgassing, Arc interruption capability, PMMA, ZnO, Radiative energy, Electric power, Arc temperature

Fabrication of chitosan hydrogels in the presence of bio-based graphene oxide

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Water pollution, as a severe environmental issue, has caused great public attention. Among many treatment methods, adsorption is regarded as an effective approach to remove pollutants from water. In this context, we developed an eco-friendly bio-based chitosan-graphene oxide (CS-GO) hydrogel with genipin (GP) as crosslinking agent for wastewater purification application. Different from modified Hummer's method for GO preparation, we converted biopolymers, such as cellulose, starch and chitosan, to nano-GO by virtue of microwave-assisted hydrothermal carbonization process. This process has unique benefits such as 1) high yields 2) high efficiency with lower energy consumption 3) green solvents without toxic catalysts. The CS-GO hydrogels showed a honeycomb three-dimension networking structure as an indication of successful crosslinking. As explored, the CS-GO hydrogels were expected to be tunable in their properties, such as swelling behaviour, mechanical performance, and thermal stability with the variation of GO and GP content. Meanwhile, GO was found to play a role in the crosslinking reaction by GP resulting in the formation of darker and more homogenous chitosan hydrogel system.

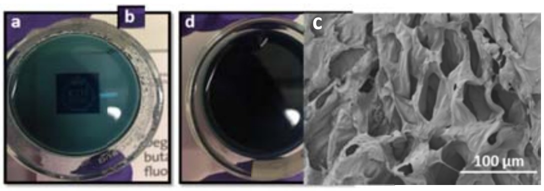

Figure 1. Visual appearance and morphology of CS-GO hydrogels. a and b are the CS-GO hydrogels with increasing GO amount from 0 to 5 mg (a: 0 mg; b: 5 mg). GO are derived from chitosan; Figure 1c demonstrates the network structure of CS-GO hydrogel with 2 mg GO derived from cellulose.

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A Comparative Study of Mechanical Properties of Table Tennis Balls

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In 2014, the state of the art table tennis balls made out of celluloid were replaced by balls consisting of different polymers for international tournaments. These balls were called "plastic balls" by the International Table Tennis Federation (ITTF). Players announced critique towards quality and playing behaviour of the new balls. The ITTF still assures for the new plastic balls identical or similar properties than with the celluloid balls. To compare the playing behaviour between plastic and celluloid, a Five Factor model consisting of spin, velocity, rebound, aero dynamical behaviour and durability is developed. These factors are split up in different influencing parameters which can be measured, calculated or modelled. As sample, balls of the brand Nittaku are measured. Less spin is found due to a small increase of the moment of inertia (0.4%) and lower friction which is measured with tribological tests. This spin loss is estimated for three commercial table tennis rubbers. The spin loss varies from 0.08 % to 17.89 %. A decrease of spin is hypothesized due to a calculated shorter collision duration. The exhibited velocity from flat strokes is assumed to be similar due to only 2% increase of cross section area which is measured through CT-scans. Tangential strokes are assumed to be slower due to decrease of spin and lack of curvature from Magnus' effect. The rebound from the racket differs due to lower friction. The rebound from the table should be similar due to similar energy loss. The energy loss is measured with hysteresis compression curves and dynamic mechanical analysis. Compression curves are examined through models from literature. The plastic ball is harder to compress. The collision duration of the plastic ball is calculated from the compression curves and is shorter. Various roughness measurements deliver no significant difference between both balls. The durability is tested with tensile tests. The plastic material ruptures and yields earlier than celluloid. The wall thickness is increased which softens the risk of forced rupture. It has to be tested if the increased wall thickness can compensate the plastic behaviour. Altogether, the test results show that at least for the sample balls the playing behaviour of the new plastic balls cannot be assessed as similar or even equal to the playing behaviour of the state of the art celluloid balls.

NEW SILK – The new road to silk

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In the recent years there has been increasing interest in replacing oil based fibers with fibers made from renewable starting materials and to find more environmentally friendly ways to produce some biological ones. Silk as a material has been used for millennia and has many desirable properties. It has nice appearance, is relatively strong and thus suitable for light weight and premium garments, and is biodegradable. However, at the moment the production costs are high and the production is geographically limited to areas in which silkworm is native species.

When the term silk is used it almost always refers to fiber made by a silkworm, usually B. Mori, but there is a plethora of other silk producing species with a wide variety of fiber properties. One of the most studied of non-silkworm silks are spider silks, as there are several different types according to the intended use and some of them, like dragline silk, can be very strong and tough.

In this project we are using biotechnology to design and prepare new types of recombinant spider silk proteins that are based on already known structures. In combining the sequences for different structural motifs we hope to be able to tailor the mechanical properties of the fiber as well as optimize the fiber formation in the spinning process. Furthermore, the recombinant spider silk proteins are produced either in bacteria or in yeast so low-value feedstock, like waste or side streams, could be used.

Extensional viscosity of a β-glucan concentrate

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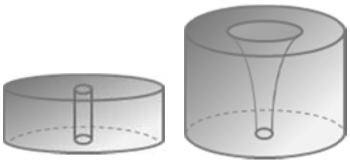
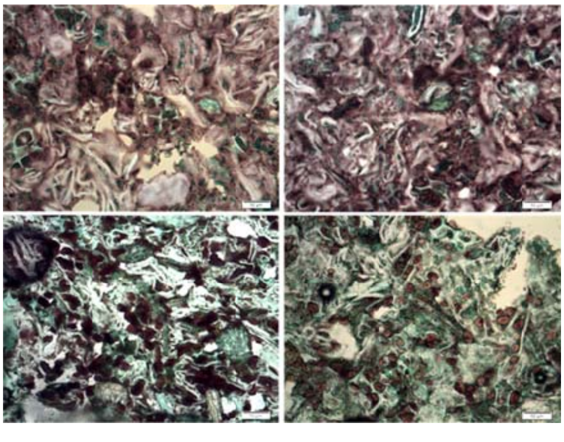
Creating a sustainable society where all materials are used to its full potential and the waste and pollutants are minimized is of crucial importance for the future of our planet. One of the main challenges which needs to be addressed is to reduce our dependence on fossil fuels for energy and materials production. The polymers in conventional plastics are produced from crude oil or gas whereas at the same time there are many material fractions and side streams within the agricultural and forestry sector which are not utilized to their full potential. One way to approach both issues would be to obtain the necessary polymeric chains from the bio-based streams instead of the fossil source and convert them into valuable products before they can be recycled, composted or burnt for energy.

The major part of plant tissues consists of cellulose, hemicelluloses and lignin. Whereas the cellulose and lignin fractions can in principle be separated and taken care of to quite a large extent, the hemicellulose fraction is often neglected and burnt for energy directly since it has no clear application area. In this project a material from the agricultural sector consisting mainly of the hemicelluloses β-glucan and arabinoxylan as well as starch is examined for its potential of being processed by conventional plastics processing techniques into something which could substitute oil-based plastics in certain applications. The main focus of the study was to assess the rheological and mechanical properties of the concentrate. In addition to measuring the more commonly reported shear viscosity, also the extensional viscosity has been examined using a hyperbolic contraction flow die fitted to a capillary viscometer. The material behaviour was further characterised using optical and confocal scanning laser microscopy. In conclusion, the concentrate showed interesting properties for further processing using conventional methods for thermoplastics.





Self-Assembly of Electrostatic Co-Crystals from Supercharged Fusion Peptides and Protein Cages

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Self-assembly is an attractive method to produce well-ordered structures of biomolecules, far more detailed and complexed systems than can be achieved through synthetic methods.[1] Electrostatic interactions are convenient in such systems, as they are generally reversible and easily controllable. Utilizing polyelectrolytes, which possess high charge density, allow stronger interactions and synthetical fine tuning the properties of the systems. Such systems show promise in biomedical applications and material engineering.[2]

Here we study self-assembling of negatively charged ferritin and viral protein cages into co-crystal structures with supercharged cationic polypeptides (K72) and their recombinant fusions with green fluorescent protein (GFP-K72). The assembling process was studied and complete assemblies characterized in aqueous media. The assembling was found to be highly dependent on the ratio of the oppositely charged components and electrolyte concentration. Assemblies of both ferritin and viral cages adopted well-defined crystalline structures, which were characterized with small angle X-ray scattering and found to possess face centered cubic structure with lattice constants of 14.0 and 28.5 nm, respectively. The recombinant proteins occupy voids within the systems, suggesting porous structures of the assemblies, which can act as protecting agents for nanoscale quest-molecules.

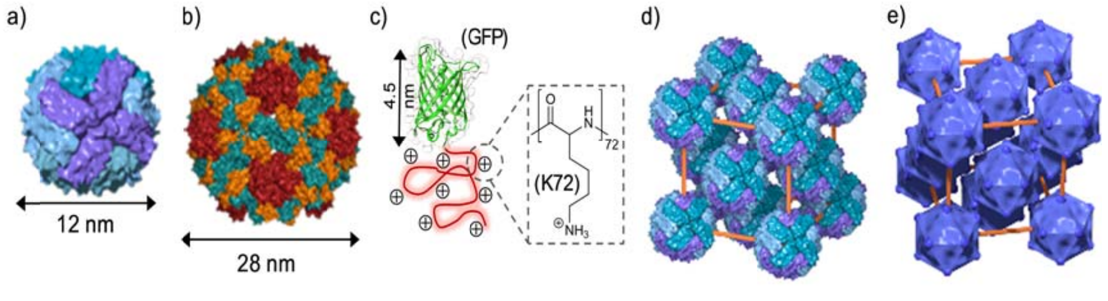

Figure 1. Building blocks of the self-assembling systems: a) ferritin cage, b) viral protein cage, c) GFP-K72. 3D models of d) ferritin - K72 and e) viral protein - K72 assemblies.

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Novel method to measure surface crystallinity of fibers and nonwovens

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The production of fibers from a polymer melt is an important process in many industrial sectors where fibers and nonwovens are utilized as hygiene and medical products, as geotextiles or as filter materials. The properties of such highly oriented products, like nonwovens or films, strongly depend on their crystallinity. As fibers are exposed to high cooling rates and draw ratios during their production, crystallinity normally is not a bulk property but a function changing with the diameter of the fiber or film and therefore bulk properties often are not informative for end consumer characteristics like a soft feel or the migration of additives to the surface.

Currently the crystallinity of polymers is determined via differential scaling calorimetry (DSC) or via X-ray diffraction (XRD). Even though DSC is an easy and fast way to determine crystallinity, it suffers several disadvantages. In DSC studies sample preparation of fiber material is difficult, results are not calibration free and heat is introduced in the measuring process which might change instable crystal structures in the polymer. XRD is able to overcome these problems but is time intensive and complicated in terms of sample preparation and evaluation of the measurements. Furthermore, it is not possible to determine surface crystallinity with both methods.

This study shows a novel approach to utilize Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR) as a highly sensitive, non-destructive and fast way to measure surface crystallinity of fibers in a penetration depth of 0,5 – 2,5 µm. Samples without crystallinity gradient produced with different cooling rates from 1 – 3500 K/min were measured via XRD and FTIR-ATR to calibrate the method (Figure 1). Subsequently fibers were produced at different processing conditions on a pilot spunbond line to verify the method and show its applicability to measure surface crystallinity of fibers and nonwovens.

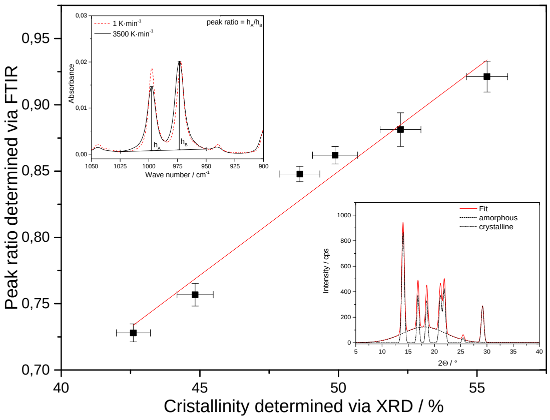

Figure 1: Calibration curve for the determination of the degree of crystallinity via FTIR measurements

New bio-based linear or branched diallyl poly(ethylene furanoate)s

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The eminent exhaustion of fossil resources does not only entail challenges of meeting modern fuel demands, but also present issues for the plastics industry, wherein most of the mass produced plastics used today are produced from either oil or natural gas. A major topic in recent research have been development of alternatives to the widely used polyethylene terephthalate (PEF), in which an analogue to the oil based terephthalic acid (TA) is sought. A lot of attention has been devoted to the compound 2,5-furandicarboxylic acid (FDCA), synthesized from glucose and other carbohydrates.1 FDCA has shown similar properties with TA and has been used to produce analogues to the PET plastics, known as polyethylene furanoate (PEF) plastic.2 In this project, we are investigating new linear or branched polymers from FDCA in combination with allyl alcohol, which can, through processes developed over the recent years3, be synthesized from glycerol (a major byproduct from biodiesel production).

Here we polymerize the diallyl ester of FDCA, diallyl furandicarboxylate (DAFDC), with ethylene glycol thermally in order to create telechelic systems, resembling PEF plastics, with allyl functionalized end groups. By variations of the feed mixture, branching of the systems with glycerol results in further increasing the allyl functionality in branched polyesters.

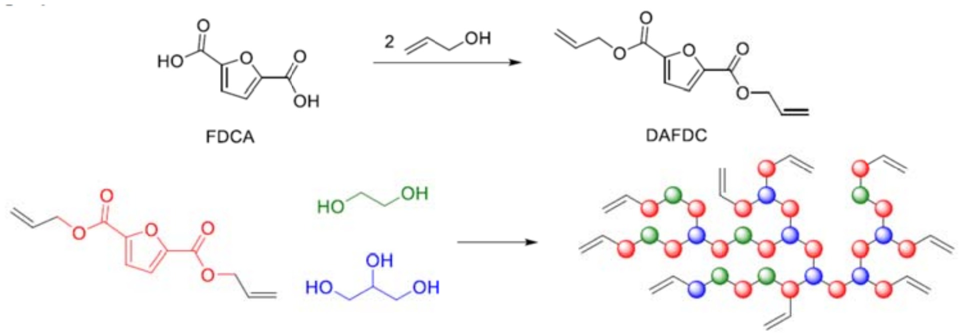

Figure 1: Synthesis of diallyl furandicarboxylate (upper) and schematic representation of the branched polyesters (lower).

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Microwave-assisted hydrothermal carbonisation of polypropylene

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Microwave-assisted hydrothermal processes can be applied for carbonization and/or liquefaction of biopolymers and biomass. Compared to conventional autoclave hydrothermal process, the advantage of microwave-assisted irradiation is the enhanced reaction rate[1]. In our group microwave-assisted liquefaction/carbonization of cellulose[2], starch[3], waste paper[4] and used coffee grounds[5] have been evaluated. Now, similar hydrothermal process was explored for carbonization of polypropylene plastics.

Polypropylene is hydrophobic and non-polar plastic. It does not absorb microwave irradiation under room temperature. However, with the synergistic effect of acidic aqueous solution and microwave irradiation, polypropylene can be effectively degraded into smaller molecules under relatively mild environment. Our preliminary study indicated that by manipulating the reaction parameters, such as reaction time, amount of acid and temperature, it is possible to obtain carbonised and/or liquefied products after microwave irradiation of polypropylene. Thus, the process provides a possible path for upcycling polyolefin plastic waste to value-added products.

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Superhydrophobic self-regenerative silicone rubber nanocomposites for electrical outdoor insulation

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The overall objective of this project is to develop new structural composite materials for high voltage outdoor insulation applications using silicone rubber (PDMS) combined with micro- and nanoparticles. The goal is to obtain hierarchical superhydrophobic surfaces, with antifogging, antifouling and self-cleaning ability. This will minimize surface leakage currents and subsequent surface flash over of the insulator [1]. In a harsh outdoor environment the surfaces will gradually erode, but in combination with the bulk properties, the surface will be self-regenerative [2].

In order to achieve both the superhydrophobic and self-cleaning ability, a combination of different sizes, deposition techniques and surface chemistry of ZnO particles has been investigated. Two different methods of chemical hydrophobization of ZnO nanoparticles were developed, based on previous studies [3,4], together with four different deposition techniques, including spraying of ROD ultrasonicated ZnO solutions. Hydrophobic and hydrophilic ZnO nanoparticles were added to pure silicone rubber (SYLGARD®184). Hydrophilic ZnO nanoparticles were treated with octadecylphosphonic acid [3] or octadecanethiol [4] using two different methods. The effect of surface chemistry and the deposition technique on the hydrophobicity has been investigated using static and dynamic contact angle measurements. The objective has been to achieve the highest static contact angle combined with the lowest possible hysteresis. Functionalization with acid resulted more suitable when using PDMS as matrix, but the differences between the deposition methods required a deeper analysis. The link between superhydrophobicity and the surface structure has been assessed by Scanning Electron Microscopy.

The next step towards a self-regenerative material is approached by the incorporation of the optimal functionalised nanoparticles into the bulk. The dynamic behaviour of silicone rubber presents a challenge for the stability of nanocomposites. Different mechanical techniques and metho1ds of integration are being investigated. Studies have been performed evaluating the effect of the curing time of the PDMS on the degree of incorporation of the nanoparticles in the surface and uniformity within the bulk. The behaviour of the nanocomposite with time and environmental conditions will be studied.

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Characterization of Biopolymers and Synthetic Polymers using Asymmetric Flow Field-Flow Fractionation (AF4) and Thermal Field-Flow Fractionation (TF3) coupled to Multi-Angle Light Scattering (MALS)

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Field-Flow Fractionation (FFF) has become a reliable analytical tool for the separation and comprehensive characterization of polymers, biopolymers, proteins and nanoparticles. Four different FFF techniques are commonly used today: asymmetric flow FFF, centrifugal FFF, thermal FFF and gravitational FFF. By coupling the FFF systems to suitable light scattering detectors, such as multi-angle light scattering (MALS) and dynamic light scattering (DLS) and concentration detectors such as UV and refractive index, the molecular weight distribution of synthetic polymers and biopolymers can be measured together with the molecular structure (degree of branching, copolymer composition and aggregation) of these samples.

In this poster the application of asymmetric flow FFF (AF4) for the characterization of biopolymers in aqueous solvents and thermal FFF for the characterization of synthetic polymers in organic solvents will be demonstrated. Several application examples will show the possibilities of the FFF techniques and the results that can be achieved when FFF separation methods are coupled to multi-angle light scattering (MALS) detection.

Thermoplastic micro-fibrillated cellulose-reinforced composites: dependence of mechanical properties on the cellulose fiber network

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Cellulose fibers are an attractive, yet elusive, reinforcing material for thermoplastics due to their high strength, low cost and abundant availability. However, cellulose as a hydrophilic material has an inherent incompatibility with a hydrophobic polymer matrix. Aggregation within the composite leads to inferior mechanical properties. We combine the use of a compatabilizing agent; the amphiphilic copolymer poly(ethylene-ran-acrylic acid), and a gelled cellulose system in order to form thermoplastic composites with improved mechanical properties. The system promotes the dispersion and optimizes the strength of the interfacial bonding between the filler and the matrix.

We report a route for manufacturing micro-fibrillated cellulose (MFC) reinforced composites of poly(ethylene-ran-acrylic acid) (EAA) using water assisted mixing. We have studied the mechanical properties of the resulting composite as a function of the number of network points in the cellulose network. In the method MFC is mixed with a micellar suspension of EAA in water. The MFC concentration in the suspension is held above the onset of gelling. Hence EAA micelles are kinetically trapped within the continuous fiber network. This phenomenon is visualized using diffusion NMR spectroscopy. Micrographs of the composites show the MFC to be well dispersed within the matrix. Dynamic Mechanical Analysis of composites containing 10wt% cellulose shows an increase in mechanical stiffness compared to the neat matrix, which correlates to the number of network points within the composite.

In summary; EAA-MFC composites of increased strength and stiffness compared to the neat matrix were prepared using water assisted mixing while controlling the MFC concentration. The mechanical properties of the composite can tentatively be fine-tuned by careful control of the number of network points in the initial aqueous suspension.

Electrical conductivities of melt spun PMMA/aligned carbon fibers/carbon black fiber composites

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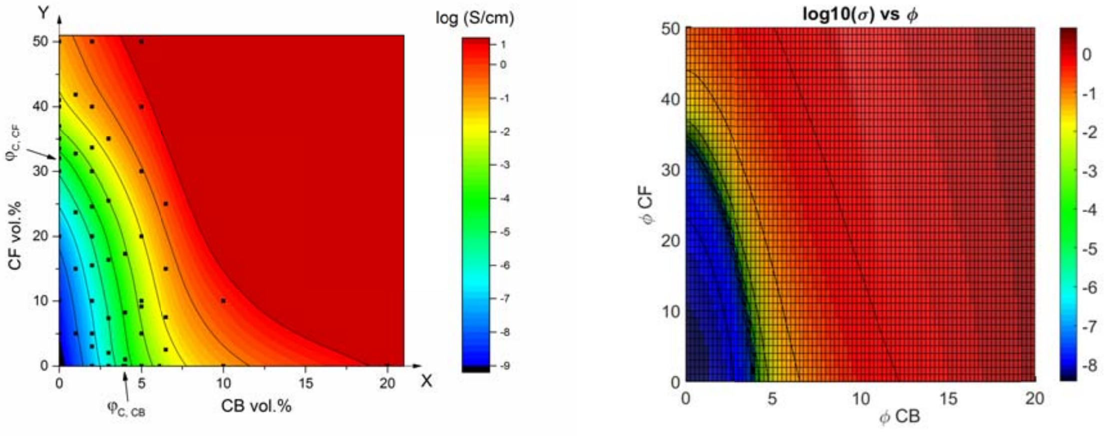
Conductive polymer composites (CPCs) have been widely used in many fields, such as anti-static materials, electromagnetic interference (EMI) shielding, sensor and conductors. Carbon black (CB) and carbon fibers (CFs) are the most commonly used conductive fillers, which can be incorporated into a polymer matrix for facilitating the formation of a CPCs. To evaluate a potential synergic effect between CFs and CB, the effect of the CFs-pathways in a PMMA/CB/CF system should be minimized. Therefore, the melt spinning process is applied in this study, in order to induce a maximum alignment of the CFs in the CPCs and consequently, to reduce the contacts between the CFs.

In this study, percolation thresholds of ternary composites of PMMA/CF/CB as well as PMMA/CF and PMMA/CB composites were investigated. A conductivity contour plot for PMMA/CF/CB composites is presented for the first time (Fig. 1 (a)). Moreover, a novel equation for predicting the electrical conductivity of composites containing two kinds of conductive fillers was proposed (Fig. 1 (b)), showing results close to corresponding experimental data. Our work comprise also systematic measurements of tensile strength for the PMMA/CB/CF composites. A novel and significantly improved effective-media equations for conductive three-component composites is given.



(a) (b)

Fig 1. (a) Experimental logarithm value of conductivity of fiber composites as a function of filler volume fraction of CFs and CB in a contour plot diagram. (b)Calculated logarithm value of conductivity of fiber composites as a function of filler volume fraction of CFs and CB in a contour plot diagram, as generated with novel equation.

Antibacterial silica with carbosilane dendritic systems on the surface

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Bacterial resistance and microorganism contamination is a huge problem, being very important the design of non-antibiotic antibacterial materials [1] for water treatment, food protection, etc. One widely study group with bactericide properties is quaternary ammonium (QA), and their introduction on material surfaces has been done to translate their activity to these materials [2].

Our group have synthesized silica with QA on the surface grouping then in small islands by the use of dendritic structures (Fig. 1). The library of dendrimers and dendrons employed will allow testing the effect in the bactericide properties of topology (dendrons vs dendrimers), generation (size) and type of QA (NMe_3^+, NMe_2H^+, NH_3^+) of dendritic systems.

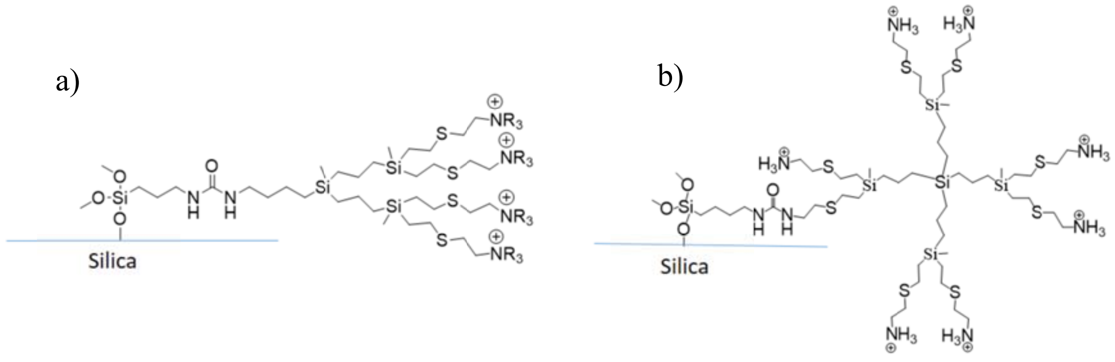

Figure 1: a) Silica with dendron on the surface. b) Silica with dendrimer on the surface.

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Transparency of suture able polycaprolactone nanofiber hydrogel compounds for medical application in the eye

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The treatment of corneal wounds in ophthalmology often requires donor tissue as replacement or wound closure material. Because of insufficient amounts of donor tissue and the inconsistent properties of these biological scaffolds a strong focus was made on development of synthetic materials. Augmented replacements need to be able to resist the force applied on the scaffold during suturing while maintaining its transparency.

Here we developed scaffolds consisting of alginate hydrogel, which were reinforced with electrospun nanofibers made out of polycaprolactone and a blend with chitosan. The transparency of our scaffolds was quantified with a UV-Vis spectrophotometer over the visible light area ranging from 400 to 800 nm. For application relevant measurements a method described by Schubert et. al. [1] was used. A line of text was printed out in different font sizes on which the scaffolds were placed to evaluate the readability of the text lines.

To examine the suture ability of the scaffolds a method developed by Küng et. al. [2] was used. A suture was passed through the sample in a distance of 1 mm to the rim before the sample was clamped in a tensile testing machine. While pulling out the suture the force load was measured which gives us the suture retention strength of the scaffolds.

Compounding both materials leads to scaffolds with high transparency (60-80 %) while maintaining enough mechanical strength for suturing the material in ophthalmic applications [3].

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Thermoplastic poly(ethylene acrylic acid) composites reinforced with cellulose nanofibrils

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Cellulose pulp fibres are well known reinforcing agents in composites. The benefits of using a natural cellulose reinforcing agent is its sustainable origin, abundance, and low cost. Highly fibrillated cellulose pulps, called cellulose nanofibrils (CNF) or microfibrillated cellulose, are small cellulose fibrils with nanoscale diameter and lengths on the micrometer scale. The advantage of CNF compared to pulp fibres is the high length to diameter aspect ratio of CNF, which is an important factor that influences the reinforcing effect in thermoplastic composites. In this work CNFs are used as reinforcement in a thermoplastic poly(ethylene acrylic acid) (EAA) matrix. A novel approach of mixing water dispersed EAA with CNF was used to avoid fibril agglomeration. Using this wet-mixing method, cellulose content of up to 70 vol. % could be achieved in the composites. The mechanical strength of CNF composites exceeded those of plain pulp fibre composites. The stiffness could be improved by a factor of 25 and the strength by a factor of 3. X-ray microtomography reveal the microstructure of the fibres and fibrils in the composites and the wet-mixing method produced well dispersed CNF reinforced composites.

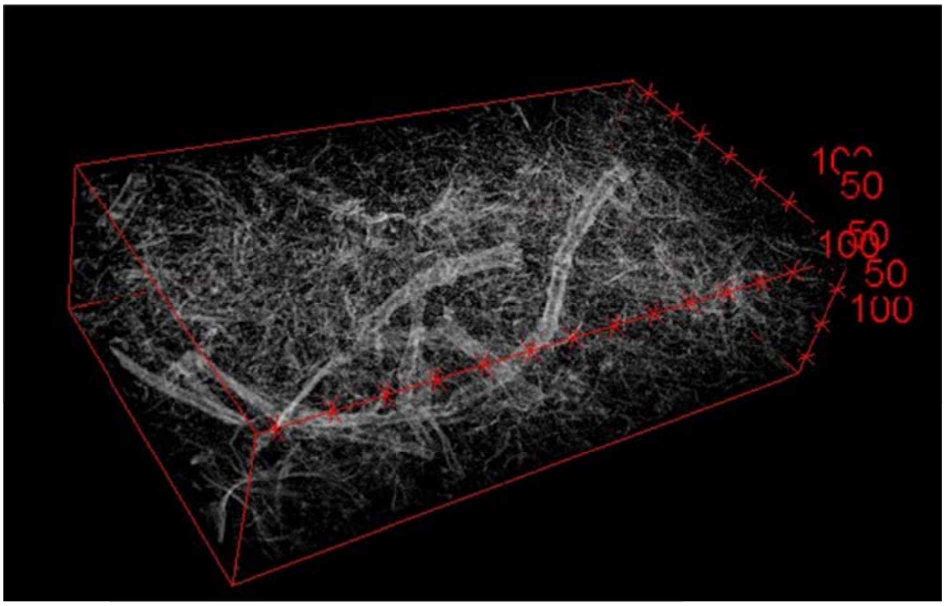

Figure 1. 3D visualization of cellulose composite material

Analysis of the poroviscoelastic behavior of covalently crosslinked hydroxyethylcellulose for biomedical applications

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Hydrogels are three-dimensional polymeric network capable of absorb large amount of water. They are composed of long hydrophilic polymer chains interconnected by cross-links, which prevent the network dissolution. They are used in several frontier fields, such as in drug delivery applications, tissue engineering applications, etc. This work is connected to the use of hydrogels for the treatment of low back pain, where the purpose is to replace degraded "Nucleus Pulposus" with a hydrogel. With the aim of further investigate the hydrogels' behavior, in this work the mechanical characterization of covalently crosslinked HydroxyEthylCellulose (HEC) was carried out and a mathematical model capable of describe the diffusion coupled with the viscoelasticity of hydrogels has been developed, implemented and tested.

The HEC was crosslinked by the Divinyl Sulfone (DVS) and the mechanical properties of the HEC gels were determined through stress relaxation tests and frequency sweeps. The frequency sweep test demonstrated a predominant elastic character and low viscous properties of the prepared HEC gels. Unconfined tests showed that increasing the degree of crosslinking of the HEC, the stress reaches higher values (for a given strain). Regarding the modeling results, an optimization procedure was performed on a stress relaxation test in order to determine the elastic moduli G_1, G_2 and the relaxation time τ. Once the parameters were estimated the model was able to predict the gel behavior at different strains.

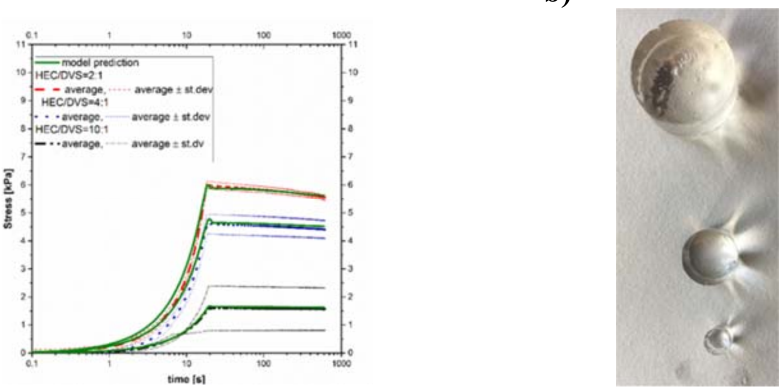
a) **b)**

Figure 1. a) Model predictions of the experimental data resulted from the unconfined compression tests for a given strain;
b) HEC hydrogels with different diameters.

From starch to multifunctional nano-graphene oxide

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Starch represents one of the most abundant and cheap natural plant biomass resources. Graphene (oxide), on the other hand, has attracted tremendous attention due to its excellent mechanical and bio-related properties. We have [1,2] demonstrated an efficient/facile route to prepare novel value-added nano-size graphene oxide (nGO) from starch. Microwave was applied firstly to hydrothermally decompose starch to carbon nanospheres (CN) [1]. CN was then transformed to nGO under oxygen-rich acidic conditions [2]. The formation of CN during microwave irradiation was related to the reactions in the soluble phase: starch hydrolyzed to glucose then dehydrated to levulinic acid and formic acid though 5-HMF as an intermediate. Meanwhile, 5-HMF carbonized/polymerized into CN, which was formed as a solid residue (Figure 1). Further oxidation of CN lead to exfoliation of nGO from the spherical CN. The obtained 0D nGO was about 20×30 nm^2 in the lateral dimension. Due to the unique small and amphiphilic structure, nGO provided unique thermal, crystal, mechanical and barrier properties in PLA/starch biocomposites [2]. It was also proved that nGO is a promising material in bone-related biomedical applications due to its biocompatibility and bioactivity in starch [3,4] and PCL scaffolds [5]. MTT assay proved that nGO is biocompatible with osteo-MG63 cells under a certain high concentration (1mg/mL). Furthermore, nGO could induce hydroxyapatite in mineralization test, reflecting excellent bioactivity. A delicate closed-loop strategy was thus demonstrated: multifunctional nGO was derived from starch and further utilized as property enhancer in starch based composites.

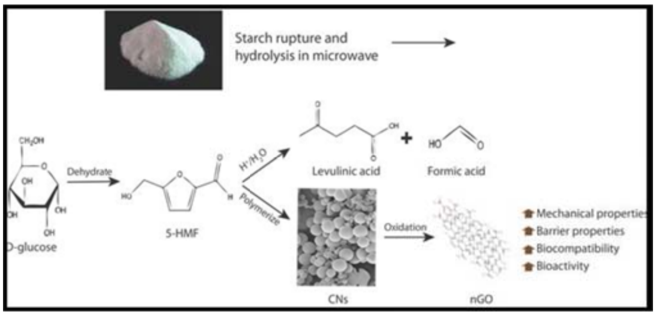

Figure 1. Transformation of starch to nGO

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Synthesis of bio-based and recyclable thermosets

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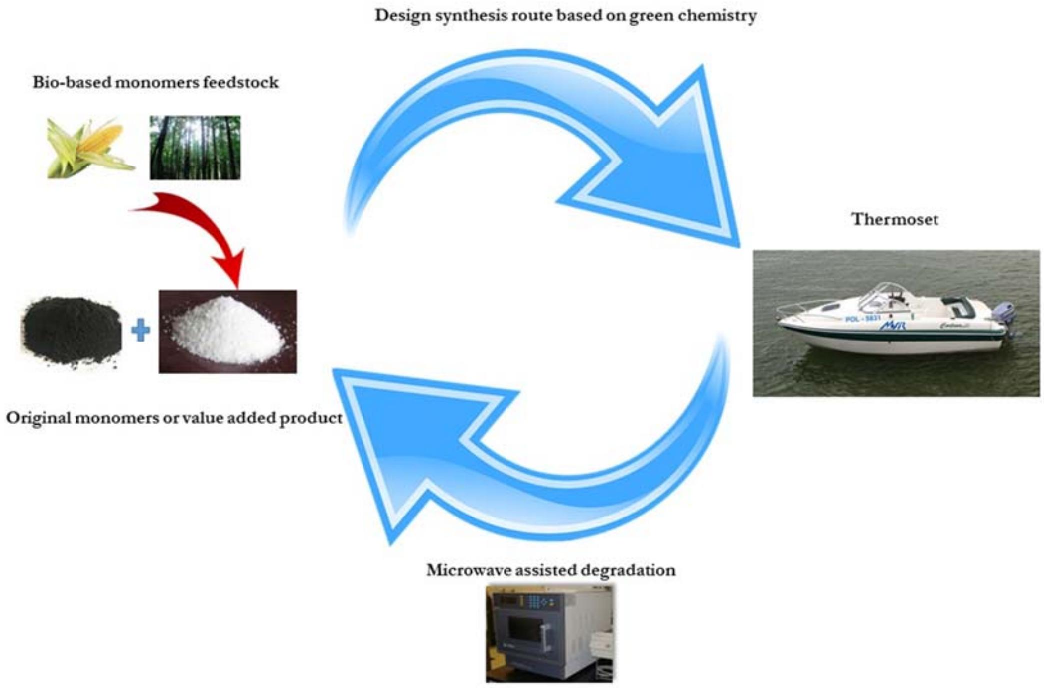
A sustainable society is an ultimate goal for a modern country considering the problem of depleting petroleum resources and growing polymer waste issues. Much interest has, therefore, been focused on the development of renewable bio-based materials. At the same time recycling of thermoplastics is rapidly developing and new recycled products have reached the market. Bio-based thermosets are in comparison with the bio-based plastics more difficult to recycle due to their inherent crosslinked structure. The aim of this project is to develop a series of strong and rigid bio-based thermosets as well as to develop a process for their recycling through microwave-assisted technology. The aim is to obtain high quality building-blocks for production of new materials in a closed-loop process. We are developing a novel series of thermosets by designing unsaturated polyester resins (UPs) and their crosslinking chemistry. The thermosets are based on isosorbide which is constituted of a bicyclic ring structure that will ensure stiffness to enhance the thermomechanical properties of UPRs. All the monomers in the UPRs are derived from renewable resource and no solvent is used during the polymerization reaction. This work contributes to development of future bio-based resin applying the principals of green chemistry.



Simulating the electric conductivity of the conductive polymer composites

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The geometrical distribution of the fillers has a large impact on the electrical properties of the composites. Many excellent theoretical studies via simulations have already been conducted in order to investigate the relationship between geometry and electrical properties. Most of these studies have however assumed an idealized isotropic orientation of the fillers, and focused on only one variable of geometrical distribution. Therefore, a universal and anisotropic platform of simulation, containing three simulation modules are explored [1]. The simulation modules are: finite element modelling (FEM), percolation threshold modeling (PTM) and electrical networks modelling (ENM). After constantly updating and improving in the past years, the simulation platform performs high degree of flexibility, high degree of automation, high efficiency and high accuracy (Fig. 1).

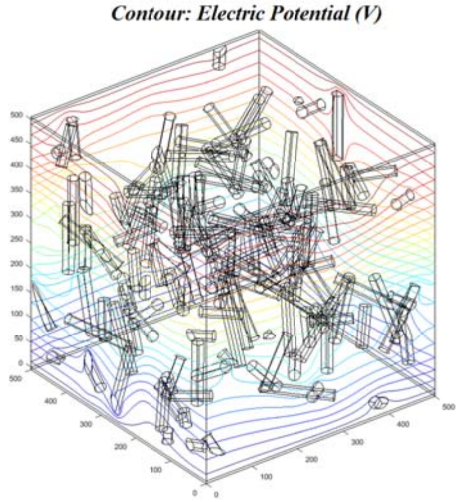

Fig. 1. A simulated contour of electrical potential of anisotropic composites with 1-D conductive fillers.

Within the platform, all the factors could be controlled as either constant or variable, and a deeper understanding of the relationship between different factors is comprehended. An experimental consideration with multiple levels of variables is carried out, and the synergistic relationship of the variables could be systematic studied. The trend of change in each variable under different environmental settings is clearly displayed and systematically studied by the simulation platform.

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Cellulose-fiber-based insulation materials with improved reaction-to-fire properties

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The poor reaction-to-fire properties of cellulosic thermal insulation need to be improved to meet the safety regulations for building materials. In this study, cellulose-fiber-based insulation foams were prepared from formulations containing mechanical pulp and commercial fire retardants. Results of single-flame source tests showed that foams developed from the formulations with 20% expandable graphite (EG) or 25% synergetic (SY) fire retardants had substantially improved reaction-to-fire properties, and passed fire class E according to EN 13501-1. The results indicated that the foams could resist a small flame attack without serious flame spreading over a short period of time. Compared with the reference foam that contained no fire retardant, the peak heat release rate of the 20% EG and 25% SY foams decreased by 62% and 39% respectively when the samples were subjected to a radiance heat flow of 25 kW m^{-2} in a cone calorimeter, which suggested enhanced reaction-to-fire properties of these foams.