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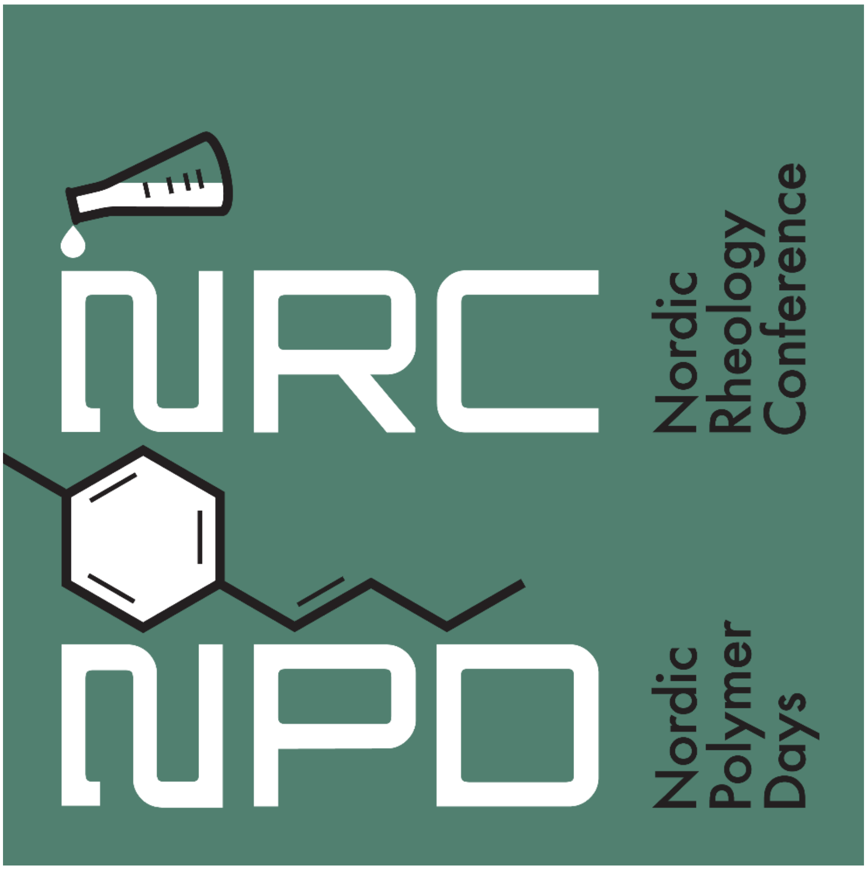

Cyberspace

August 18-20, 2021

Dear Participant

Nordic Polymer Days (NPD) and Nordic Rheology Conference (NRC) are annual meetings circulating among the Nordic countries. Both have a long history - in 2021 NPD will be organized for the 57th time and NRC for the 31st time. This year's conference is also the third of the combined NRC-NPD, the previous ones having been held in 2011 and 2016. Yet this time everything is different – instead of a physical meeting gathering scientists to one of our Nordic cities, the COVID-19 pandemic restrictions have forced us firstly to postpone the conference by one year and eventually to organize the event as a virtual conference.

This year the conference is a joint effort of the Society for Wood and Polymer Chemistry in Finland (SPPY) and Nordic Rheology Society (NRS). This collaboration resulted in a top-quality programme attracting colleagues in the field of biomaterials, polymer science and rheology from all over the world. The organisers are pleased to welcome the conference participants to enjoy the stimulating talks, informal virtual atmosphere and discussions with colleagues and friends. We encourage young scientists and students to have discussions with world-class experts and use this unique opportunity for networking.

We wish to thank all who have contributed organising this event: plenary speakers, exhibitors, contributing universities, research institutes and companies, and participants.

Conference Chair, Dr. Olli-Ville Laukkanen, RWTH Aachen University

Conference Co-chair, Dr. Sami Hietala, University of Helsinki

Conference Co-chair, Dr. Sami-Pekka Hirvonen, University of Helsinki

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NRC&NPD2021 conference program

Sessions of the Nordic Rheology Conference in blue background

Sessions of the Nordic Polymer Days in green background

Please note that all times are in Eastern European Summer Time (EEST, UTC+3)

Wednesday, August 18

EEST	Blue Hall	Green hall	Red hall
9:45-10:00	Opening ceremony		
10:00-10:40	Plenary 1: Kiyohiko Igarashi *"Enzymatic degradation and synthesis of crystalline cellulose"*		
10:40-11:10	Break & Mingle		
	Session: Rheology of biopolymers	**Session: Polymer synthesis**	**Session: Sustainable polymers**
11:10-11:30	Tuukka Levä: *"Immobilized Photosynthetic Cell Factories – Multicomponent Hydrogels from Nanocellulose and Alginate for Cell Entrapment"*	Vikram Baddam: *"Polycation stabilized nanoparticles obtained via PISA: salt induced higher ordered morphologies"*	Linnea Cederholm: *"δ-Lactones in a Circular Economy"*
11:30-11:50	Prakash Baranivignesh: *"Experimental investigation on the effect of fibre consistency on rheology of aqueous foams in pipe flow"*	Jukka Niskanen: *"1,2,3-triazole based poly(ionic liquids) as solid dielectric materials"*	Jenevieve Yao: *"Microwave-hydrophobized lignin/PLA blends for fused filament fabrication 3D printing"*
11:50-12:10	Sylwia Wojno: *"Phase transitions of cellulose nanocrystal suspensions via rheo-PLI and nonlinear oscillatory shear techniques"*	Dirk Kuckling: *"Backbone vs. side-chain: (light-) degradable polymers for triggered drug release"*	Arianna Rech: *"Waste-based biopolymer slurry for 3D printing with recycled materials"*
12:10-12:30	Aayush Kumar Jaiswal: *"Rheological Properties of High-Consistency Enzymatically Fibrillated Cellulose Suspensions"*	Muhammad Waqas Ali: *"Synthesis and Characterization of multi responsive hybrid microgels for controlled drug delivery with maximum drug loading capability"*	Wenxiang Xuan: *"Levulinic acid: Sustainable building-block for diverse plasticizer architectures"*
12:30-13:30	Lunch break		
13:30-14:10	Plenary 2: Anne-Marie Hermansson (Carl Klason Rheology Award Lecture) *"Structure related rheology of food and biopolymers systems"*		
	Session: Food rheology	**Session: Biopolymers**	**Session: Sustainable polymers**
14:15-14:35	Mats Stading: *"Bolus rheology of texture-modified food"*	Jingwen Xia: *"Phase-separation of Cellulose from Ionic Liquid upon Cooling: Preparation of Microsized Particles"*	Nitin Valsange: *"Preparation and investigation of biobased aliphatic polyesters based on a rigid spirocyclic dicarboxylate derived from levulinic acid"*
14:35-14:55	Johanna Andersson: *"Sound analysis of swallowing a shear-thinning fluid"*	Vladimir Aseyev: *"Regeneration of Cellulose from Ionic Liquids in a Form of Particles"*	Charalampos Pronoitis: *"Biobased and Functional Polyamides and Polyhydroxyurethanes"*
14:55-15:15	Mats Stading: *"A mechanical model of the human throat for swallowing rheology"*	Matti Leskinen: *"Regeneration of cellulose beads from [DBNH][OAc]DMSO; a study on the bead formation process and effects of drying on cellulose structure"*	Hossein Baniasadi: *"Bio-based long-chain aliphatic polyamides"*
15:15-15:45	Break & Mingle		
	NRC industry workshop **Hosted by Fredrik Innings & Gustaf Mårtensson**	**Session: Biopolymers**	**Session: Polymer composites & processing**
15:45-16:05		Anish Gulati: *"Behaviour of Tetrabutylammonium Carboxymethyl cellulose in organic solvents"*	Dirk W. Schubert: *"Novel theoretical self-consistent mean-field approach to describe mechanical properties of composites and polymer solutions"*
16:05-16:25		Suvi Arola: *"The role of ions and surface water in nanofibrillated cellulose networks"*	Yingwei Ouyang: *"Thermomechanical Reinforcement of Polyethylene/Polypropylene Blends for High Voltage Cable Insulation by Compatibilisation with a Styrenic Block Copolymer"*
16:25-16:45		Bas van Bochove: *"Photo-curing biopolymers for tissue regeneration; individually designed composites by stereolithography"*	Linda Salminen: *"Tough materials through ionic interactions"*

Thursday, August 19

EEST	**Blue Hall**	**Green hall**	**Red hall**
9:55-10:00	Opening of the day		
10:00-10:40	Plenary 3: Robert Luxenhofer *"An old pony is teaching us new tricks - Poly(2-oxazoline)s and poly(2-oxazine)s: From self-assembly to drug-delivery and 3D printing"*		
10:40-11:10	Break & Mingle		
	Session: Rheology of sustainable materials	**Session: General rheology**	**Session: Functional polymers**
11:10-11:30	Tuna Baydin: *"Optimization and Improvement of the Thermal Stability of Fish Gelatin"*	Olli-Ville Laukkanen: *"Interfacial shear and dilatational rheology of polyelectrolyte microgel monolayers at the oil-water interface"*	Justina Vaicekauskaite: *"Field Concentration Use in Electroluminescent Devices"*
11:30-11:50	Catherine T. Nordgård: *"CLEX alginate gelling technology: a versatile tool for production of biomaterials"*	Gustaf Mårtensson: *"Production of satellites during impact of dense suspensions on a flat surface"*	Ida Östergren: *"3D-printing of Plastic Plasmonic Hydrogen Sensors"*
11:50-12:10	Dipankar Ghosh: *"Enhanced Mechanical Stability in Multi-component Supramolecular Gels Based on Enantiomers"*	Roland Kádár: *"Progress and challenges on relating 'nonlinear oddities' in oscillatory shear to structural buildup in nanostructured fluids"*	Tony Tiainen: *"Capture of CO2 by using acrylate based polymers with amine functionalities"*
12:10-12:30	Deepika Malhotra: *"Enhancing the mechanical compatibility of natural biomaterials with native human skin"*	Dragana Arlov: *"Developing an improved methodology to measure viscosity of hot-swelling starch"*	Chonghui Li: *"Magnetochromic elastomer with controllable instant color changes"*
12:30-13:30	Lunch break		
13:30-14:10	Plenary 4: Bernhard A. Wolf *"Large scale fractionation of polymers and advanced viscometric methods"*		
	Session: Rheology of biopolymers	**Session: Advances in rheometry**	**Session: Functional polymers**
14:15-14:35	Antti I. Koponen: *"The effect of consistency on the shear rheology of aqueous suspensions of cellulose micro- and nanofibrils"*	Jörg Läuger: *"Rheo-optical tools for polymer applications"*	Sami Hietala: *"Poly(N-acryloyl glycinamide) microgels for encapsulation of catalysts"*
14:35-14:55	Leevi Viitanen: *"Effect of surfactants on the rheology of cellulose nanofiber suspensions"*	Christian Fengler: *"Low-field RheoNMR: In-situ correlation of local segmental mobility with mechanical properties during hydrogel synthesis"*	Dominik L. Braunmiller: *"Static and dynamic control of magnetic microgels"*
14:55-15:15	Meri Lundahl: *"Effect of carbon nanomaterials on the rheology and spinnability of cellulose solutions"*	Henri G. Burhin: *"A new and highly efficient method to measure the steady shear viscosity and wall slip of rubber compounds. Closed boundary rheometer (RPA)"*	Nabanita Hazra: *"Capillary Driven Self-Assembly of Ellipsoidal Composite Microgels at the Air/Water Interface"*
15:15-16:45	Poster session & Social activities		

Friday, August 20

EEST	Blue Hall	Green hall	Red hall
9:55-10:00	Opening of the day		
10:00-10:40	Plenary 5: Tiina Nypelö *"Wood-based hemicelluloses: What are the key properties to enable future applications?"*		
10:40-11:10	Break & Mingle		
	Session: General rheology	**Session: Biopolymers**	**Session: Functional polymers / Sustainable polymers**
11:10-11:30	Katarina Dimic-Misic: *"Limitations on rheological properties of particulate suspensions arising from addition of a mesoporous ancillary mineral: exemplified by pin coating of a functional gas filter layer"*	Jon Trifol: *"3D-printed thermoset biocomposites based on Forest Residues by Delayed Extrusion of Cold Masterbatch (DECMA)"*	Sepideh Zokaei: *"Electrically Conducting Elastomeric Fibers with High Stretchability and Stability"*
11:30-11:50	Augusto Cannone Falchetto: *"On the Rheology of Asphalt Mastic Containing Mining Filler"*	Emile R. Engel: *"Melt processing of cellulosic fibres with only water as plasticiser"*	Xiaoya Li: *"Nonionic antimicrobial hyperbranched polyesters with indole or isatin functionalities"*
11:50-12:10	Arild Saasen: *"Properties of Dense Barite Sediments from Water-Based Drilling Fluids Oscillatory Viscosity Measurements of Wet Barite Powder"*	Roberta Teixeira Polez: *"Cellulose nanofibers/lignin particles/tragacanth gum nanocomposite hydrogels for biomedical applications"*	Smita V. Mankar: *"Synthesis And Lca Of Vanillin-Based Spirocyclic Diol Toward Fiber And Packaging Applications"*
12:10-12:30	Mahmoud Khalifeh: *"Rheological Characteristics of Oil-Based and Water-Based Drilling Fluids"*	Maryam Mousa: *"Bio-based lactones – Exploring their free-radical polymerization and polymer properties"*	Harald Silau: *"Valorization of lignin for coating applications"*
12:30-13:30	Lunch break		
13:30-14:10	Plenary 6: Minna Hakkarainen *"Carbon dot/polymer composites for biomedical, environmental and packaging applications"*		
	Session: Non-Newtonian fluid mechanics	**Session: Biopolymers**	**Session: Polymer composites & processing**
14:15-14:35	Janaki Umashanker: *"The shear and extensional rheology of aqueous xanthan gum solution using the Giesekus multi-mode model"*	Tuuli Virkkala: *"Hemicellulose cross-linked nanocellulose as immobilization matrix for photosynthetic cell factories"*	Angelica Avella: *"Synergic effect of water in reactive melt crosslinking of thermoplastic/thermoset poly(ε-caprolactone)/cellulose nanocrystals biocomposites"*
14:35-14:55	Christos K. Georgantopoulos: *"Qualitative modeling to predict the extrusion flow instabilities in polybutadiene sample: Influence of die geometry"*	Ville Rissanen: *"Nanocellulose-Based Immobilization Matrices For Photosynthetic Cell Factories"*	Muhammad A. Munawar: *"Highly Oriented Electrospun Conductive Nanofibers of Biodegradable Polymers-Revealing the Electrical Percolation Thresholds"*
14:55-15:15	Dragana Arlov: *"Predicting pressure drop in pipes with tomato paste and concentrated orange juice. One successful and one failed prediction"*	Nesibe Dogan: *"Cellulose nanocrystal-based bio-nanocomposite matrix for cell immobilization with continued photosynthetic activity"*	Ezgi Ceren Boz Noyan: *"Processing and properties of polyethylene plastics packaging waste"*
15:20-16:00	Closing ceremony		

Plenary lectures

Enzymatic degradation and synthesis of crystalline cellulose

Kiyohiko Igarashi [1,2,]

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Advances in enzyme technology let us know detailed mechanisms of cellulose degradation and synthesis in molecular level. We recently published how processive cellulases evolved from non-processive enzymes. This process is similar to "convergent evolution" like relationship between shark and dolphin, which have similar shape of body while they are quite different species each other. Processive cellulases have common feature with asymmetric subsite covered by loops, and these structural features are well conserved in processive cellulases.

In enzymatic synthesis of cellulose, we have launched cellodextrin phosphorylase and its substrate to International Space Station, and synthesized cellulose crystal under microgravity to understand the effect of gravity for cellulose synthesis. Since density of cellulose is about 1.5, cellulose synthesized at ground is always precipitated, while the space cellulose was quite homogeneous gel-like material.

Structure related rheology of food and biopolymers systems

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Structure related rheology play an important role for the understanding of product properties. First, we need a basic understanding of the material under consideration. From a structural point of view this is complicated as we have to cover a broad range of length scales, starting from the molecular level of the biopolymer characteristics to the behavior in a multiphase system and further implications on the macro scale. This means that knowledge is required from the nanometers to millimeters and a combinations of microscopy techniques are needed.

In many cases information about the microstructure can help us to understand the rheological behaviour of a product. With regard to the rheology, it is important to consider both the strength and rheology during structure formation as well as the failure properties. This is especially important for food and consumption products, where the breakdown performance will determine whether we like product or not. From a fundamental point of view, micro rheology in combination with microscopy can reveal how structure respond to stress concentrations as well a crack propagation in initial stages of break down.

In a real situation the properties of a product are determined by the process and to follow ant control the rheology is crucial in order to obtain products with the desired properties. In precision engineering the rheology can be tuned in unit operations, providing there is a proper understanding of the process-structure rheology relationships. Finally, the dynamics of complex systems are important. Structure as well as rheology have a bearing on mass transport properties such as diffusion of water as well as active components. New microscopy approaches, scattering techniques and the potential to handle big data sets open up new possibilities to increase our understanding of complex structure- rheology relationships.

An old pony is teaching us new tricks - Poly(2-oxazoline)s and poly(2-oxazine)s: From self-assembly to drug-delivery and 3D printing**

Lukas Hahn[1], Haider S. Malik[1], Michael M. Lübtow[1], Theresa Zorn[2], Josef Kehrein[3], Anna-Lena Ziegler[1], Vladimir Aseyev[5], Christoph Sotriffer[3], Ann-Christin Pöppler[2,], and Robert Luxenhofer[1, 5]*

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**This contribution is dedicated to the memory of Prof. Françoise Winnik.

The polymer families of poly(2-oxazoline)s and poly(2-oxazine)s have been known for decades, but even though in early work by Zalipsky et al. their potential as alternative to PEG for the fabrication of stealth liposomes was noted [1], they did not see wide spread attention. With promising first-in-human results for a poly(2-oxazoline)-drug conjugate (SER-214)[2] and other exciting academic development in the last decade [3], interest in poly(2-oxazoline)s and – more recently – poly(2-oxazine)s seems to be increasing significantly. We have studied in particular new amphiphilic block copolymers and their self-assembly in recent times, with a focus on novel monomers and monomer combinations, and have found very interesting structure property relationships with respect to the solubilization of hydrophobic drugs [4] and temperature induced self-assembly and gelation. Of particular interest are observations highlighting the importance of the hydrophilic block of amphiphilic block copolymers in some of these self-assemblies, either in drug solubilization [5] or in the self-assembly via interaction with the hydrophobic block [6].

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Large scale fractionation of polymers and advanced viscometric methods

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The lecture starts with a short description of methods providing access to technically interesting amounts of polymers that are freed from harmful components, like too short/long chains or other components. Its main part presents some recent developments in the field of the flow behaviour of polymer solutions and polymer melts.

The basis of a new look at some fundamental problems of rheology rests on the following approaches and observations, respectively.

- A universal definition of the intrinsic viscosity, enabling its reliable determination for polyelectrolyte solutions in pure water, i. e. in the absence of extra salt.[1]
- The modeling of the viscosities of polymer solutions over the full range of compositions by means of two to three adjustable parameters only.[2]
- The introduction of the *intrinsic bulkiness* - as the analogue of the intrinsic viscosity - for vanishing solvent content of the solution.[3]
- The treatment of shear thinning as a first order disentanglement process enabling the reliable extrapolation of measurements outside the Newtonian regime to zero shear.[4]
- The introduction of clear-cut criteria for the determination of viscometric cross-over concentrations in contrast to cross-over concentrations under equilibrium conditions.[5]

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Wood-based hemicelluloses: What are the key properties to enable future applications?

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Wood-based polymers are notorious for the renewable origin and intrinsic non-toxicity. Polymer engineering, however, poses various other demands regarding processing, solubility, and reproducible physico-chemical properties. I will give an overview on the opportunities and challenges of wood-based polymers for materials engineering with focus on the polysaccharides and introduce current work on wood xylans. Wood xylans are renewable natural materials that have potential for future use in bio-based engineering and we continuously work towards film applications. The poor water interaction of xylans hinders dissolution and film production but can be overcome by chemical modification of xylan to alter its properties [1].

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Carbon dot/polymer composites for biomedical, environmental and packaging applications

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Carbon dots (CDs) have captivated tremendous interest in multiple applications due to attractive properties from good biocompatibility to intriguing optical properties. Here we will present a facile microwave-assisted route for preparation of CDs from various biomass resources[1] and show examples of the great value and versatility of these multifunctional CDs to enhance the properties of biobased materials in packaging,[2,3] biomedical[4] and environmental[5] applications. The zero-dimensional amphiphilic CDs provide unique thermal, mechanical and barrier properties in polylactide (PLA) and PLA/starch composites for packaging applications. CDs incorporated into biomedical scaffolds demonstrate good biocompatibility and attractive bioactivity by inducing calcium phosphate mineralization on the surface of the scaffolds. This makes CDs a promising additive for bone-related biomedical applications. Furthermore, CDs can assist in drug loading and release from biomedical scaffolds. CDs also stabilized porous bioresorbable scaffolds and improved the electrospinnability of starch and PLA fibers. In environmental applications the rheological properties, swelling ratio, degree of crosslinking and adsorption capacity of chitosan and carboxymethyl cellulose hydrogels could be tuned by addition of CDs. Recently we also demonstrated that incorporation of CDs in cellulose acetate rendered the material enhanced degradability under open environment relevant conditions.[6] This was achieved by photocatalytically activated deacetylation, the bottleneck for biodegradation of cellulose acetate. The weight loss of CD modified cellulose acetate after 30 days in simulated sunlight was 43% or 53% for materials aged in artificial sea water and air, respectively. This can be compared to 4% and 12% weight loss for cellulose acetate without CDs under same conditions.

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Wednesday, August 18

NRC

Session: Rheology of biopolymers

Immobilized Photosynthetic Cell Factories – Multicomponent Hydrogels from Nanocellulose and Alginate for Cell Entrapment

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The development of immobilized photosynthetic microbial cell factories has recently been highlighted as a promising pathway to sustainably produce a range of chemicals, including biofuels[1] and polymer precursors[2]. However, the cell immobilization matrices must be improved to withstand the forces present in a photobioreactor. In addition to the wet-state mechanical requirements, the matrices need to be biocompatible, transparent, and porous to enable photosynthesis within them. With a global trend of sustainability, the matrices would preferably be biodegradable and of natural origin. Recently, TEMPO-oxidized cellulose nanofibers (TCNF) have been shown to outperform conventional matrix structures made from polymeric alginate. However, additional crosslinking with synthetic polyvinyl alcohol (PVA) is required in TCNF matrices to achieve sufficient wet strength.[1, 2] Here, we created immobilization matrices by physically cross-linking TCNFs with ionically crosslinked alginate to make self-standing thin-layer hydrogels with interpenetrating network structures. The objective of the study was to apply the double network (DN) technique[3] in dilute conditions suitable for photosynthetic cells. We discovered that the addition of TCNF in the multicomponent hydrogels with 1 wt% total solid content improves the mechanical properties of the hydrogels under shear stress, and that the physical crosslink between TCNF and alginate can replace the covalent PVA crosslink used in the TCNF reference material. These findings showcase the potential of "solid-state" cell factories as an alternative to conventional suspension cultivation of cells.

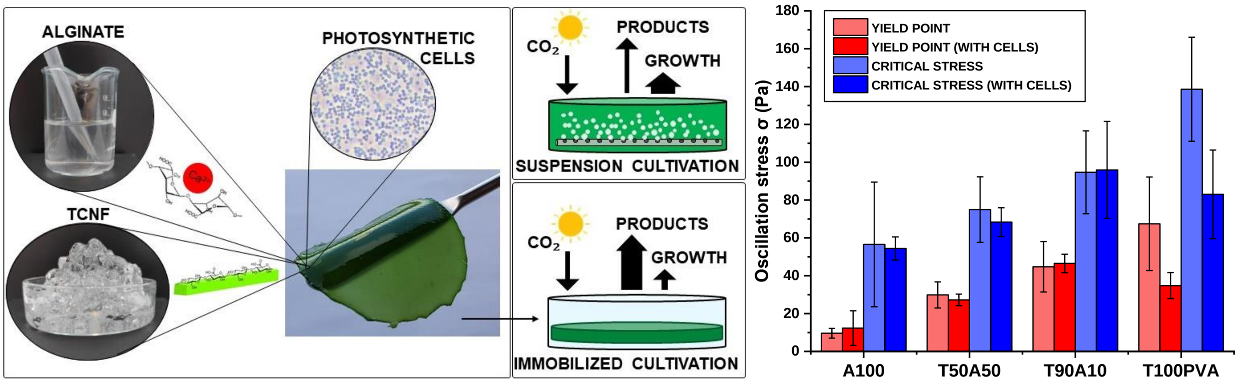

Figure 1. A: Concept of an immobilized photosynthetic cell factory. B: Yield point and critical stress values for different immobilization matrices from alginate (A) and TCNF (T) with and without immobilized cells.

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Experimental investigation on the effect of fibre consistency on rheology of aqueous foams in pipe flow

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Due to recent development of foam forming for making fibrous structures (instead of traditional water forming), understanding on the rheology of aqueous fiber foam has become a necessity [1]. However, this topic has been almost completely neglected in the existing academic literature; there are only two earlier papers on this topic [2][3], and most basic questions remain unanswered. Here we present results on the effect of fiber consistency on the rheology of aqueous fiber foams. Hardwood (birch) fibers were used at mass consistencies of 2, 3, 4 and 5%. Air content was 70% and SDS was used as the surfactant. The measurements were performed with a pipe rheometer, as normal rheometer geometries are unsuitable for these materials. In addition to shear rheology, slip flow at the pipe walls was also studied. The viscosity behaviour of the foams followed accurately a power law with all consistencies. Flow index was n ~ 0.4 and it decreased slightly with increasing consistency. The consistency index K was linearly dependent on consistency. The interaction between the fibers is thus clearly weaker in foam than in pure water. The slip behavior was similar for all consistencies.

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Phase transitions of cellulose nanocrystal suspensions via rheo-PLI and nonlinear oscillatory shear techniques

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Cellulose nanocrystals (CNC) extracted from the abundant, renewable natural polymer cellulose, show significant potential for many applications, either as material on its own or as renewable reinforcement in polymers. The intrinsic interaction between cellulose nanocrystals results in hierarchical ordering in CNC suspensions. Cellulose nanocrystals (CNCs) can self-assemble into nematic and chiral nematic structures, exhibiting birefringence above a critical concentration. In this work we explore CNC phases through a combination of rheo-PLI (polarized light imaging) and nonlinear oscillatory shear (Fourier- Transform Rheology and stress decomposition). Aqueous CNC dispersions with concentrations spanning the biphasic (BP) and liquid crystalline (LC) phases (2-9 wt% CNC), as identified based on birefringence, steady shear and linear viscoelastic oscillatory shear data, were investigated. From nonlinear rheological point of view, for the lowest concentration that approaches the concentrated isotropic - BP transition, a significant angular frequency dependence on the third relative higher harmonic (I 3/1) in terms of both scaling exponents, including non-quadratic scaling, and magnitude was recorded. At the transition to LC, I 3/1 suggests multiple scaling laws in the MAOS region, including a quadratic scaling strain amplitude range. All concentrations exhibit nonlinear intra-cycle strain stiffening behavior, with weak angular frequency dependence. Already for BP concentrations, a transition from intra-cycle shear thickening to intracycle shear thinning was recorded. The intra-cycle shear thickening behavior was significantly increased for CNC concentrations in the LC phase.

Rheological Properties of High-Consistency Enzymatically Fibrillated Cellulose Suspensions

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Cellulose nanomaterials (CNMs) are promising renewable, bio-based and biodegradable materials, which have been explored for numerous applications in packaging, electronics, biotechnology, etc. These exciting applications have led to the development of various CNM production methods. However, challenges related to production costs still prevail and often the resulting material is at low consistency, typically between 1–5%, which limits logistics. If one up-concentrates the material to high consistency, the resulting high viscosity makes it difficult process the material further into products. To overcome these challenges, a high-consistency enzymatic fibrillation (HefCel) technology was developed at VTT, allowing nanocellulose production at 10%–25% consistency with significantly lower energy consumption compared to other manufacturing methods [1]. The material also possesses much lower viscosity than the other conventional grades of CNMs.

This work studies the rheological behavior of CNMs prepared using the HefCel technology. The effect of enzyme dosage and the raw material type on the CNM flow properties is explored. Three different bleached chemical pulps viz. never-dried softwood, once-dried softwood, and once-dried hardwood pulp were used along with three different enzyme dosage levels to each pulp type to produce nine different HefCel grades. All HefCel grades were characterized for their rheological behavior and the flow behavior was also compared to other conventional CNM grades (Figure 1). Moreover, morphology of the HefCel grades was correlated with their corresponding rheological behavior in order to determine a structure-property relationship.

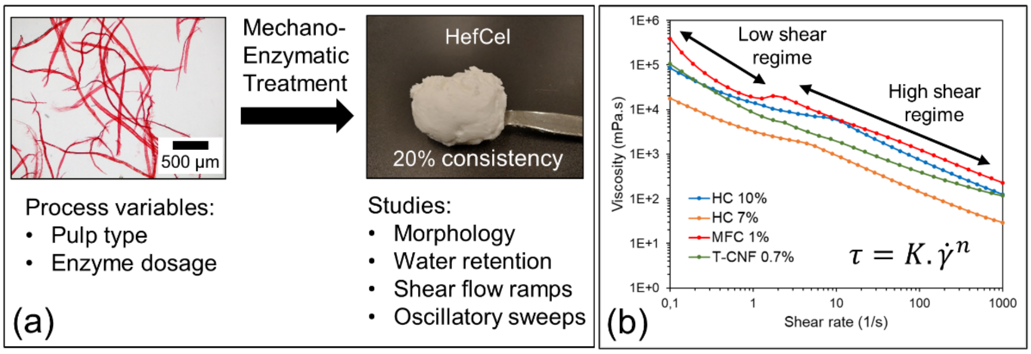

Figure 1. (a) Experimental scheme of the study, and (b) forward shear ramps for HefCel (HC) samples at 7 and 10% consistency as compared to microfibrillated cellulose (MFC) and TEMPO-oxidized cellulose nanofibrils (T-CNF). The flow curves were divided into flow regimes and power law fitting was done for each regime [2].

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Wednesday, August 18

NRC

Session: Food rheology

Bolus rheology of texture-modified food

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Healthy individuals apply unconscious, but well-coordinated strategies for oral processing producing easy-to-swallow boluses. However, for an increasing proportion of the population the actual swallowing causes problems. Swallowing disorders, or dysphagia, affects 40% of the ones older than 70 due to dementia, trauma or medication side effects. Dysphagia management consists of intake of texture-modified foods with texture depending on the severity of the disorder. The food texture is modified according to common practice and guidelines, whereas it is actually the rheological properties of the bolus that affects safety and ease of swallowing rather than the food itself.

Bolus rheology was determined for five healthy subjects for a set of such solid foods regularly given to dysphagia patients. The softest class was gel food, then a smooth timbale which both were compared to the corresponding regular, un-modified food. The foods investigated were bread, cheese, tomato and the combination as a sandwich, all for the respective texture class: gel, timbale and regular food. The subjects chewed until ready to swallow and the expectorated bolus was immediately measured for complex shear modulus and viscosity, and moisture and saliva content were determined.

Rheometry shows that texture-modification influenced bolus rheology with decreased viscosity and modulus for increased degree of modification. Also saliva content as well as chews-to-swallow decreased with degree of modification. Overall, the bolus saliva content was lower for the combination (sandwich) than for the individual components. The phase angle for all boluses was also relatively constant, indicating a similar bolus structure. All boluses of the texture-modified foods showed high extensional viscosity, which is important for bolus cohesiveness.

Bolus rheology rather than food texture determines if a food is safe to swallow and the results show that the intended texture-modification is reflected in the flow properties of the respective boluses.

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Sound analysis of swallowing a shear-thinning fluid

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Dysphagia or problem in swallowing is common among elderly, which is especially an issue in countries having a high number of elderlies in their population. The reasons are numerous, among them are stroke and sarcopenia. The common way to detect dysphagia is the observation of swallows with videofluoroscopy. However, these facilities are costly and rare. GOKURI is an AI-powered smartphone-based point of care neckband type device for the assessment of the swallowing function.[1] The device, which has been developed for liquid boluses, uses the sound of the bolus moving alone the pharynx as well as the sound from swallowing related anatomical events such as the nasal passage closing or the closing of the upper esophageal sphincter to evaluate the frequency profile and detect the length of a swallow.[1] In this study, edible model fluids exhibiting Newtonian, shear-thinning and a Boger flow behaviour containing water, maltodextrin and xanthan gum in different concentrations while having the same viscosity at a shear rate of 50 s^{-1} were developed.[2] Those model fluids were ingested and the sound spectra recorded using GOKURI and were compared to plain water. Within the 8 test subjects, the results indicated that there was a significant difference in swallowing duration between water and the shear-thinning fluid, see Figure 1. The swallows had large individual variations and a mean of 0.91 (±0.22) seconds. Water was 0.13 s faster to swallow than the shear-thinning fluid with a significant difference with 95% confidence interval. We hypothesize that the shear-thinning fluid is elongated in the throat as it has high extensional viscosity due its xanthan content as compared to water.

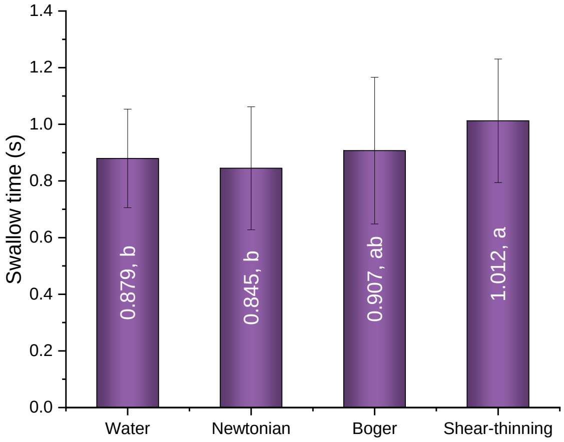

Figure 1. Mean swallowing durations of water as compared to model fluids. Different letters denote significant differences (*$p<0.05$*).

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A mechanical model of the human throat for swallowing rheology

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The human throat is a complex, active channel transporting both food and air to our internal organs. The upper part, the pharynx, is critical for correct swallowing and rely on coordination between breathing and food transport. A multitude of disorders may occur which are collectively referred to as dysphagia. There is a strong correlation between dysphagia and age, and it affects 10-30% of all people aged 65 and above. In Sweden, the fraction of the population older than 65 is 20% and in Japan, it is approaching an outstanding 30%, as compared to the global average which is less than 10%. Life expectancy is also expected to increase globally. Persons suffering from dysphagia must drink thickened beverages and eat texture adjusted foods.

The product development of thickeners and texture-adjusted foods require confirmation of the effect on swallowing. This can be done in a mechanical model of the throat before involving dysphagia patients. A previous research model, the "Gothenburg Throat" [1] has been modified for product development and its function verified. This new model is robust and easy to use and regulate through a touch screen interface. Swallowing of water and thickened water in the model simulate swallowing disorders showed aspiration of the water but as in vivo not for the thickened water.

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Wednesday, August 18

NPD

Session: Polymer synthesis

Polycation stabilized nanoparticles obtained via PISA: salt induced higher ordered morphologies

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Polymerization induced self-assembly (PISA) has emerged as a versatile tool to study self-assembling of block copolymers especially with controlled radical polymerization techniques. In PISA, the block copolymers undergo in situ self-assembling during the polymerization, where solvophilic blocks are chain extended with other monomers that form solvophobic blocks. Nanoparticles with different morphologies like spheres, worms and vesicles can be synthesized by PISA. The final morphology depends on several parameters like the lengths of hydrophobic and hydrophilic blocks, temperature, solvent, salt, and pH.[1] When the solvophilic block is a polyelectrolyte, charge repulsions in the particle corona inhibit the growth of higher order morphologies. In these cases, PISA leads to only spherical particles. However, higher-order morphologies can be achieved when the charge density in the corona is diluted either with non-charged stabilizers or by using copolymers of ionic and nonionic units.[2] It has been shown that polycations may undergo phase separation in aqueous salt solutions with either lower or upper critical solution temperature (LCST or UCST). Particularly, the styrene-based polycations can easily undergo phase separation compared to other polycations.[3,4]

In this work, poly[(vinylbenzyl) trimethylammonium chloride] (PVBTMAC) has been used as a stabilizer in PISA and has been extended with diacetone acrylamide DAAM. A whole spectrum of particle morphologies was obtained simply by changing the reaction medium from pure water to aqueous salt solutions; no dilution of the cationic charges with non-charged comonomers or with non-charged polymers was needed. Hydrophobic triflate ions induce an UCST behavior in nanoparticles obtained with PISA. To conclude, using PVBTMAC as the stabilizer in PISA one can induce morphological changes by adding NaCl. On the other hand, adding LiOTf (triflate) to the dispersions leads to thermoresponsive particles.

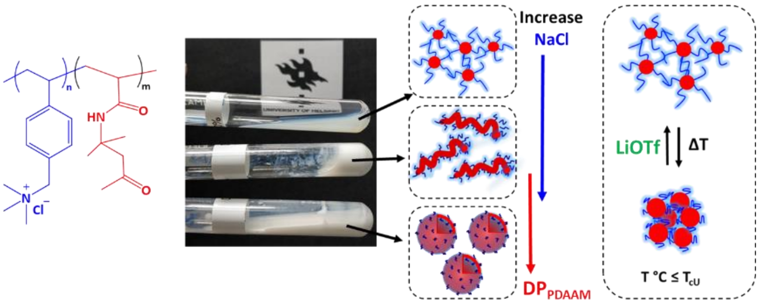

Figure 1. Morphological transitions in PISA of PVTMAC-PDAAM, and thermoresponsive behavior in triflate solutions.

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1,2,3-triazole based poly(ionic liquids) as solid dielectric materials

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Polyionic liquids (PIL) are an important addition to polymeric dielectrics in organic electronics due to their versatility. 1,2,3-triazole based PILs are an emerging field among polymeric dielectrics in organic electronics.

The copper-catalyzed azide-alkyne cycloaddition (CuAAC) 'click' reaction is a robust and straightforward synthetic route to obtain 1,2,3-triazole based poly(ionic liquids) (PILs) from poly(4-vinylbenzylchloride). Charge in the polymer can be introduced either by alkylating the 1,2,3-triazole group or by using an alkyne that carries a charge. Thusly, the polymer backbone is unaffected, but the charge and the polymer architecture can be manipulated by the choice of alkyne, azide-containing group, and the alkylating group. PIL properties are also affected by the choice of counterions. We prepared both positively and negatively charged PILs carrying either inorganic (Na^+ or Cl^-) or organic counterions 1-butyl-3-methyl-imidazolium ($C4mim^+$) or 1-butyl-3-methyl-imidazolium ($TFSI^-$).

The nature of the counterions had a significant influence on the conductivity of metal-insulator-metal (MIM) capacitors when the dielectric properties were characterized by electrochemical impedance spectroscopy at room temperature. The ion mobility of the positively charged PIL was significantly improved after substituting the Cl^- counterion with $TFSI^-$, as was the transition frequency of the capacitor, due to the T_g decreasing from 80 to 8 °C after the ion exchange. For the negatively charged PIL, the counterion exchange from Na^+ to $C4mim^+$ had little effect on the conductivity, as the T_g of the polymers remained above room temperature.

The tunable aspect of the chemistry, transition frequencies, conductivity, and high capacitance densities make 1,2,3-triazole based PILs good dielectrics in organic thin-film transistors, compared to traditional polymer dielectrics.

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Backbone vs. side-chain: (light-) degradable polymers for triggered drug release

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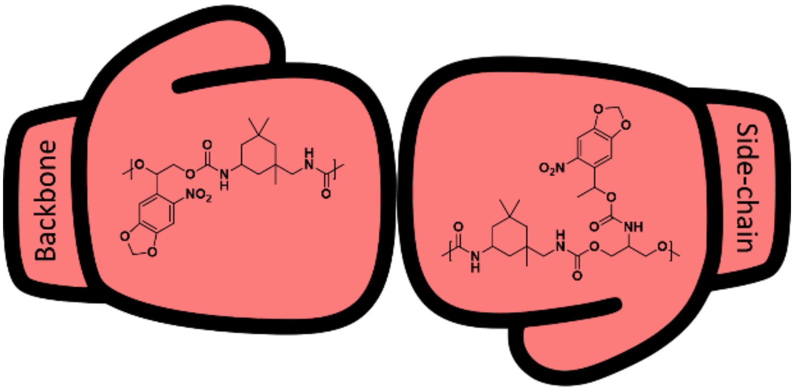
For an effective pharmacotherapy an optimal accumulation of a drug within an affected part of the body is required. Furthermore, a controlled release of the drug at the target site is required. This can be realized by "intelligent" systems utilizing different triggers like light, pH value or redox properties to release the drug in a controlled fashion.[1] Colloidal drug delivery systems based on novel switchable polymers are investigated allowing an effective drug transport into cells and tissues. Hence, on one side the intracellular pH shift in endolysosomal compartments is used to effectively degrade the polymer and release the drug. Furthermore, the increased concentration of reductive glutathione (GSH), which especially can be found in tumor cells, is used for the degradation of redox-sensitive polymers. Additionally, light switchable polymers are investigated that can release the embedded drug from the drug carrier after a short period of irradiation.[2] Here, we report novel polymers which are based e. g. on 6-nitropiperonal and differ in the implementation of the light-cleavable unit. Degradation of these backbone- or side-chain-cleavable polymers was analyzed by UV/Vis spectroscopy and SEC. Furthermore, nanoparticles were fabricated and characterized by photon correlation spectroscopy as well as scanning electron microscopy to evaluate the suitability for drug delivery application. [3] The final goal is the development of drug delivery systems being able to respond to different stimuli.



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Synthesis and Characterization of multi responsive hybrid microgels for controlled drug delivery with maximum drug loading capability

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Multi responsive Poly (NIPAM-AAA-AAm) hydrogels with three different concentrations of allyl acetic acid (AAA) were prepared by free radical emulsion polymerization and confirmed by FT-IR spectroscopy. By increasing the concentration of AAA, the size of the hydrogel increases which dynamic laser light scattering and turbidity of the gels decreases determined. Poly (NIPAM-AAA-AAm)/ Ag hybrid microgels were prepared by insitu reduction of Ag ions and confirmed by UV-Visible and XRD spectroscopy. The optical properties were determined by UV-Visible spectroscopy. To determine the amount of nanoparticles TGA has been used. P (NIPAM-AAA-AAm)/Ag hybrid with 3% AAA content have 32.5% of Ag NPs while hybrid with 9% AAA content contain 38.9% of the inorganic part. TEM images show the uniform distribution of the inorganic part in the hybrid systems with average size of 10-28 nm. These results show that p (NIPAM-AAA-AAm)/Ag hybrid with 9% AAA content have maximum drug loading capability.

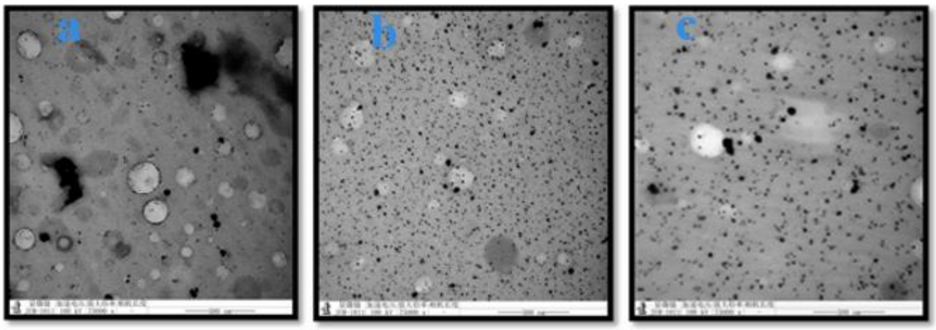

Figure 1. TEM images of the hybrid microgels with (a) 3 % (b) 6% and (c) 9 % of the allyl acetic acid content.

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Wednesday, August 18

NPD

Session: Biopolymers

Phase-separation of Cellulose from Ionic Liquid upon Cooling: Preparation of Microsized Particles

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Cellulose is an historical polymer, for which its processing possibilities have been limited by the absence of a melting point and insolubility in all non-derivatizing molecular solvents. More recently, ionic liquids (ILs) have been used for cellulose dissolution and regeneration, for example, in the development of textile fiber spinning processes[1]. In some cases, organic electrolyte solutions (OESs), that are binary mixtures of an ionic liquid and a polar aprotic co-solvent, can show even better technical dissolution capacities for cellulose than the pure ILs. Herein we use OESs consisting of two tetraalkylphosphonium acetate ILs and dimethyl sulfoxide (DMSO) or γ-valerolactone (GVL), as co-solvents[2]. Cellulose can be first dissolved in these OESs at 120°C and then regenerated, upon cooling, leading to micro and macro phase-separation. This phenomenon much resembles the upper-critical solution temperature (UCST) type thermodynamic transition. This observed UCST-like behavior of these systems allows for the controlled regeneration of cellulose into colloidal dispersions of spherical microscale particles (spherulites), with highly ordered shape and size. While this phenomenon has been reported for other IL and NMMO-based systems, the mechanisms and phase-behavior have not been well defined. The particles are obtained below the phase-separation temperature as a result of controlled multi-molecular association. The regeneration process is a consequence of multi-parameter interdependence, where the polymer characteristics, OES composition, temperature, cooling rate and time all play their roles. The influence of the experimental conditions, cellulose concentration and the effect of time on regeneration of cellulose in the form of preferential gel or particles is discussed.

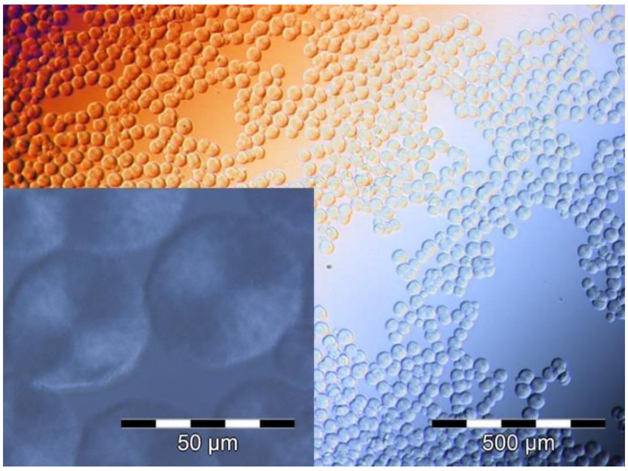

Figure 1. *Regular micro-sized particles regenerated from a cellulose-OES mixture of tetrabutylphosphonium acetate:DMSO = 70:30 wt. % upon cooling.*

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Regeneration of Cellulose from Ionic Liquids in a Form of Particles

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Ionic liquids (ILs) have been used for dissolution of cellulose and its further regeneration in a form of fibers used, for example, in the textile production. Organic electrolyte solutions (OESs) are used instead of pure ILs in some cases. OESs are binary mixtures of an IL and a polar aprotic co-solvent and can show better dissolution capacity for cellulose than that of pure ILs. Here we report on the preparation of spherical particles from homogeneous cellulose solutions. Studied OESs consist of 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]), tributylmethylphosphonium acetate ([P_{4441}][OAc]), or tetraalkylphosphonium acetate ([P_{4444}][OAc]) as ILs with dimethyl sulfoxide (DMSO) or γ-valerolactone (GVL) as co-solvents in various ratios. Our approach to the particles preparation combines material science with physical chemistry of polymers in solutions. The particles are formed upon changing thermodynamic quality of solution, which can either be achieved by addition of a precipitant (*e.g.* water) or by changing temperature. Formation of the spherical solid-like multi molecular aggregates upon cooling below the phase separation boundary is a new phenomenon for cellulose. Suggested methods are simple in practice though requires further R&D processing.

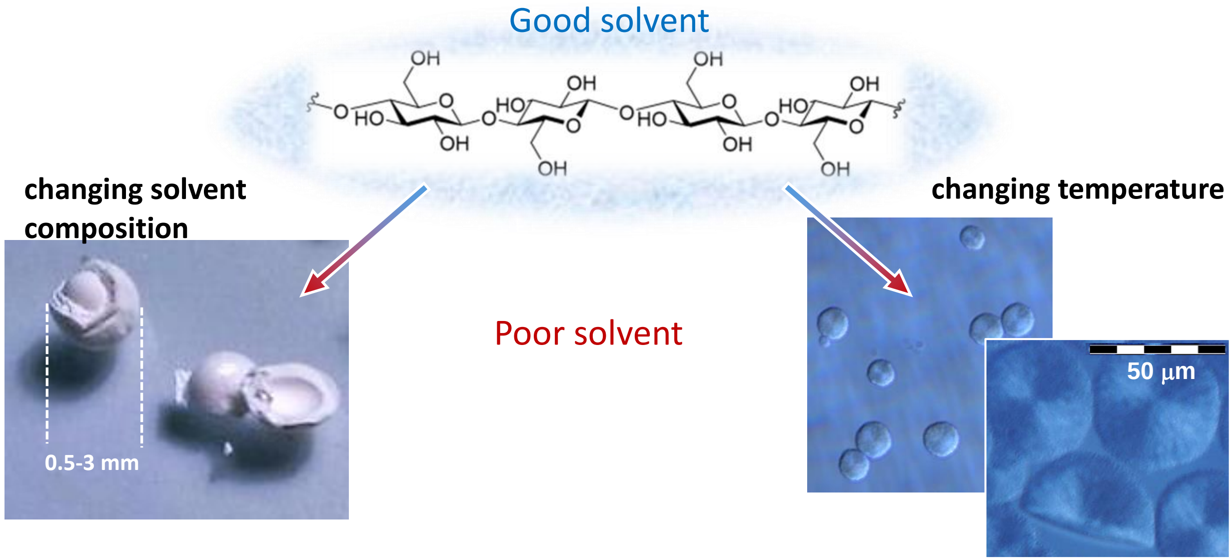

Figure 1. Cellulose beads can either be prepared using water as a precipitant or by changing temperature of solutions. Dilute solutions of cellulose in OESs are required in both cases.

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Regeneration of cellulose beads from [DBNH][OAc]DMSO; a study on the bead formation process and effects of drying on cellulose structure

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Superbase ionic liquids (SBILs) are direct-dissolution cellulose solvents with many attractive properties, such as mild dissolution conditions and recycleability.[1] Furthermore, cellulose/SBIL dopes are by large less viscous than traditional cellulose/solvent systems. For instance, [DBNH][OAc] with co-solvent DMSO dissolves up to 10 wt% of microcrystalline cellulose at only 60 °C. Regeneration of these solutions and subsequent drying enables the cellulose to be fashioned into solid particles (figure 1).

In the present study, cellulose beads were prepared by drop-wise regeneration of cellulose/[DBNH][OAc]:DMSO dope into H_2O, followed by drying. The regenerated cellulose was revealed as rather amorphous under WAXS analysis: total crystallinity was in the range of 15-25% (cellulose II). By altering the drying method, the bead bulk density could be controlled from >1,5 g/cm3 (air-drying) to <0,1 g/cm3 (freeze-drying & supercritical-CO_2-drying). The supercritically-dried aerogel beads exhibited high mesoporosity and specific surface areas of up to 450 m2/g, which makes them highly attractive for adsorption related applications.

The effect of different drying conditions on bead structure, analysed using SAXS and SEM, revealed a relatively complex internal composition. Additionally, SEM micrographs and SAXS analysis of the dried beads and a never-dried sample illustrated the presence of spherical structures likely deriving from spinodal-decomposition, which were used as a model system to study cellulose hornification. In conclusion, these findings further our understanding of cellulose regeneration from SBILs in relation to final cellulose micro- and nanostructure.

Figure 1. H_2O-cryogel and xerogel cellulose beads prepared by regeneration of cellulose/[DBNH][OAc]:DMSO dope via drop-wise addition into antisolvent followed by freeze- and air-drying respectively.

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Behaviour of Tetrabutylammonium Carboxymethyl cellulose in organic solvents

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The field of polyelectrolytes has garnered a lot of interest over recent years, mostly owing to the role played by them in many biological as well as industrial processes. The Carboxymethyl cellulose (CMC) based polyelectrolytes are actively utilized as a viscosity modifiers. However, the sodium salt of CMC, the most commonly used CMC salt, is primarily insoluble in organic solvents, which limits its applicability. In this study, we have replaced the Na counter-ion with the Tetrabutylammonium ion which enhances its solubility in a broad range of organic solvents. This has enabled us to explore the microscopic and macroscopic properties of the TBACMC polyelectrolyte in solution phase using Small-Angle Neutron Scattering (SANS) and rheological measurements.

We are investigating the properties such as the correlation length (ξ), overlap concentration (c*), entanglement concentration (c_e), intrinsic viscosity etc. to understand the role of solvent characteristics, such as dielectric constant, on the aforementioned properties. The SANS data shows a correlation peak in the mid-Q region which decreases in prominence increase in concentration and, eventually, disappears into a shoulder beyond a certain concentration. This final concentration, however, is different for different solvents. Simultaneously, the rheology studies have shown some interesting trends. For instance, we observe a weaker than expected relation between c* and solvent dielectric constant for the various TBACMC systems.

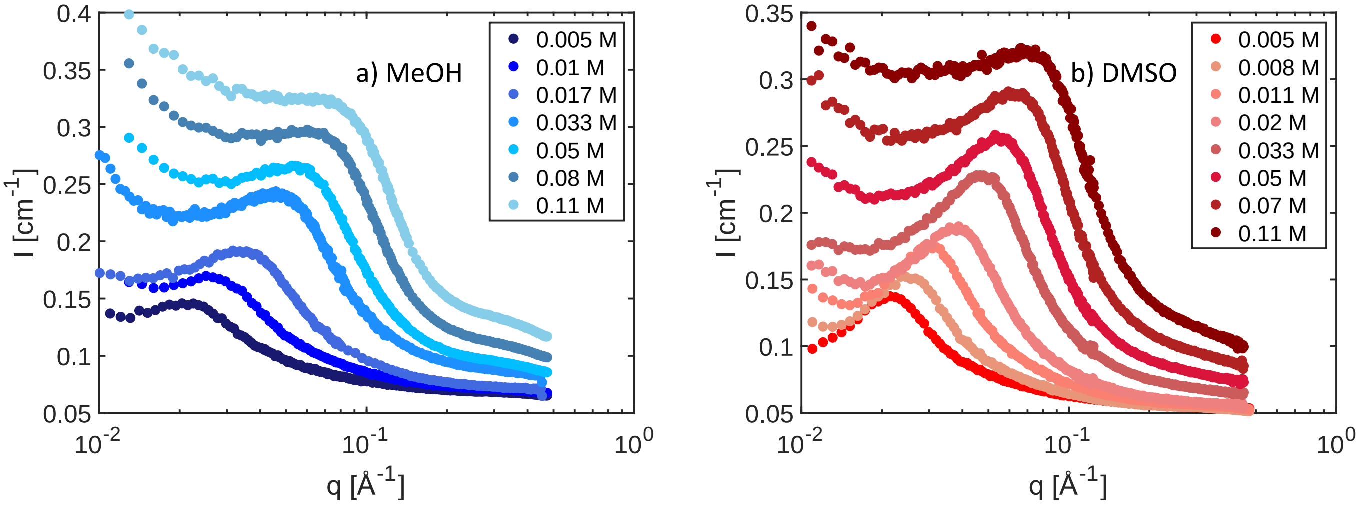

Figure 1. SANS data for TBACMC in a) Methanol and b) DMSO

The role of ions and surface water in nanofibrillated cellulose networks

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Cellulose nanomaterials have received considerable and consistent academic and industrial attentions for more than a decade due to their renewable nature, biodegradability, and superior properties compared to synthetic (nano)materials.[1,2] Wood sourced cellulose nanofibril (CNF) hydrogels are versatile materials as their preparation is straightforward, the starting material is abundant and several methods, including chemical modification, leads to various types of CNF materials with slightly different materials properties. The CNF hydrogels are tough and strong and they are shear thinning and thixotropic in nature.[3] The hydrogels have shown potential for example in high value applications in pharmaceutical and biomedical fields due to non-toxicity and biocompatibility.[4] The major difference of CNF hydrogels compared to polymeric hydrogels is that the CNF hydrogels are formed by colloidal nanoparticles not individual molecules. This in turn means that the system has a large and active surface area that has an effect on the material's behaviour. The gelation mechanism is due to entanglement of the fibrils, fibril-fibril interactions, and electrostatic stabilization.[4] The hydrogel structure can be further stabilized by cross-linking with physical, ionic or covalent methods. Salts have been shown to cause flocculation and increase in elasticity of CNF hydrogels. Several research groups have studied the effects of ions (either by addition of salt[5–7] or decrease in pH[7,8]) in CNF hydrogel networks at concentration above 10 mM of ions. They have concluded that decreasing the pH or adding ions destabilizes the hydrogel network by ions replacing water on the fibril surface and decrease in electrostatic repulsion between fibrils leading to flocculation.

In this work, we studied the effects of different ions at low concentrations between 0.25 and 50 mM on unmodified CNF hydrogel properties and structure by small deformation oscillatory rheology experiments. From the data we gain information on for example, the structure and relaxation of the hydrogel network but also transitions occurring within the system from gel to strong gel. In order to explain our results, we used molecular modelling to show that salt ions interacting with the fibril surface strongly order the bound water rather than replace the water. These interactions and ordering of water affect the effective interactions between the fibrils via the increased order in the water layer, which in turn cause increased strength and amount of interactions between fibrils. In conclusion, the salt ions, regardless of their species, provide stronger interaction sites for the fibrils and thus act as cross-linkers in the CNF hydrogel system causing increase in elasticity of the hydrogel and ultimately flocculation.

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Photo-curing biopolymers for tissue regeneration; individually designed composites by stereolithography

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Additive manufacturing of bioactive polymers and composites opens up new avenues for precisely designed and customized scaffolds and implants. Stereolithography (SLA) is based on the principle of photocuring of prepolymers in the pre-designed voxel-areas. Here, individually designed scaffolds for tissue regeneration were prepared by SLA. Following initial printing tests, upscaling was achieved by prototyping and resin optimization. Photocuring poly(trimethylene carbonate) (PTMC) was used for the polymer matrix. Tricalcium phosphate (TCP) and nano-hydroxyapatite (nHA), both well-known for their bone inducing properties, were used as composite materials. Ceramic contents of up to 40 wt% TCP or nHA could successfully be obtained. The properties of the obtained ceramic/polymer composites were evaluated both *in vitro* and *in vivo* on rabbit and minipig bone defect models.

Composite scaffolds provided an osteoconductive surface in the critical rabbit cranial defect inducing osteoblast infiltration. Functionalization of the scaffolds with bioactive molecules BMP and ZA led to improved scaffold osteoinductivity with enhanced mineralized tissue deposition. In a 24 week study of large mandibular defects in minipigs, the custom implants were biocompatible and generally well tolerated, exhibiting osteoconductive properties and bone ingrowth. However, the large PTMC/TCP implants showed higher incidence of necrosis and infection, potentially due to their large size which may have led to sub-physiologic pH levels, causing infection. More research is required to fully understand the pathogenesis.

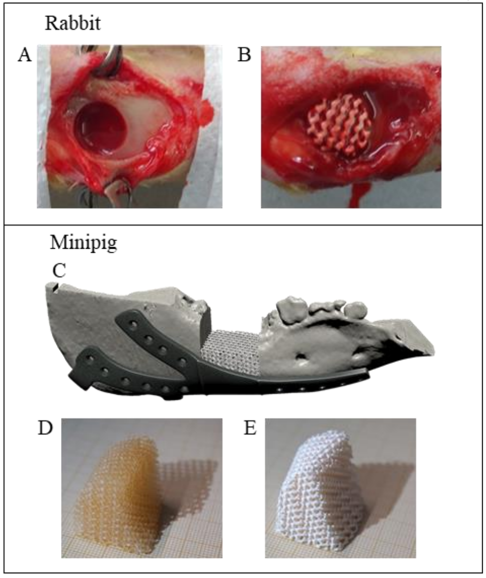

Figure 1. A-B: Implantation of 8mm PTMC/nHA scaffold in rabbit tibia. C: 3D model of custom scaffold and titanium plate in the mandibular defect model. D-E: Printed 25mm PTMC neat scaffold (D) and PTMC/TCP composite scaffold (E).

Wednesday, August 18

NPD

Session: Sustainable polymers

δ-Lactones in a Circular Economy

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In the strive towards a circular polymer economy, ring-opening polymerization (ROP) of heterocyclic monomers is gaining attention. In particular, ROP of substituted five-six membered cyclic structures, owing to their low to moderate ceiling temperature (T_c), exhibit great potential for closed-loop materials. Although the low T_c is facilitating chemical recyclability, this comes with the drawbacks of low thermodynamic stability and high to moderate equilibrium monomer concentrations. To meet the thermodynamic properties in the synthesis step, the polymerization is often performed in bulk, at ambient temperature or lower, in order to reach high monomer conversions. However, the polymer is still sensitive to unzipping in e.g. processing steps.

In this work,[1] we have developed an end-capping strategy based on copolymerization kinetics, utilizing the compositional drift that may occur when one of the comonomers has a slower copolymerization rate compared to the other comonomer. By copolymerization of δ-decalactone (δDL) with the more thermodynamically stable ε-decalactone (εDL), a copolymer with an increased εDL concentration towards the chain ends could be obtained. Hence, the P(δDL-co-εDL) demonstrated a higher thermodynamic stability compared to the PδDL homopolymer. To illustrate the role of macromolecular structure on the thermodynamic behaviour, δDL was also copolymerized with ε-caprolactone (εCL). Moreover, depolymerization and chemical recycling of P(δDL-co-εDL) was triggered by benzyl alcohol (BnOH) as external nucleophile.

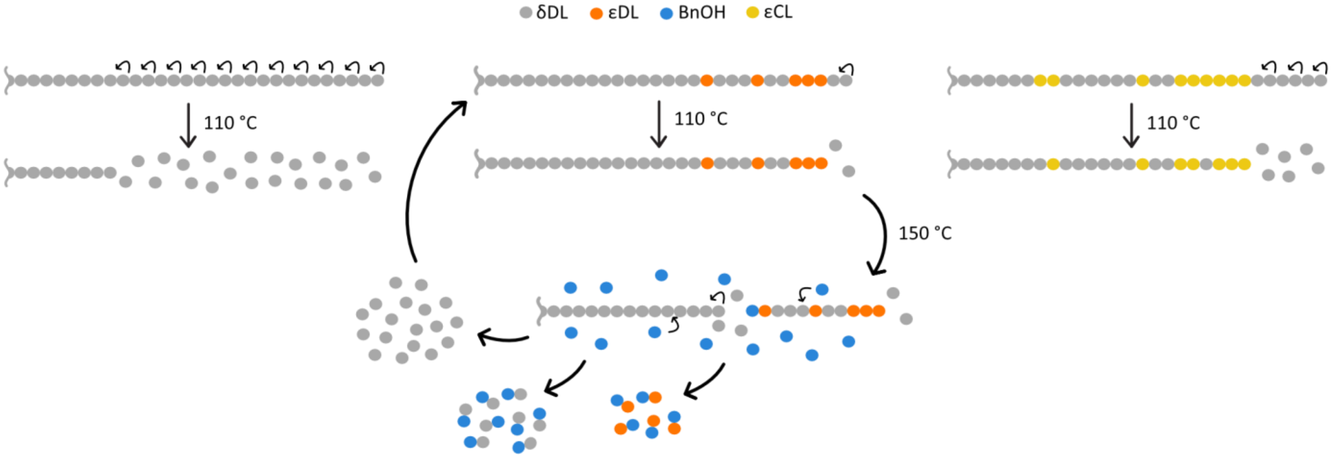

Figure 1. The macromolecular structure determines the thermodynamic stability. The recyclability of P(δDL-co-εDL) can be triggered by BnOH as external nucleophile.

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Microwave-hydrophobized lignin/PLA blends for fused filament fabrication 3D printing

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As one of the main components of wood, lignin exists in copious amounts in nature and is generated in large scales as a sidestream in the pulping industry. In spite of its widespread availability, lignin still remains an underutilized resource as it is typically combusted for energy production. Efforts to valorize lignin as a component in polymer blends or composites are hindered by the hydrophilic nature of lignin that results in poor compatibility with non-polar matrices. In this study, we demonstrate a microwave-assisted hydrophobization strategy *via* esterification, which yields lignin ester derivatives through fast reaction times (10 min) and high efficiency (>90 % degrees of substitution). The successful hydrophobization of lignin was exemplified as polylactide (PLA) blends of up to 50 wt% hydrophobized lignin could be melt-extruded into filaments that were utilized in fused filament fabrication (FFF) 3D printing. Despite the high lignin loading levels, the 3D printed materials remarkably exhibited retained mechanical properties (41.6 MPa ultimate tensile stress and 2.1 % elongation) comparable to neat PLA (50.7 MPa ultimate tensile stress and 3.2 % elongation). Further demonstrating the beneficial effects of lignin in polymer blends, the materials exhibited both UV-shielding and antioxidant activity, exhibiting up to three times the UV absorbance of neat PLA, scavenging up to 55% of DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical, and increasing oxidation induction temperature (OIT) of the 3D printed materials by up to 40 °C.

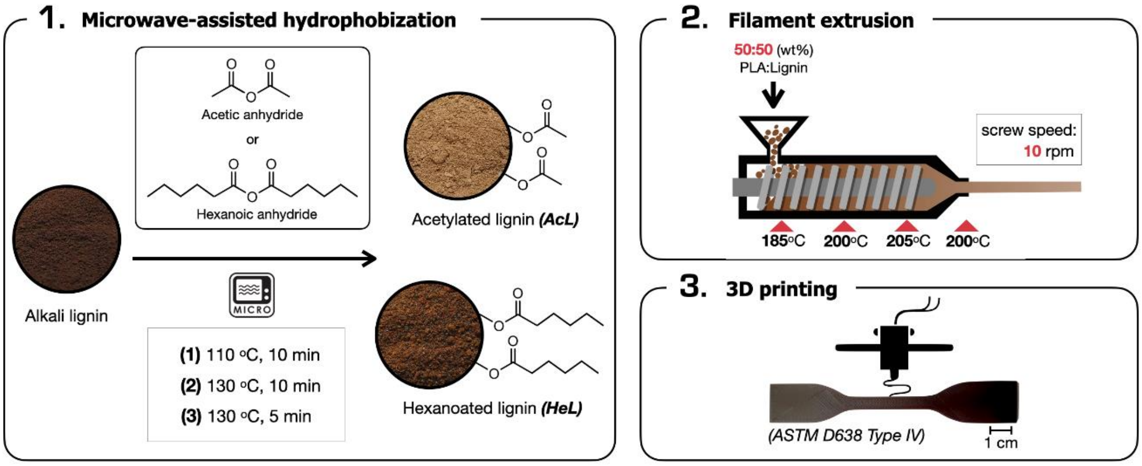

Figure 1. Schematic diagram of lignin hydrophobization and subsequent filament extrusion and 3D printing.

Waste-based biopolymer slurry for 3D printing with recycled materials

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Due to the growing population, and dependence of society on petroleum-based materials, the amount of oil required for plastic production is projected to be increasing over the coming 30 years. It is therefore essential to find more sustainable sources for raw materials, either through improving the recycling of materials in general or by introducing new bio-based components. [1]

This study investigates new biopolymer composites made from water-based slurries suitable for 3D printing, where waste materials are used as fillers and biopolymers are used as binders, with the aim of increased use of biomaterials in architectural-scale uses where 3D printing is used as fabrication context. Ultimately, the aim is to print fast and on a large scale by using low-cost and sustainable materials to prepare new sustainable building materials.

Starting from a base recipe made by water as the base of the slurry, cellulose insulation (CI) and sawdust (SD) as waste material or fillers, glycerol as plasticizer and xanthan gum (XG) as biopolymer binder. The role of each ingredient was investigated in detail, with respect to shrinkage during the curing time, printability, mechanical and rheological properties.

One of the major challenges in printing slurry-based systems is the inherent shrinkage of the system, when water is evaporating from the printed material. The results showed that increasing the plasticizer and decreasing the water lead to a reduction in shrinkage and deformation in the final material by keeping good slurry flowability and printability. However, the increase of glycerol caused a significant reduction in elastic modulus, for this reason, the remaining components were adjusted to regain a higher elastic modulus in the final material. First, the fillers were evaluated, finding that increasing the amount of cellulose insulation over the amount of sawdust leads to an increase in elastic modulus but also to an increase in shrinkage. Secondly, the binder effect was evaluated by increasing its concentration and attempting its crosslinking with the use of salt ions, such as calcium and borax ions. It was found that the higher the concentration of XG the stronger the effect of the crosslinkers and that this leads to higher modulus in the final material, higher firmness of the slurry during printing and improved resistance of the final material to water. Lastly, inclusion of a minor amount of clay (vermiculite) as an additive to improve the mechanical properties and cohesiveness of the system was attempted, showing that the values of elastic modulus that were lost with the increase in glycerol could be regained.

These results led to the optimization of the waste-based slurry and the understanding of how to tune its properties. Subsequently, the project aims at up scaling and testing of the recipe on different geometries.

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Levulinic acid: Sustainable building-block for diverse plasticizer architectures

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Levulinic acid was utilized as the main building–block for designing several series of linear and branched ketone or ketal functional biobased plasticizers for polylactide (PLA). Exploring this versatile building-block could contribute to fueling the upgrade of petroleum-based plasticizers to more sustainable choices. PLA is a degradable and biobased material and should be plasticized with green plasticizers for flexible applications to retain the fully biobased nature. Preferably the new plasticizer-candidates should be low migrating and provide constant performance during the materials service-life. If the plasticizer has additional functions beyond plasticization, it can be a significant plus. The challenge of developing plasticizers with designed structures accentuates the balance of high performances and environmental impacts.

Here, the benefits of levulinic acid were illustrated by two intriguing studies. The first study highlighted the potential of levulinic acid based flexible plasticizer architectures. Biobased ethylene glycol and glycerol were esterified with levulinic acid to form linear and branched structures with ketone groups. The ketone groups were further transformed into ketals by ethylene glycol to vary the hydrophilicity/hydrophobicity and architecture of the plasticizers. A commercial biobased plasticizer, acetyl tributyl citrate, was set as a reference for comparison. The PLA films plasticized by 20 % of the four synthesized levulinates demonstrated significant plasticization with substantially decreased glass transition temperatures (T_g) (e.g., ethylene glycol dilevulinate shifted the T_g down to 15 °C) and increased the elongation at break (from 5 % for pure PLA to 446 % or higher). Furthermore, the branched plasticizer with ketal groups helped to preserve the processing window of PLA plus provided a high Young's modulus as determined by tensile testing. The PLA hydrolysis rate in three simulants (water, ethanol solution and acetic acid solution) remained similar to unplasticized PLA. The second study demonstrated the possibility to obtain dual-functioning plasticizers by exploiting the natural aromatic compound eugenol and the green platform chemical levulinic acid. Aromatic eugenol was esterified with levulinic acid with two different feed ratios to obtain eugenyl levulinates containing ketone and varied concentrations of phenol and hydroxyl groups. Valeric acid esters were prepared for comparison and they helped to elaborate that the ketone groups of levulinic acid were subjected to nucleophilic addition and linked to the aromatic rings, leading to altered architectures and hydrophilicity of the plasticizers through higher content of hydroxyl groups. The PLA films incorporating 30 % of the three synthesized plasticizers exhibited satisfying plasticization, reflected by decreased T_g (e.g., eugenyl valerate enabled a decline in T_g of 43 °C) and increased elongation at break (eugenyl levulinates improved elongation to 400 - 480 %). Moreover, the two eugenyl levulinates and one eugenyl valerate, all significantly inhibited the growth of *Staphylococcus aureus*, and the eugenyl levulinate with the highest phenol-, carboxyl- and alcohol group content inhibited the growth of *Escherichia coli* as well.

Overall, levulinic acid was demonstrated as a promising building-block for effective biobased plasticizers for PLA.

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Preparation and investigation of biobased aliphatic polyesters based on a rigid spirocyclic dicarboxylate derived from levulinic acid

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Over last two decades, the development of biobased plastics has gained significant interest due to the serious environmental impact of fossil-based plastics, including the depletion of fossil resources and generation of greenhouse gas (GHG) emissions.[1] Lignocellulose-derived chemical building blocks have received increasing importance for the development of alternative monomers for polymer production.[2,3] Among them, levulinic acid has been recognized as platform chemical for preparation of various polymer precursors.[4] In the present work, a rigid spiro-diester monomer with a low greenhouse gas emission was prepared by combining ethyl levulinate and pentaerythritol (Figure 1). Aliphatic polyesters with moderately high molecular weights were synthesized by polycondensations of the spiro-diester with 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and 1,4-cyclohexanedimethanol, respectively. Subsequently, the fully aliphatic ketal-functional polyesters were investigated with regard to thermal and dynamic rheological properties.

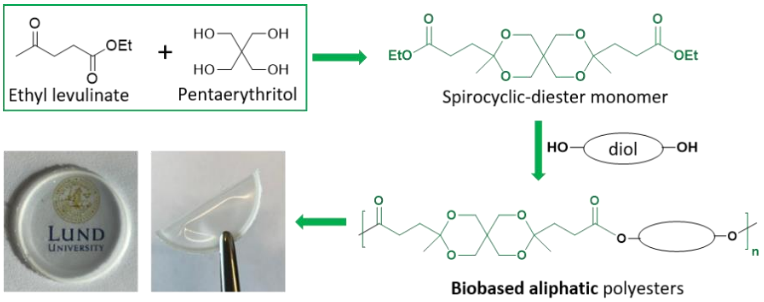

Figure 1. Synthesis of the spiro-diester monomer and different biobased aliphatic polyesters

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Biobased and Functional Polyamides and Polyhydroxyurethanes

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Polyamides (PAs) and polyurethanes (PUs) are two important classes of polymers with many commercial applications. They are utilized in large industries such as construction where rigid and flexible PU foams are used for insulation and cushioning, and the automotive industry where many car parts are made of PAs due to their high strength and thermal stability. Despite their great utility, PAs and PUs present downsides in terms of non-sustainable production processes and chemicals employed. PAs usually require high temperature and low pressure during their synthesis and harmful isocyanates are employed for the synthesis of PUs. To overcome these challenges, we have developed more sustainable synthetic routes based on a ring-opening aminolysis reaction of cyclic diesters and cyclic carbonates towards PAs and PUs respectively. We utilized biobased monomers and eliminated the use of solvents, toxic reagents and harsh reaction conditions.[1,2,3] Thermoplastic PAs with fiber-formation ability were prepared with a wide property range depending on the structure of the diamines reacting with ethylene brassylate, the cyclic diester employed. Through the same route, it is also possible to realize uncommonly encountered, yet strong (σ_b = 17 MPa) and flexible (ε_b = 176 %) thermoset PAs with shape-memory property due to crystalline regions locked within the amorphous network. PUs with pendent hydroxyl groups along the backbone, named polyhydroxyurethanes (PHUs) can be synthesized by an isocyanate-free method through the aminolysis of cyclic carbonates. The pendent hydroxyl groups were employed for the ring-opening polymerization of ε-caprolactone (CL) leading to graft copolymers with novel structure. The reaction could be performed in bulk due to the rational design of the PHU structure enabling its dissolution in the CL monomer. The molar mass of the grafted PCL chains can be easily modulated by varying the –OH:CL ratio, impacting the thermal properties of the copolymers. Finally, by combining the versatility of the ring-opening aminolysis pathway with a dynamic chemical motif, reversible PA and PU networks can be prepared.

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Bio-based long-chain aliphatic polyamides

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Plastic materials derived from renewable resources are gaining a growing interest in scientific research and industry to replace petroleum-based ones. Polyamides (PAs) are among the most frequent engineering polymers with excellent thermal and mechanical properties with various industrial applications such as automobile parts, packaging, and electrical and electronic devices. In the current study, a series of relatively long-chain aliphatic PAs were synthesized through the reaction between a bio-based dicarboxylic acid and petroleum-based diamines. The samples revealed significant tensile strength, tensile modulus, and toughness compared with the commercial ones. Furthermore, they showed relatively lower melting points and significantly lower water uptake capacity, making them exciting candidates for certain engineering applications. Moreover, the effect of the addition of some mineral- and bio-based fillers on different properties of the developed PAs was investigated. It was found that the mineral fillers, i.e., surface-modified graphene, clay, and silicon dioxide, dramatically improved the thermomechanical properties of the matrix. Besides, these relatively low melting point PAs were interesting candidates for bio-fillers, i.e., microcrystalline cellulose and lignin, regarding the high thermal sensitivity of those fillers [1–4].

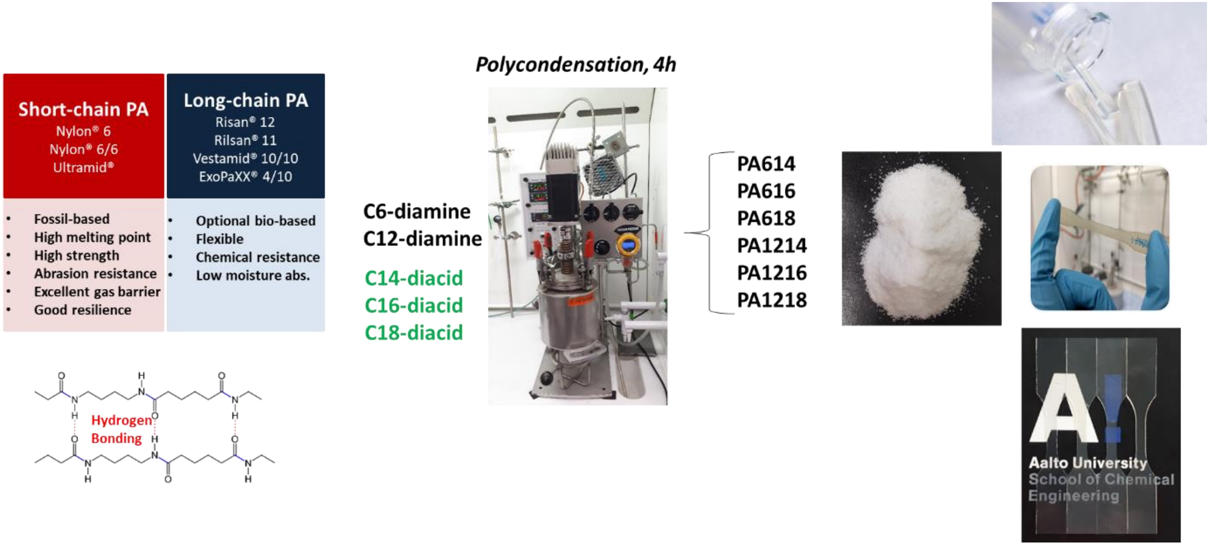

Figure 1. Representation of bio-based long-chain aliphatic polyamides synthesis

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Wednesday, August 18

NPD

Session: Polymer composites & processing

Novel theoretical self-consistent mean-field approach to describe mechanical properties of composites and polymer solutions

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A novel theoretical approach, which yields a non-linear differential equation for the mechanical properties of fiber filled composites as a function of the volume fraction of the filler and the fiber orientation, is shown and simply solved. Furthermore, the transfer to polymer solutions is shown and gives a physical explanation for various well-known empirical relations and numerical values including the Huggins constant and exponent of power-laws for the concentration and molar mass dependence of the polymer solution viscosity.

Furthermore, the exponent of power-law molar mass dependence of the polymer melt viscosity "3.4" is derived without a reputation model, only considering packaging as shown in the following figure combined with self- consistency:

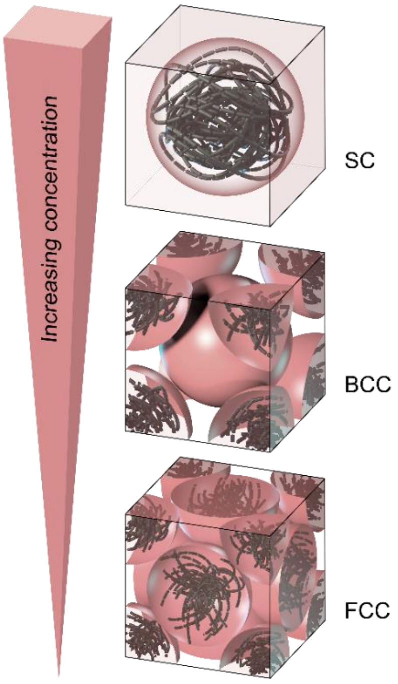

Figure 1. Packaging scenarios for polymers in solution and melts. Reference volume (elementary cell) of a spherical object, where the reds spheres represent a solid particle or an enveloping sphere of a polymer chain in the case of a polymer solution. From top to bottom the concentration increases, starting with simple cubic (sc), passing a body-centered-cubic (bcc) going to a face-centered-cubic (fcc) structure.

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Thermomechanical Reinforcement of Polyethylene/Polypropylene Blends for High Voltage Cable Insulation by Compatibilisation with a Styrenic Block Copolymer

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High voltage direct current (HVDC) cables play an important role in facilitating our shift from fossil fuels to renewable energy. They transmit electrical power efficiently over long distances, allowing renewable energy infrastructures to be integrated into large power grids. Robust insulation materials are crucial in underground and undersea high voltage cables to ensure high cable performance over the cable lifetime. The mechanical flexibility and excellent electrical insulating properties of low-density polyethylene (LDPE) makes it attractive for HVDC cable insulation applications. However, LDPE has a low melting temperature and requires thermomechanical reinforcement to cope with the high temperatures experienced during cable operation. This can be achieved by adding a higher melting polymer like polypropylene (PP), but the incompatibility between LDPE and PP means that high PP content is needed for sufficient thermomechanical reinforcement, resulting in materials that are too stiff at low temperatures. We found that adding small amounts of a linear triblock copolymer polystyrene-b-(ethylene-co-butylene)-b-polystyrene (SEBS) to a PP/LDPE blend with just 24 wt% PP resulted in the formation of salami-like microstructures in coalesced domains of PP/SEBS in the LDPE matrix (Figure 1), and significantly improved thermomechanical properties. Not only did these ternary blends demonstrate excellent creep performance at elevated temperatures, but also displayed excellent electrical insulation properties even superior to that of neat LDPE. Our findings show the potential of SEBS/PP/LDPE ternary blends as an attractive insulation material for HVDC cables of the future.

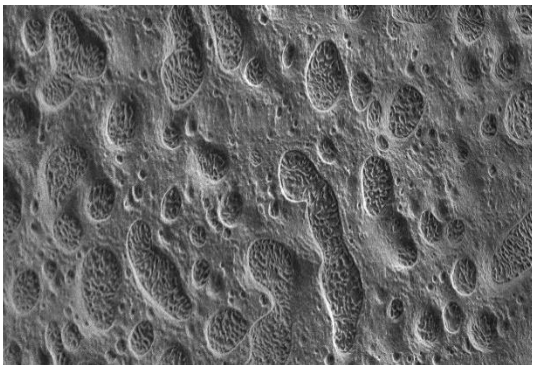

Figure 1. SEM micrograph of the cryofractured and etched surface of the SEBS/PP/LDPE ternary blend

Keywords: high-voltage power cable insulation, polyethylene, polypropylene, copolymer, thermoplastic

Tough materials through ionic interactions

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Additive manufacturing (AM) has emerged an increased demand of new, rapidly photopolymerizable materials. Photopolymerized materials are widely used, but often suffer from insufficient toughness.[1] Hence, new methodologies are needed to improve them. Polymer networks are commonly classified as either physical or chemical networks. The chains of a chemical network are connected by covalent bonds, whereas those of a physical network are connected through non-covalent interactions.[2] Classically elastomers have been crosslinked via permanent covalent bonding, while ionic or electrostatic interactions provide an alternative way to crosslink polymers.[3]

This research explores a new, widely applicable approach for preparing photopolymers with excellent mechanical properties. This is realized by crosslinking traditional non-charged monomers with a chemical crosslinker and a dynamic crosslinker: a salt that contains polymerizable double bonds in both its anion and cation. Chemical crossliker stabilizes the form and the ion pairs in the dynamic crosslinker act as sacrificial bonds that break and reform under deformation.[4] A simplified illustration of the materials' design is presented in Figure 1.

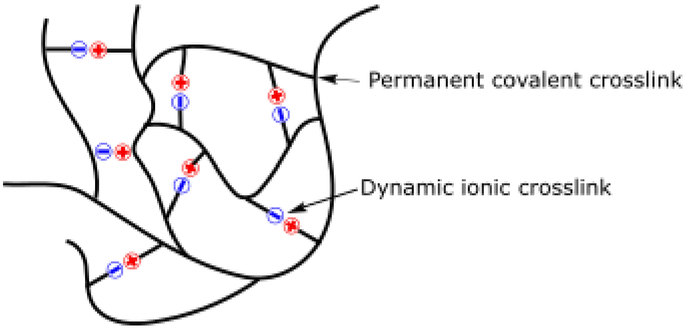

Figure 1. The material design.

Butyl acrylate based materials were prepared successfully with varying concentrations of chemical and dynamic crosslinkers. Chemical crosslinking decreased the elasticity of the materials but did not significantly affect their strength. Dynamic crosslinker enhanced the mechanical properties significantly. The methodology was tested with two dynamic crosslinkers and can be generalized to other monomers as well.

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Thursday, August 19

NRC

Session: Rheology of sustainable materials

Optimization and Improvement of the Thermal Stability of Fish Gelatin

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Fish gelatin is a popular alternative to mammalian gelatins due to ecological and ethical concerns and, religious and cultural preferences[1]. Although gelatin from cold water species have lower gel strength and lower gelling and melting temperatures compared to mammalian gelatins, warm water fish gelatins have similar rheological properties with mammalian gelatins[2,3]. However, warm water fish gelatin exhibits low thermal stability, especially at above its equilibrium sol-gel transition temperature which is common in warm climates[4]. To improve the thermal stability of fish gelatin, different combinations of two different sugar alcohols, sorbitol and xylitol, and a non-reducing sugar, sucrose, were added to the fish gelatin gels. The gelling-melting kinetics as well as gel strength of these gels were analysed using small amplitude oscillatory shear measurements. Short-term stability tests performed at 55 °C for 20 hours indicated that the heat stability of fish gelatin gels improved with increasing concentrations of sugar alcohols. In addition, sucrose exhibited the smallest decrease in storage modulus (G'_{max}) compared to sugar alcohols.

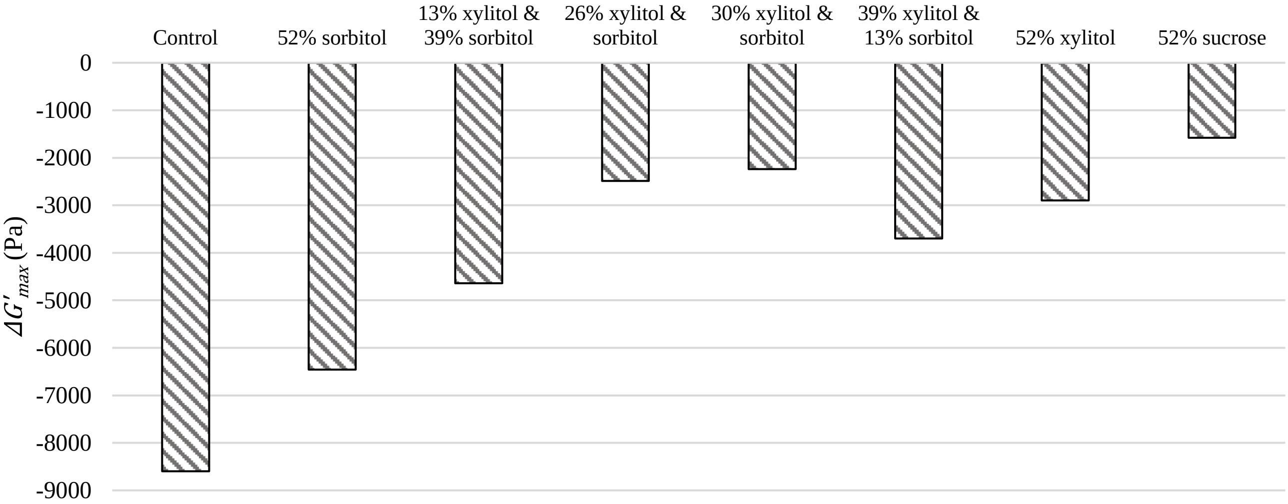

Figure 1. The change in the storage modulus (G'_{max}) of fish gelatin gels with 52% sorbitol, xylitol or sucrose after 20 hours incubation at 55 °C. Control gel does not contain any sugar alcohols or non-reducing sugars.

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CLEX alginate gelling technology: a versatile tool for production of biomaterials

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The combination of cells and hydrogels has significant potential in many biomedical applications including (but not limited to) tissue engineering, regenerative medicine, organs on a chip, *in vitro* drug testing and diagnostics. Alginates, which form hydrogels in the presence of divalent cations (typically calcium) are highly biocompatible and widely utilised as the hydrogel matrix in such systems. ClexBio's proprietary gelling technology, CLEX[1,2], allows alginate hydrogel formation with precise control to complement the excellent biocompatibility and enables the use of microfluidic devices to form hydrogel microstructures containing delicate biological cargo such as living cells. Importantly, CLEX provides effective, controlled gelling of alginates with varying molecular weights and compositions, including peptide modified alginates, allowing for the creation of hydrogels with application tailored properties. Here we present rheological analysis of the gelling kinetics, elastic moduli and phase angles of hydrogels produced from varied alginates and alginate blends using the CLEX gelling technology.

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Enhanced Mechanical Stability in Multi-component Supramolecular Gels Based on Enantiomers

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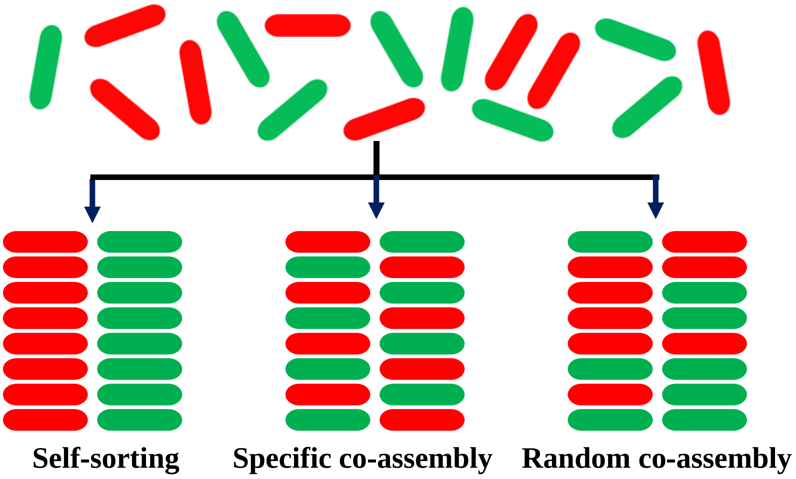
Supramolecular multi-component gels have emerged as a special class of functional soft material as it offers fine-tuning of the gel-state properties.[1] Mixing two or more gelators lead to self-recognition at the molecular level (Scheme 1), and the individual gelator molecules can form separate fibres (self-sorting), or they can co-assemble in a specific (specific co-assembly) or random way (random co-assembly).[1] We are interested in chiral gelators due to their potential applications in chiral nanomaterials, chiral recognition and asymmetric catalysis.[2] Enantiopure gelators (*RR*- or *SS*-) based on amino acid derivatives with urea/amide moieties were synthesised[3, 4] and multi-component gels (*R*+*S*) were prepared by mixing equimolar *RR*- and *SS*-gelators. The self-assembly of the multi-component gels was probed by various microscopic techniques and X-ray diffraction. The thermal stability of the gels was evaluated by gel-sol transition temperature and the mechanical strength was analysed by rheology. Oscillatory amplitude sweep and frequency sweep experiments revealed that the mixed gel displayed enhanced mechanical strength compared to the enantiopure gelators in both urea and amide-based gels. For the urea gelators, the rheological experiments were complemented by studying the mechanical properties under high deformation, determined by uniaxial compression measurements.[3] I will discuss the comparison of the mechanical strengths of the single-component enantiopure gels and the multi-component mixed gels by rheology. This study will demonstrate how rheology can be used to probe the self-assembly of multi-component gels, and the rheological measurements will be corroborated with other standard gel characterisation techniques.



Scheme 1. Various self-assembly modes in multi-component gels.

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Enhancing the mechanical compatibility of natural biomaterials with native human skin

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It is well known that skin is a viscoelastic material, and it is necessary to know its linear viscoelastic (LVE) properties for developing skin equivalents [1, 2]. There is not enough data in literature for the same, especially for the commercially available skin models. Our work focused on the generation of *ex vivo* native human skin and 3D models LVE reference data using oscillatory shear rheology for the development of skin scaffolds [3].

Next step involved a custom-made method to prepare process-convenient skin scaffolds by tuning the rheological properties of hydrogels composed of a few naturally occurring polysaccharides [4]. The dependence of intrinsic elastic modulus (G'_0) on the concentration of the principal hydrogel component variant, i.e., kappa (κ)-carrageenan is shown in Fig. 1. It showed a good match with the native counterpart. Additionally, caffeine permeation study was done and the hydrogels showed improved barrier features with increasing κ-carrageenan concentration [5].

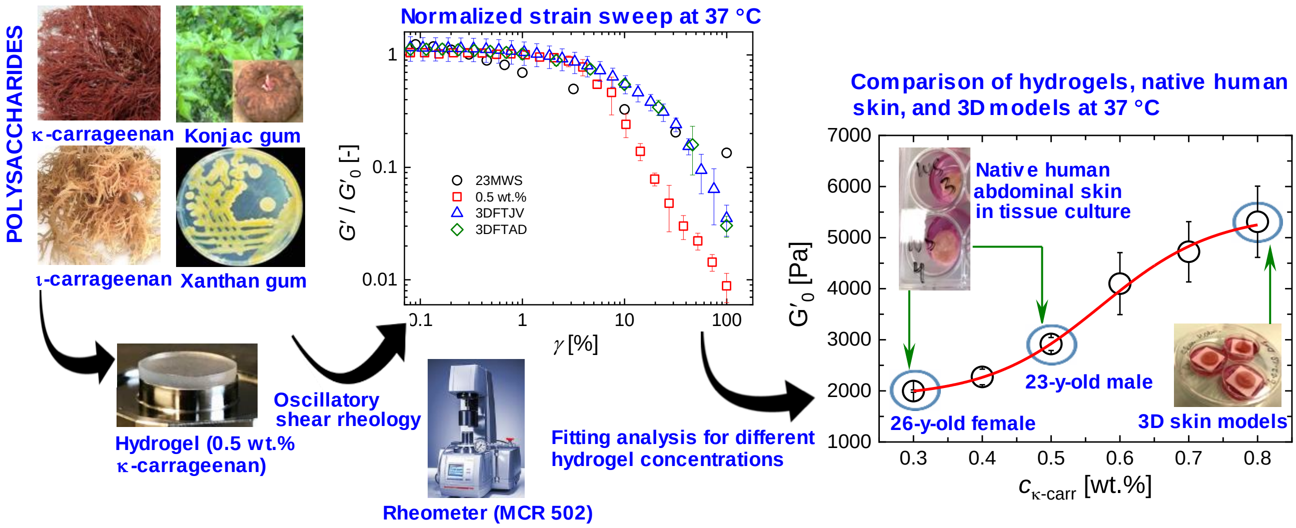

Figure 1. Work flow towards mimicking native human skin mechanical properties.

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Thursday, August 19

NRC

Session: Rheology of biopolymers

The effect of consistency on the shear rheology of aqueous suspensions of cellulose micro- and nanofibrils

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While the raw material type and the production method of cellulose micro- and nanofibrils (CMNF) strongly affect the absolute values of the rheological parameters of their aqueous suspensions, the dependence of these parameters on consistency, *c*, is found to be uniform [1]. The consistency index and yield stress of CMNF suspensions follow generally the scaling laws $K \sim c^{2.43}$ and $\tau_y \sim c^{2.26}$, respectively, and a decent approximation for flow index is $n = 0.30 \times c^{-0.43}$. The variability of reported scaling exponents of these materials is likely mainly due to experimental uncertainties and not so much due to fundamentally different rheology. It is suggested that the reason behind the apparently universal rheological behavior of CMNF suspensions is the strong entanglement of fibrils; the flow dynamics of typical CMNF suspensions is dominated by interactions between fibril flocs and not by interactions between individual fibrils.

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Effect of surfactants on the rheology of cellulose nanofiber suspensions

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Increasing concerns on human effect on the environment has risen demand for novel biobased materials to replace those environmentally hazardous, often based on fossil fuels. Prominent replacement candidates are many forms of cellulose nano fibers (CNF) with rich variety of textures and applications [1]. One example of such materials are foams based on CNF suspensions which offer lightweight, strong and elastic materials for e.g., insulating and packing applications [2]. Practical manufacturing processes of such foams require the understanding of the rheology of CNF suspensions mixed with surface-active molecules. The present study compares the rheology of plain CNF suspensions with suspensions with those involving surfactants. The rheology is measured in a setup consisting of concentric cylinders geometry shown in Fig 1(a). Recently various imaging techniques have been incorporated to rheological measurement setups to get further insights on the heterogeneous flow behavior often associated to materials with similar structure [3]. Here, we choose a regular camera with a mirror setup that allows us to image the surface of the sample during the experiment as seen in Fig 1(b). From such images we can calculate the tangential velocity at the surface as a function of the distance from the rotating inner cylinder. In the experiments we find that addition of surfactants causes hysteresis in the flow curves measured either starting from high or low shear rates: The flow curves get highly dependent on the sample history. While some CNF suspensions are known to manifest this effect even without surfactant [4] this was not the case in our TEMPO oxidized CNF. An example of such flow curve is shown in Fig 1(c). Monitoring the velocity at the surface reveals that the deformation is completely localized near the rotating inner cylinder in the increasing shear rate ramp (Fig 1(c) orange) while on the decreasing shear rate ramp the material flows through the whole gap (Fig 1(c) blue). We suspect that the surfactants interact with the surface of CNF molecules and weaken the network structure between the molecules resulting in the observed flow behavior. A further microscopy study on the structure of the CNF suspension would be interesting to conduct in the future.

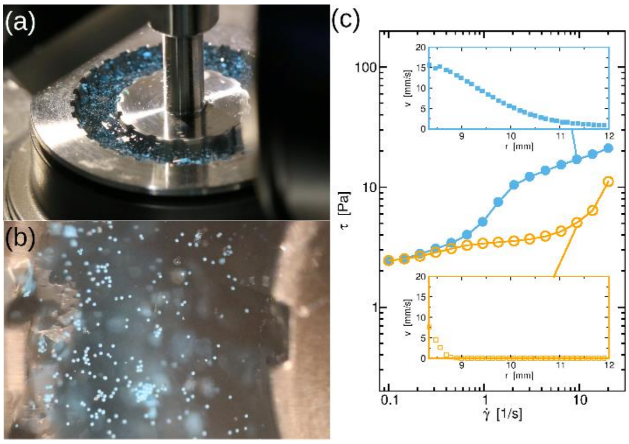

Figure 1. (a) Concentric cylinders setup (b) Sample with tracer beads (c) Flow curve and velocity profiles

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Effect of carbon nanomaterials on the rheology and spinnability of cellulose solutions

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Incorporation of carbon nanomaterials in cellulosic fibres has several potential benefits, such as adding reinforcement, electrical conductivity and a graphitic templating effect when the fibres are used as carbon fibre precursors [1,2]. In order to disperse these materials into a cellulosic fibre, they should be spun together with cellulose. Herein, hybrid spinning dopes were prepared by mixing different carbon nanomaterials (graphite, carbon nanotubes and graphene oxide) with cellulose solutions in ionic liquid. The viscoelastic behaviours of the obtained dopes were analysed at different temperatures and spinnability tested at temperatures that facilitated a zero shear viscosity of ~40 000 Pa s.

The effect of the additive on rheology depended on the additive type: two-dimensional graphene oxide increased both the complex viscosity and elastic behaviour of the dopes at a sufficiently high concentration. When the graphene was exfoliated from graphite, it even made the dope fully gel-like and thus unsuitable for spinning. In contrast, one-dimensional carbon nanotubes increased the elasticity significantly less and decreased the viscosity and activation energy (i.e., temperature sensitivity of the zero shear viscosity). The lowered activation energy correlated with mildly impaired spinnability.

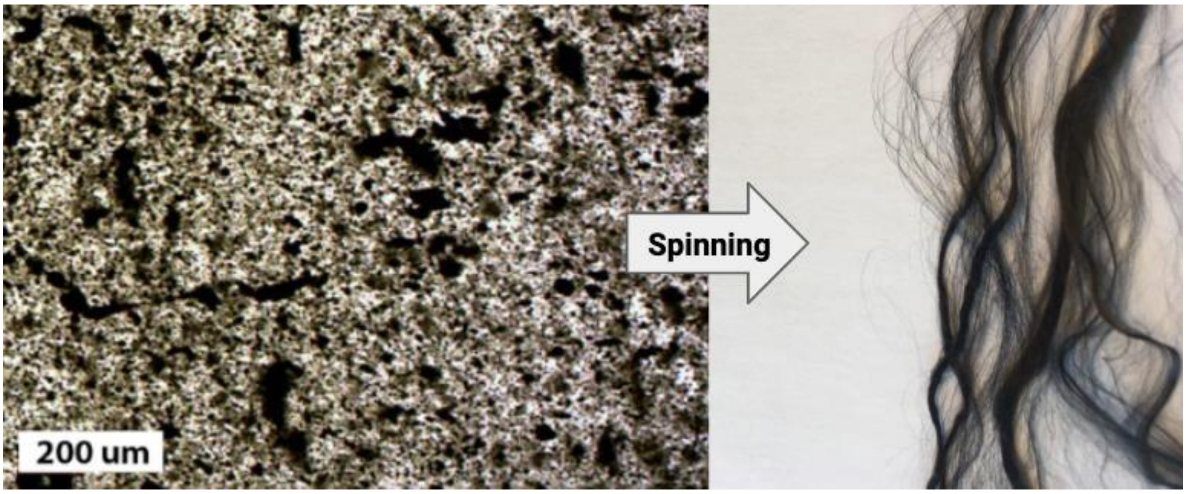

Figure 1. Optical micrograph of cellulose and graphene oxide in ionic liquid and photograph of the ensuing fibre

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Thursday, August 19

NRC

Session: General rheology

Interfacial shear and dilatational rheology of polyelectrolyte microgel monolayers at the oil-water interface

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Numerous industrial applications require precise control over the stability of emulsions and foams. The use of smart emulsifying agents such as stimuli-responsive microgels allows for on-demand inversion or breaking of the system by mild changes in external conditions [1]. Microgels are three-dimensional, crosslinked polymer networks that are of colloidal size and swollen by the solvent [2]. As opposed to hard colloidal particles, the softness of microgels can be tuned by varying their crosslink density. Microgels adsorb spontaneously to fluid interfaces, making these interfaces viscoelastic. The mechanical stability of microgel-laden interfaces and, thus, emulsion stability depend on the softness (deformability) of the microgels as well as on the viscoelastic properties of the microgel monolayer at the interface [3,4].

In this study, pH-responsive polyelectrolyte microgels are synthesized by incorporating methacrylic acid (MAA) in poly-N-isopropylacrylamide (pNIPAM)-based microgels [5]. The interfacial shear rheology of the polyelectrolyte microgel monolayers at the decane-water interface is investigated under controlled surface pressure using a custom-made setup where a modified double wall ring (DWR) geometry is positioned in a Langmuir trough. The dilatational rheological properties are characterized by means of oscillating barrier and step compression measurements in a Langmuir trough, as well as by performing oscillating pendant drop measurements upon microgel adsorption to the interface.

The investigated microgel monolayers generally exhibit highly elastic behavior both in shear ($G^{s\,\prime} \gg G^{s\,\prime\prime}$) and dilatation ($E^{s\,\prime} \gg E^{s\,\prime\prime}$). We correlate the rheological properties of the monolayer with the two-dimensional phase behavior of the microgels which is associated with an isostructural phase transition between a non-close-packed and close-packed arrangement [6]. The effect of pH on the shear and dilatational rheological properties at different compression states is discussed. Two distinct relaxation mechanisms are observed in the microgel monolayers.

Acknowledgements: The authors thank the Deutsche Forschungsgemeinschaft (DFG) for funding within SFB 985 “Functional Microgels and Microgel Systems“. O.V.L. acknowledges the Alexander von Humboldt Foundation for financial support.

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Production of satellites during impact of dense suspensions on a flat surface

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The development of electronic components is continuously pushing manufacturers to produce smaller and more densely packed components circuit boards. This rapid development could hardly have been sustained without efficient, flexible and highly accurate manufacturing methods. The inherent limitations of the deposition process of solder paste onto the circuit board, such as deposit positioning and individual volume control, are alleviated by digital processes, such as jet printing, where individual volumes of a high-viscosity, high volume fraction suspension are forced through a nozzle by an electronic actuator [1]. As deposit volumes decrease, the demands on increased positioning accuracy and volume repeatability are increasing. Another deposit quality that is important is the production of satellites that can be produced both during the break-off process of the trailing fluid filament, as well as during impact on the substrate.

In this study, the production of satellites produced during the impact of the fluid body on the surface is studied. High-speed imaging is used to capture the impact process using an industrial printing head. The production of droplets of dense suspension is produced using a piezo-based ejection technology controlled by a voltage waveform that can be manipulated to affect the speed of the emerging droplet. The dense suspension used consists of a mixture of spherical granules of a SnAgCu metal alloy with an approximate diameter of 20 μm and a resin-based carrier fluid. The volume fraction of the dense suspension is 86 wt%. The paper will present data concerning the effect of droplet speed and volume on the production of impact satellites. The size of the produced satellites is studied, together with the effect of the specific surface material.

Figure 1. Imaged jetting sequence seen in a cross-sectional view. From left to right snapshots at 10 ms, 30 ms, 50 ms, 100 ms and 200 ms.

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Progress and challenges on relating 'nonlinear oddities' in oscillatory shear to structural buildup in nanostructured fluids

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The nonlinear oscillatory shear material response of complex fluids has been shown to exhibit peculiar behavior, i.e. 'nonlinear oddities'. By 'oddities' we refer mainly to (i) non-quadratic scaling of the third relative higher harmonic ($I_{3/1}$) with the strain amplitude in the medium amplitude oscillatory shear region (MAOS) and (ii) strong dependence on the applied angular frequency in $I_{3/1}$ and of the viscous third relative Tschebyshev coefficients ($v_{3/1}$). We have previously correlated such 'oddities' to percolation in nanostructured fluids. Here we provide an overview of progress and challenges based on our work on polymer-based nanocomposites, nanocellulose suspensions and pressure sensitive adhesives. In polymer nanocomposites based on conductive fillers unique nonlinear 'oddities' are recorded for filler concentrations corresponding to the electrical percolation threshold in both $I_{3/1}$ and $v_{3/1}$. For supercritical concentrations, the 'oddities' further develop and include $I_{3/1}$ scaling exponents equal to zero as well as multiple scaling laws (three regions) within MAOS. For a given filler morphology, there appears to be little influence of the molecular topology of the polymer matrix, and the non-linear behaviour could therefore be mainly related to the filler morphology and dispersion levels. In suspensions, (mainly focused on aqueous cellulose nanocrystals (CNC) suspensions), similar 'oddities' can be also observed, however, their relationship to gelation is more challenging to assess (similarly also for adhesives). For aggregating CNC suspensions 'oddities' of type (i) in the form of single and three-scaling regions, and (ii) could be observed. Grafting of surface groups having various topologies can qualitatively mimic the nonlinear behaviour of untreated samples at higher concentrations. In self-assembling CNC suspensions, the nonlinear behaviour appears to correspond to the particular phase investigated, with differences in behaviour especially between biphasic and liquid crystalline phases.

Developing an improved methodology to measure viscosity of hot-swelling starch

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The knowledge about starch and its behaviour is increasingly important since starch, as a texture modifier causes significant viscosity changes in food products during heat treatment, even at very low concentrations. Accurately analysing the absolute viscosity of starch during processing, is essential to define the most efficient processing solution for each individual food product. However, due to the tendency of uncooked granules to sediment, the temperature sensitivity, and the strong time dependent behaviour of starch, accurately determining the behaviour of starch is scientifically challenging. These are well-known problems which are extensively described in literature [(1-4]) but not solved.

In this work, a methodology to assess the rheological behaviour of hot-swelling starch was investigated by performing a temperature ramp and flow curve in a rheometer. These currently applied methods showed challenges such as sedimentation and poor measurement repeatability. The challenges were solved in the temperature ramp by increasing the constant shear rate and starting the measurement without surveillance time. Furthermore, it was concluded that a low heating rate is essential to accurately determine the gelatinization temperature.

For the flow curve, different absolute measuring systems were needed before gelatinization and after gelatinization. A heating interval, regulating the heating rate and heating time, decreased sedimentation and improved the measurement repeatability. In addition to this, the measuring point duration in the flow curve was decreased to closely follow the behaviour of the sample in a shorter measuring time. The improved methodology showed an almost three times higher viscosity after gelatinization by preventing sedimentation. However, one limitation with this method remains, it needs to be customized for each measuring system since the temperature controllers work differently in different heating devices (air, peltier or electrical heating).

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Thursday, August 19

NRC

Session: Advances in rheometry

Rheo-optical tools for polymer applications

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Rheological methods reveal information on macroscopic material properties. However, the mechanical material properties are strongly dependent on the underlying microstructure. Therefore information on the microstructure is often valuable for a better understanding of the rheological behavior. Simultaneous use of rheological and optical techniques, i.e. of rheo-optical methods, is helpful to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids and polymeric materials in particular. Different optical methods such as small angle light scattering, microscopy (polarized, fluorescence, confocal), spectroscopy (NIR, IR, Raman), birefringence and dichroism, as well as pure visualization techniques have been employed.

In this paper, the use of rheo-optical techniques suited for polymer application is discussed. Microscopy and especially polarized microscopy and SALS at elevated temperatures provide structural information in the micro meter range on flow induced orientation or phase transition phenomena. A rheo polarized imaging techniques called SIPLI (shear induced polarization light imaging) combines a visualization technique with measurements of local stresses through the detection of the birefringence [1]. By employing parallel-plate geometries, different shear rates are present throughout the sample, from a maximum shear rate at edge of the sample to a zero shear rate in the center of the plate. With SIPLI the whole plate is observed and the birefringence can be displayed over the full range of shear rates within one single experiment. Applications presented include simultaneous SIPLI and the rheology of the oriented lamellar phase of block copolymers, cellulose and block copolymer solutions. In addition, a direct relation between the shish formation and the polymer melt viscosity upturn during flow-induced crystallization of semi-crystalline polymers is demonstrated.

During phase transition, the physical as well as chemical properties of polymers change dramatically. While the viscoelastic properties can usually be characterized with a rheometer, no chemical information is obtained by the mechanical testing. The interpretation of rheometric results often relies on empirical models and a more phenomenological approach. For directly relating the changes in rheological behavior to chemical changes, we employ Raman spectroscopy in situ with rheology [2]. The phase transition from the crystalline to liquid state for different polymers was monitored for a temperature range from 70 to 150 °C. This phase transition resulted in a higher viscosity, as well as an alteration of vibrational bands in the Raman spectrum, reflecting the conversion from a crystalline to an amorphous structure. Having both viscoelastic and spectroscopic information on a sample allows a detailed characterization, and interpretation of the sample behavior on the molecular level. Special emphasis has been given to an accurate temperature control up to 400°C in order to take full advantage of the potential of the various rheo-optical techniques for polymeric applications.

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Low-field RheoNMR: In-situ correlation of local segmental mobility with mechanical properties during hydrogel synthesis

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The crosslinking copolymerization of acrylic acid (AAc) and *N*, *N*'-methylenebis(acrylamide) (MBA) with varying degrees of crosslinking (*DC*) was studied using a unique combination of rheology and low-field time domain ^{1}H NMR (TD-NMR), referred to as RheoNMR. This device allows for a direct quantitative correlation of macroscopic mechanical properties with the segmental mobility (<10 nm) of the polymer chains during gelation. The segmental mobility is probed continuously by ^{1}H NMR transverse relaxation (T_2) measurements which give an insight into the time-evolution of the nanoscopic network structure. The rheological analysis of the gelation kinetics for varying *DC* values reveals a loss of crosslinking efficiency with increasing *DC* ($G' \sim DC^{0.36}$). Simultaneous TD-NMR measurements show a characteristic stretched exponential ($\exp[(-\tau/T_2)^{\beta}]$) decay of the transverse magnetization where the stretching exponent β is decreasing from 0.90 to 0.67 as function of increasing *DC*. Since β^{-1} is related to the width of the T_2 distribution, this decreasing trend of β indicates the formation of a more heterogeneous network on the nanoscopic scale at higher *DC* values, and therefore, can be associated with the formation of dynamically different connectivity defects, e.g. loops and dangling ends. This finding is consistent with the aforementioned macroscopic loss in crosslinking efficiency and TD-NMR is able to quantify this loss based on molecular properties reflected in β. Moreover, the TD-NMR experiment is for the first time exploited as a polymer concentration probe by using a T_1 filter that substantially suppresses the contribution of solvent (residual monomer or HDO) to the NMR signal intensity. With this approach the NMR signal intensity is directly proportional to the polymer concentration which enables the in-situ monitoring of polymer formation during gelation. The direct correlation of G' with the polymer concentration (c_{poly}) reveals a characteristic scaling with an exponent of 2.3. This is consistent with the theoretical prediction of G' considering its concentration dependency ($G' \sim c_{\text{poly}}^{2.3}$) based on polymer dynamics in semi-dilute entangled polymer solutions.

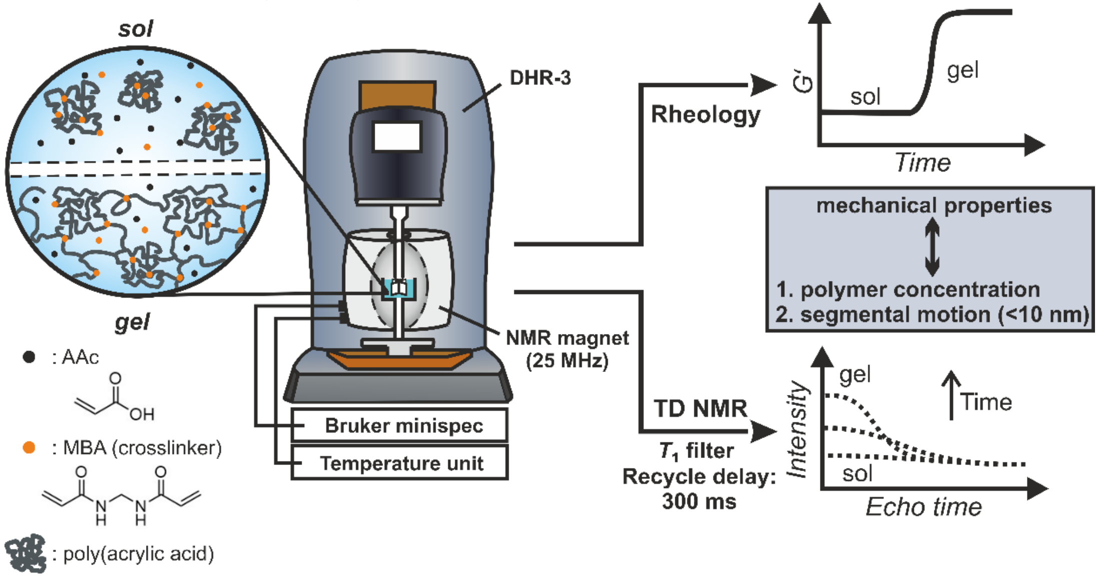

Figure 1. Schematic of the RheoNMR setup with the respective experimental observables.

A new and highly efficient method to measure the steady shear viscosity and wall slip of rubber compounds. Closed boundary rheometer (RPA).

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Steady shear viscosity of rubber compounds is commonly measured using a capillary rheometer. This instrument however is requiring numerous tests to achieve the required corrections for true viscosity calculation to be used in modern flow simulation. These corrections are entrance pressure drop (Bagley), non-Newtonian flow (Rabinovitch), and wall slip, making this test highly time-consuming and rather inaccurate. Particularly wall slip is difficult to apprehend essentially due to the complexity of rubber compound formulations.

The use of a cone/cone, cone/plate closed boundary rheometer (RPA) enables the measurement of true steady shear viscosity. The replacement of one grooved die by a highly polished die provides a suitable tool for wall slip measurements. Since the instrument has closed boundary conditions, the test cavity pressure can be varied to further study the influence of pressure on wall slip.
This instrument and die combination has successfully measured steady shear viscosity with high repeatability without correction. The results fit well with other rheometers/viscometers when no-slip conditions are assured. The closed boundary configuration prevents edge fracture as commonly experienced with open boundary rheometers on high viscosity, high elasticity materials. The comparison of results using grooved dies (no-slip) and polished dies (slip) readily provides wall slip velocity under constant pressure. The results of wall slip versus shear stress follow a power-law function as per Navier's slip law $-[F_{(V)} = -k(V_r)^e]$.
This method is unique in separating shear rate from pressure effects on wall slip. It, therefore, questions pressure-driven flow instruments which are using pressure measurement for shear stress calculation inducing a pressure gradient along the die length.

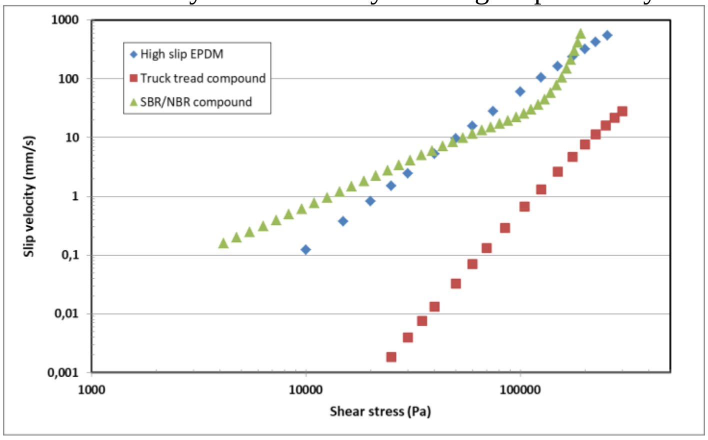

Figure 2: Slip velocity for 3 largely different rubber compounds.

Finally, in strictly no-slip conditions, a yield stress value was found for a highly filled material, similarly to high concentration suspension. Below this yield stress value, the slip ratio $[\frac{Slip\ velocity}{Apparent\ velocity}]$ for this compound is found to be equal to 1 so moving solely by pure slip, as quoted in a previous publication by Dilhan M. Kalyon[1].

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Thursday, August 19

NPD

Session: Functional polymers

Field Concentration Use in Electroluminescent Devices

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Wearable electronics[1] and soft screens[2, 3] are fields attracting great attention, and scientists are working on new ways to produce soft and stretchable electroluminescent (EL) devices. Most electroluminescent devices are based on phosphorescent materials, such as zinc sulfide (ZnS). Zinc sulfide is one of several types of electroluminescent phosphor that emits light under alternating electric field and it is widely applied in EL glass panels, plastic panels, and EL wires.[1, 4]

In this work, we fabricated dielectric elastomer actuators (DEAs) by using silicone elastomer as a dielectric and polyacrylamide (PAAm) hydrogel as an electrode. The fabricated DEAs are coated with an electroluminescent layer to create soft electroluminescent devices. These devices were previously tested[5] and it was found that such DEAs have short lifetimes due to the high field concentration along the electrode edges. In this work, we show that the amplification effect of field concentration can be used in so-called hydrogel-elastomer EL devices to reduce the working voltage and we do so by making two types of EL hydrogel-elastomer devices.

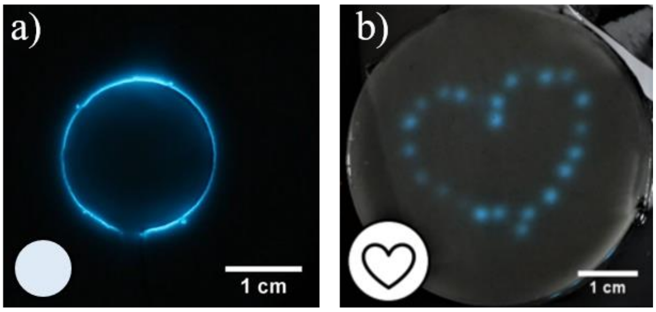

Figure 1. Electrode patterns for devices working in the dark, under a voltage of amplitude 2.7 kV and frequency 1 kHz. a) Pattern for hydrogel electrodes; b) Pattern for copper wire electrodes.

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3D-printing of Plastic Plasmonic Hydrogen Sensors

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Cost efficient hydrogen (H_2) sensors are a vital part to ensure safety in the emerging hydrogen economy. To enable the fabrication of plasmonic sensors with methods that are less elaborate than nanolithography, we have introduced plastic plasmonic nanocomposite materials[1], which allow to combine the advantages of plasmonic sensing with the versatility of polymer processing. This approach is however limited by the typically slow diffusion of H_2 through the polymer matrix, resulting in long response times on the order of minutes in case of, e.g., poly(methyl methacrylate).

In this talk, we discuss how the use of an amorphous fluoropolymer matrix together with colloidal Pd nanoparticles prepared by continuous flow synthesis, results in a highly scalable composite that has a high H_2 diffusion coefficient of 10^{-5} cm^2 s^{-1}.[2] Hence, hydrogen sensors based on this composite are no longer limited by the diffusion of H_2 through the composite and therefore display a response time as short as 2.5s.

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Capture of CO_2 by using acrylate based polymers with amine functionalities

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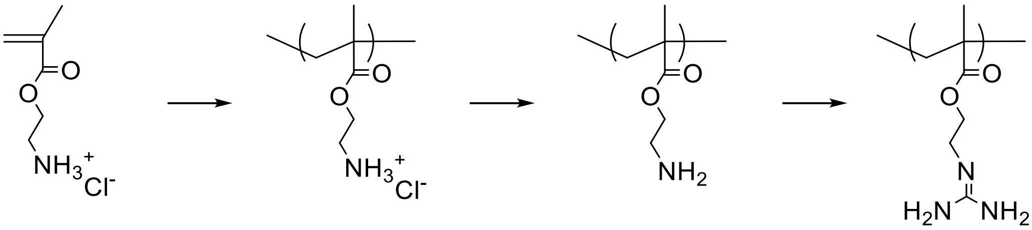
With the increasing amount of CO_2 contributing into the greenhouse effect in the atmosphere, the need for technologies to reduce the excess CO_2 is increasing.[1] Most of the carbon capture technologies (CCT) in development today are based on physi- and chemisorption.[2] Both techniques require a different approach chemistry wise and can be implemented as solids or liquids.[3] The carbon capture technologies today are still inadequate to reduce the amount of CO_2 to acceptable levels due to the high cost of these techniques.[4]

As solid polymer membranes and liquid amines are already implemented commercially in CCT, it would be sensible to try to combine the two.[3] This would bring the benefits of a solid substrate (physisorption) impregnated with amines (chemisorption) implemented in a raw material, that can be processed according to specific application. We synthesized a series of acrylate based polymers with varying amine functionalities using RAFT in low temperature aqueous conditions and studied the CO_2 absorbance of the dry solid raw powder. The results are promising and point to a comparably high and selective CO_2 absorption even before any advanced processing techniques. The desorption temperatures are also below 100 °C indicating possible energy savings during regeneration of the material.



Scheme 1. Synthesis route of polymers.

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Magnetochromic elastomer with controllable instant color changes

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A novel magnetochromic elastomer has been developed by dissolving magnetic nanoparticles (MNPs) in a low viscosity liquid and emulsifying the solution in polydimethylsiloxane (PDMS). In the presence of an external magnetic field, the MNPs are aligned in order along the direction of the magnetic field and thereby cause transparency of the material (Figure 1), achieving a switch on/off function of the material. The influence of particle size and size distribution on the magnetochromic effect is discussed. Compared to the non-treated commercial magnetic particles, ultrasonicated citric acid-treated MNPs with smaller primary particles and narrower size distribution exhibit better dispersion of particles in poly(ethylene glycol)-200 (PEG200). The silicone elastomer with 40 parts per hundred rubber (phr) PEG200 encapsulating 3 wt% citric acid-MNPs achieves a fast and reversible color change under an external magnetic field. The better coloration efficiency and faster response time of magnetochromic elastomer open up for a variety of applications, such as sensors[1] and anticounterfeiting labels[2].

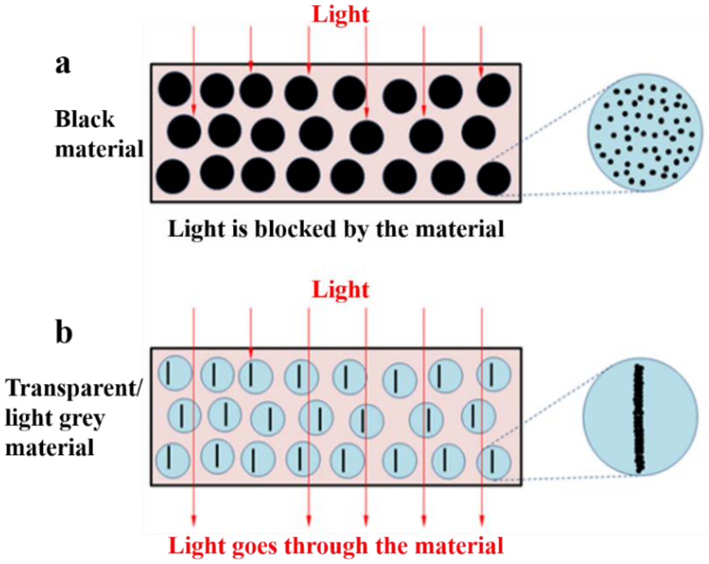

Figure 1. Schematic representation of magnetochromic properties of liquid-silicone elastomers containing MNPs. (a) The initial state of the elastomer. (b) The MNPs rearrange when exposed to a magnetic field.

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Poly(N-acryloyl glycinamide) microgels for encapsulation of catalysts

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Poly(N-acryloyl glycinamide) (PNAGA)[1] is a non-ionic polymer that shows upper critical solution temperature-type (UCST) behavior in water and saline solutions, rendering it insoluble at low temperatures and soluble at elevated temperature. By utilizing this property during the aqueous precipitation polymerization of N-acryloyl glycinamide at low temperature in presence of crosslinker, thermosensitive microgels are easily prepared.[2] These thermosensitive colloidal particles can then be utilized as smart catalytic carriers. The encapsulation of metal nanoparticle catalysts, enzymes or both simultaneously enables efficient and tunable catalytic transformations.[3,4]

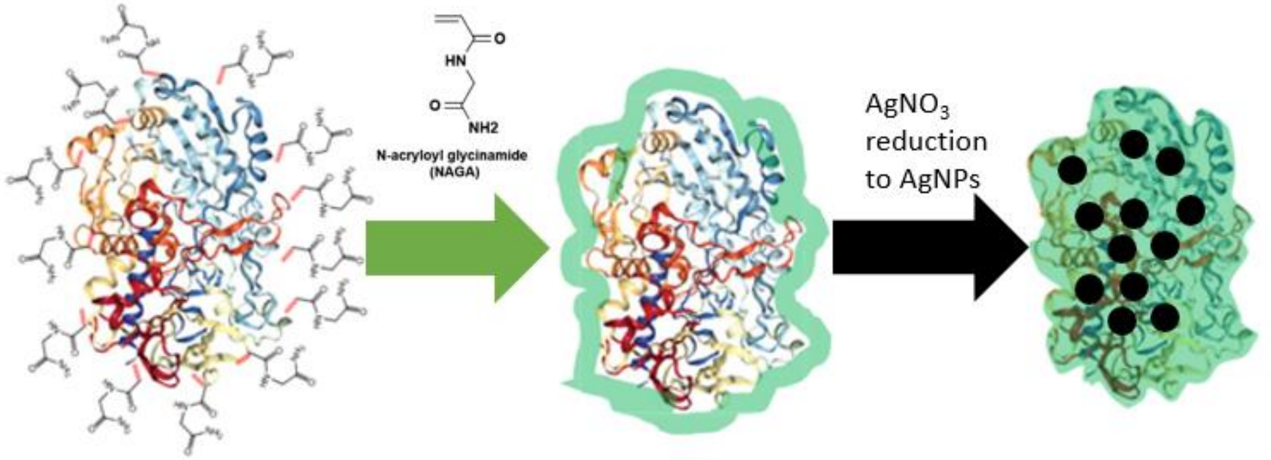

Figure 1. Synthesis of microgel catalyst system combining both enzymatic and metal catalysis.

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Static and dynamic control of magnetic microgels

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Microscale anisotropic building blocks have been receiving increasing attention in respect to their use as model systems to study complex phase diagrams, dynamics and self-assembly processes and for their biomedical applications. Tissue engineering is one of them, where rod-like magnetic microgels loaded with superparamagnetic iron oxide nanoparticles (SPIONs) were found to direct cell growth when aligned under a homogeneous magnetic field [1]. We are currently aiming at controlling the magnetic orientation and actuation of such microgels using ferrimagnetic maghemite spindles as anisotropic magnetic fillers instead of SPIONS [2]. Polyethyleneglycol microgels of various shapes were designed through two different synthesis methods. Rod-like microgels were produced using particle replication in non-wetting templates (PRINT), and "any-shaped" microgels via stop-flow projection lithography (SFL) [3]. The maghemite spindles were pre-aligned and self-assembled into dipolar chains during the microgel synthesis as evidenced by the examination of the resulting composite microgels by scanning electron microscopy (SEM) (Figure 1A). This procedure allows us to pre-program the orientation of the composite microgels parallel or perpendicular to the applied magnetic field as shown in Fig. 1B,C. The actuation of these systems by an external rotating magnetic field further offers the possibility to dynamically align the microgels rods with an orthogonal magnetic moment in the third dimension (Figure 1D). We conclude with the extension of this strategy to more complex shapes and its application for the design of magnetic micro-actuators (Figure 1E).

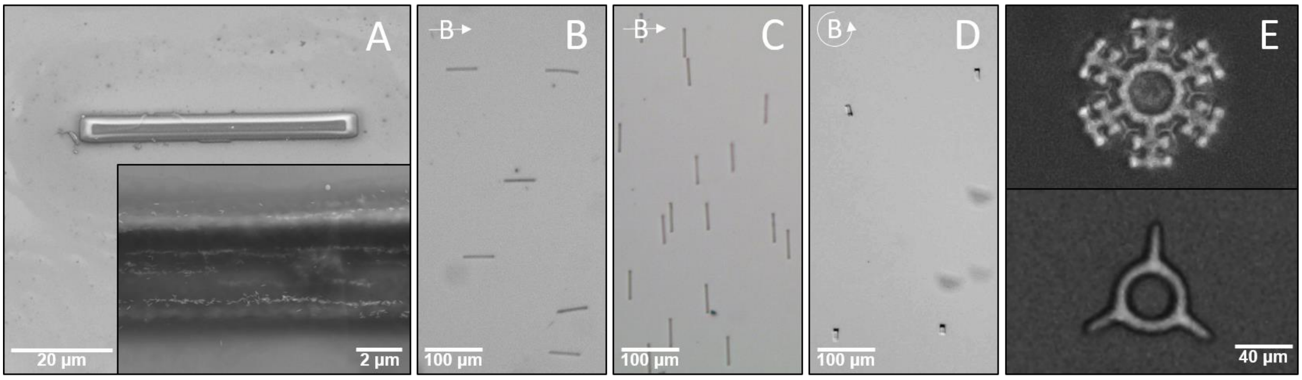

Figure 1. (A) SEM image of incorporated maghemite nanoparticles inside a rod-like microgel. (B,C) Bright field micrographs of the composite microgel alignment parallel and perpendicular to the applied magnetic field. (D) Vertical alignment of the composite microgels with an orthogonal magnetic moment under rotating field (70 mT, 10 rpm). (E) "Any-shaped" geometries obtained by SFL for the design of magnetic actuators.

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Capillary Driven Self-Assembly of Ellipsoidal Composite Microgels at the Air/Water Interface

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We investigate the spontaneous capillary driven self-assembly of composite prolate shaped microgels. The microgels consist of a polystyrene (PS) core surrounded with a cross-linked fluorescently labelled poly(N-isopropylmethylacrylamide) (PNIPMAM) shell. The aspect ratios of the composite microgels can be finely adjusted upon uniaxial stretching the particles embedded into polyvinyl alcohol films [1]. The fully characterized particles present an aspect ratio ρ varying from 1 to 8.8 as estimated from laser confocal microscopy (CLSM) in their swollen conformation at 20°C. We follow their spontaneous interfacial self-assembly at the air-water interface using bright field and fluorescence microscopy. A transition is observed from an apparently random assembly into compact clusters for ρ=2.1 to a side-to-side assembly into long chains for ρ=8.8. The transition occurs between ρ=2.6 and 3.3 for which a trigonal and trigonal/side to side coexistence assembly are respectively identified. The influence of the composite microgel softness and anisotropy on the assembly is discussed as well its influence on the interfacial tension derived from time-resolved pending drop measurements.

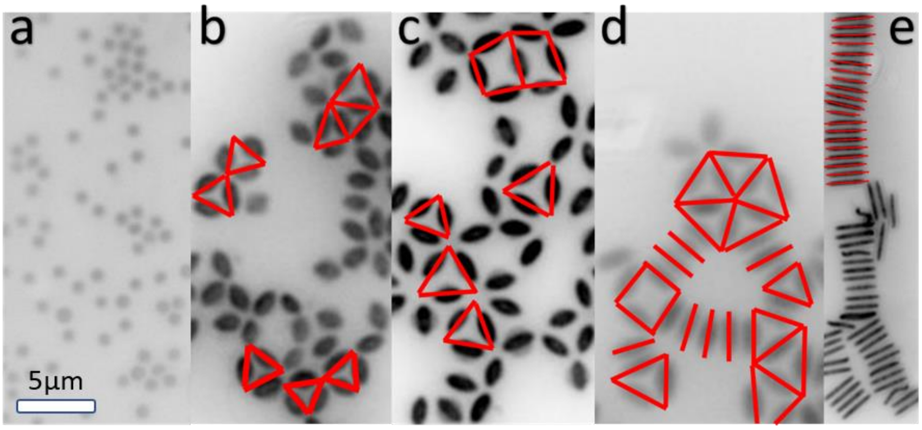

Figure 1. Colour inverted fluorescence micrographs of spherical composite microgels (a) and ellipsoidal composite microgels with an aspect ratio ρ equal to 2.1 (b), 2.6 (c), 3.3 (d) and 8.8 (e) assembled at the air-water interface at 20°C. Some of the typical assemblies are highlighted with red lines.

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Friday, August 20

NRC

Session: General rheology

Limitations on rheological properties of particulate suspensions arising from addition of a mesoporous ancillary mineral: exemplified by pin coating of a functional gas filter layer

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Unlike established paper coating, the requirements for particulate functional coatings often lead to the omission of polymer dispersant, normally used to achieve homogeneous aqueous colloidal dispersion. Dispersant is avoided so as to retain the particle surface functionality, resulting in heterogeneous complex rheology. We take an example from a novel development for an NO_x mitigation surface flow filter system, in which the desired reaction of GCC with NO_2 results in in-situ CO_2 generation, Eq. (1).

$$\begin{gathered} CaCO_3 + H_2O + 2NO_{x\,(=1,2)} + \tfrac{1}{2}\,O_2 \rightarrow Ca(NO_{2,3})_2 + H_2CO_3 \\ H_2CO_3 \rightarrow H_2O + \boxed{CO_2}\uparrow \end{gathered} \tag{1}$$

Inclusion of a mesoporous ancillary mineral has been proposed to capture the CO_2 [1]. The coating is applied onto a planar substrate in the form of a pixelated array of droplets using pin coating to maximise gas-contact dynamic [1,2]. A 2D array of protruding pins is loaded by submersion in the aqueous coating colour, and transferring the adhering droplets onto the substrate by surface contact, Figure 1. The flow is driven by meniscus wetting of the substrate (fibrous cellulose in this case) causing lateral spread and bulk permeation, followed by filament formation upon retraction of the pin array. We have studied the stress-related viscoelastic and dilatant structure behaviour of the material suspension, and found that adopting an ancillary mineral that absorbs water, and functionally gas, exemplified by perlite naturally occurring porous volcanic glass) is preferable to one that additionally immobilises surface water, e.g. sepiolite (a needle-like water adsorbing mineral) to reduce structuration and dilatancy as a function of solids content.

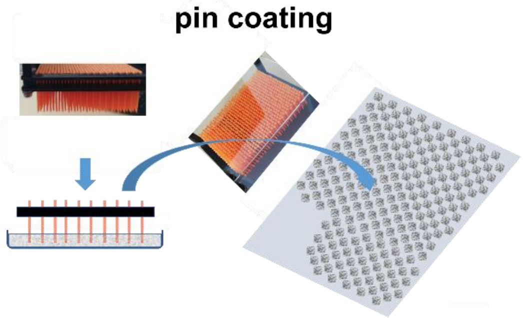

Figure 1. Schematic of pin coating onto a fibrous substrate [1]. *Copyright owned by authors.*

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On the Rheology of Asphalt Mastic Containing Mining Filler

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Low temperature cracking is a deleterious phenomenon for asphalt pavements built in cold climates. As the temperature rapidly decreases, thermal stresses develop in the restrained asphalt surface layer and, when the temperature reaches a critical value, cracking occurs. A simple solution to address this issue relies on the use of soft asphalt binders with high relaxation characteristics, which limits the accumulation of high stress and the formation of cracks. However, these types of materials may lead to large permanent deformation at high temperatures, limiting their application to real pavement constructions.

In this research, the possibility of obtaining stiffer asphalt binders by adding fine filler obtained from the mining industry was investigated. Two different types of asphalt binders were selected and from each binder, three different types of asphalt mastics were prepared based on the amount of the selected mining filler: 5%, 10%, and 25%. Low temperature three-point bending and temperature-frequency sweep tests were performed by Bending Beam Rheometer (BBR) and Dynamic Shear Rheometer (DSR) (1) to evaluate the low and high temperature properties of asphalt binder and corresponding mastics. From the experimental measurements, creep stiffness, *m*-value, thermal stress, and shear complex modulus were calculated and then graphically and statistically compared.

It was observed that asphalt mastic containing 5% of filler presents similar properties at low temperature and better performances at high temperature compared to the corresponding asphalt binder. On the other hand, asphalt mastics containing a higher amount of fines (10% and 25%) are much more brittle compared to the original binder at low temperature, even though higher rutting resistance to permanent deformation was observed. Figure 1 provides a schematic graphical abstract

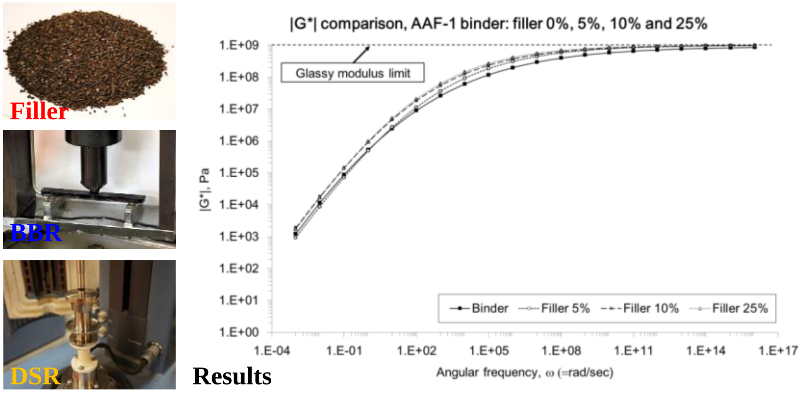

Figure 1. Graphical abstract

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Properties of Dense Barite Sediments from Water-Based Drilling Fluids Oscillatory Viscosity Measurements of Wet Barite Powder

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At the end of the lifetime of an oil or gas well, it is necessary to plug back the well and demolish the surface production equipment [1,2]. In these processes it is often necessary to remove parts of downhole piping and equipment. Most wells have been drilled with densified drilling fluids. Throughout the lifetime of the production period, most of the weighting agents have been settled out in the different annuli behind the production tubing and following casings[3]. The purpose of this article is to present measurement data that will relate to the necessary force to pull a casing from a region where the weighting agent barite has settled out. In addition to barite, drilling fluids contain salts, chemicals, polymers and other particulate materials to control the needed properties. In the current experiments, sediments in two types of drilling fluids were investigated. The sediments were analysed before and after a 30 day storage at at a temperature of 50°C. The drilling fluids were a KCl/polymer based drilling fluid and a bentonite mud. The viscoelastic properties of the sediments were analysed using a plate – plate configuration. The measurement values show very high G' and G'' values. However, the values relate to the compactness and grain-grain interaction of the sediments, and do not imply the existence of any viscoelasticity.

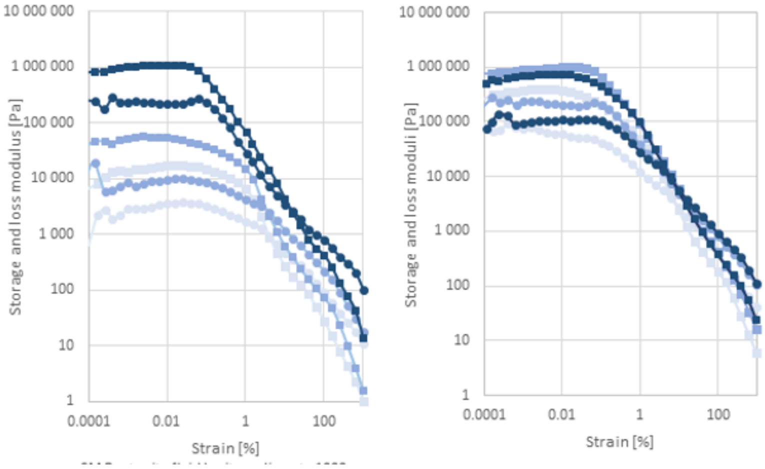

Figure 1. Examples of storage and loss moduli of barite settlements prior to and after 30 days storage at 50°C

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Rheological Characteristics of Oil-Based and Water-Based Drilling Fluids

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Drilling fluid plays a crucial role in well construction with regards to maintaining the well integrity and hole cleaning. API/ISO standards intent to help engineers to characterize the viscosity of fluids at different shear rates, temperatures, and pressures to model the viscosity profile of drilling fluids. Although the realm of rheology is beyond the viscometry, few researchers from petroleum industry have used the rheology to characterize performance and properties of drilling fluids. Werner et al.[1] studied viscoelastic properties of drilling fluids and their influence on hole-cleaning. Oltedal et al.[2] characterized rheological properties of oil-based drilling fluids. In this article, we aim to run set of characterization of rheological state and rheological behaviour of oil-based and water-based drilling fluids after hot rolling.

This study may help petroleum engineers to characterize drilling fluid by studying its rheology. The rheological measurements are conducted in shear rate ranging between 0 to 1020 (1/s), and constant shear stress. Time dependent behaviour of the fluids, stress relaxation behaviour, creep and recovery behaviour, stress sweep (storage modulus), storage stability, frequency sweep, gel strength, yield stress, zero shear viscosity and oscillatory analyses are among the parameters to be measured. Anton Paar rheometer MCR 302 is used in this study. Such study may help engineers and researchers to better understand hole-cleaning, barite sag, cutting transport, mechanisms of fluid loss and formation damage, and managed pressure drilling while comparing rheological properties of the fluids.

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Friday, August 20

NRC

Session: Non-Newtonian fluid mechanics

The shear and extensional rheology of aqueous xanthan gum solution using the Giesekus multi-mode model

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Xanthan gum can be used as an experimental analogue for certain oil well drilling fluids as it is rheologically similar yet physically simpler. This paper presents rheology data in shear and extension for xanthan gum at 10 g/L concentration. These data are compared to predictions made with the multi-mode Giesekus constitutive equation using a unified set of parameters to model both the shear and extensional rheology.

Low shear rate rheology (0.05 to 500 s^{-1}) was acquired using an ARES rotational rheometer. The steady shear rheology is similar to that reported by Martín-Alfonso, *et al*. (2018). The viscoelastic response of xanthan gum was measured using oscillatory tests on an ARES rheometer within the linear viscoelastic range. The extensional data for xanthan gum was obtained using a filament thinning rheometer: the Cambridge Trimaster (HB4). Flow visualisation tests were conducted on a fully contained dual piston rheometer: the Multi Pass Rheometer (MPR) at high shear rates (400 to 10,000 s^{-1}) with a contraction-expansion geometry. A low concentration of sand particles was included to act as tracers to highlight the flow structure.

The Giesekus model used with eight modes gave a reasonable fit to the entire set of steady shear, oscillatory shear, step strain stress relaxation and filament thinning data. These Giesekus parameters were then used to model the flow within the MPR's contraction-expansion geometry using OpenFOAM with the RheoTool plugin, developed by Pimenta, *et al*. (2017). Figure 1 presents a comparison of the flow observed within the MPR and simulation data obtained at a maximum Weissenberg number of order 10^7.

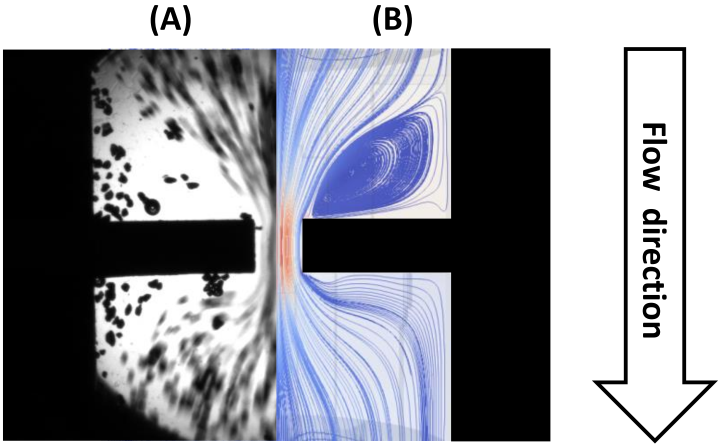

Figure 1: Comparison of contraction flow test streamlines at piston speed 10 $mm.s^{-1}$. MPR experimental setup (A) and the OpenFOAM simulation (B) with the slit die geometry.

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Qualitative modeling to predict the extrusion flow instabilities in polybutadiene sample: Influence of die geometry

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The extrusion flow instabilities[1] of a commercial polybutadiene (PBD) sample are investigated as a function of slit and round capillary die geometries. Qualitative models[2,3] are used to fit the experimental data for the spatial characteristic wavelength (λ) of extrusion flow instabilities. A new qualitative model for slit die geometry (rectangular cross-section) is derivative based on the theoretical concept of the “two layers” extrudate and the force balance at the die exit region. Correlation between the ratio of the extensional and shear stresses at the die exit area and the characteristic dimension, height H and diameter D, of the dies is presented. A geometry-dependent correlation[4] is used to predict the spatial characteristic wavelength (λ) of the extrusion flow instabilities from a round capillary die to a slit die and vice versa.

ACKNOWLEDGMENTS

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Predicting pressure drop in pipes with tomato paste and concentrated orange juice. One successful and one failed prediction.

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As a food processing lines manufacturer with diverse product complexity, an understanding of fluid dynamics in a pipe system corresponding to the rheological properties and flow behaviour is substantial. This will be beneficial to design suitable equipment and prevent processing-related issues, i.e. lowering filling performance, over-dimensioning pumps, excess energy consumption, etc.

Therefore, the objectives of this study were to predict the pressure drop in the straight pipe by using the rheological parameters using the typical high viscous food liquids, i.e. orange juice concentrate, fermented milk or yoghurt, and tomato puree. The rheology parameters were measured using a rotational rheometer described in literature [1-2] and the pressure drop measurement were obtained using a pressure drop rig, as shown in Figure 1.

The orange juice concentrate had a better pressure drop prediction than yoghurt and tomato puree due to its rheology simplicity. However, two other products had more complexity that complicated the rheological measurements in different ways as reflected in the pressure drop experiment. Yoghurt had an obvious thixotropy behaviour, while tomato puree had both thixotropy and rheopexy behaviour with an oscillatory effect during measurement.

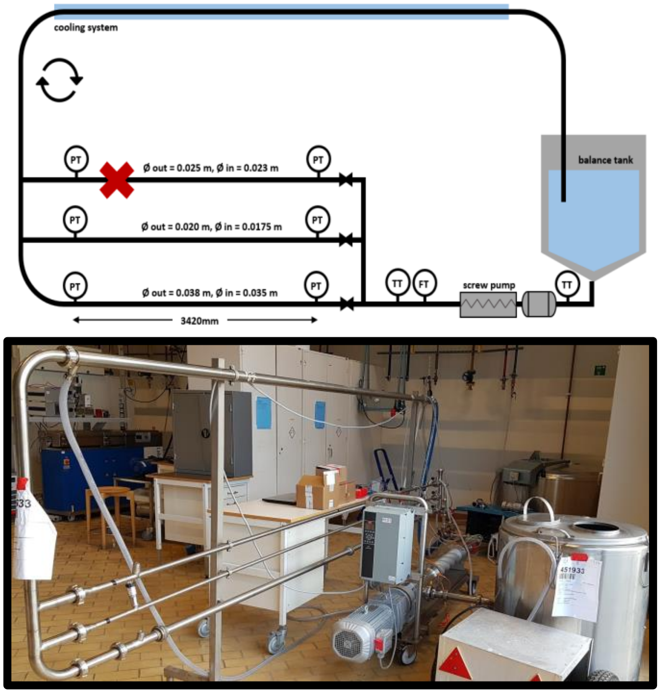

Figure 1. Showing the experimental rig for pressure drop measurements

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Friday, August 20

NPD

Session: Biopolymers

3D-printed thermoset biocomposites based on Forest Residues by Delayed Extrusion of Cold Masterbatch (DECMA)

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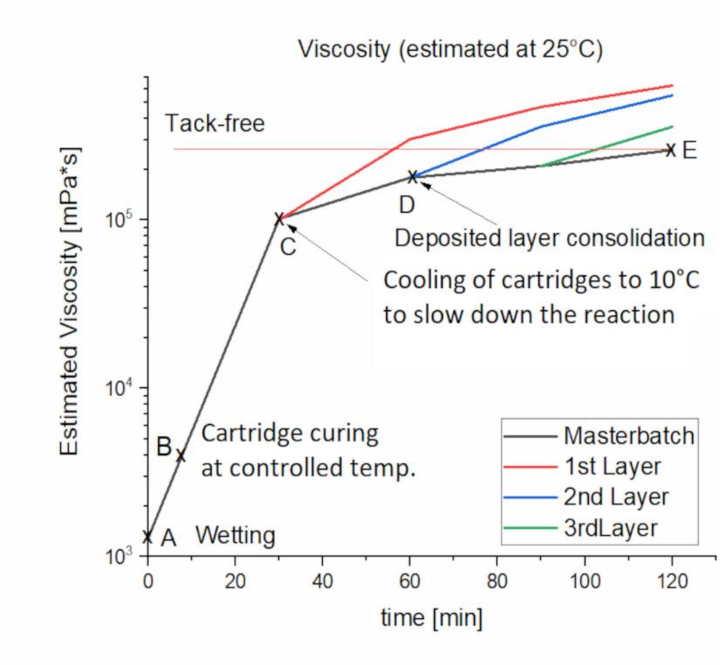
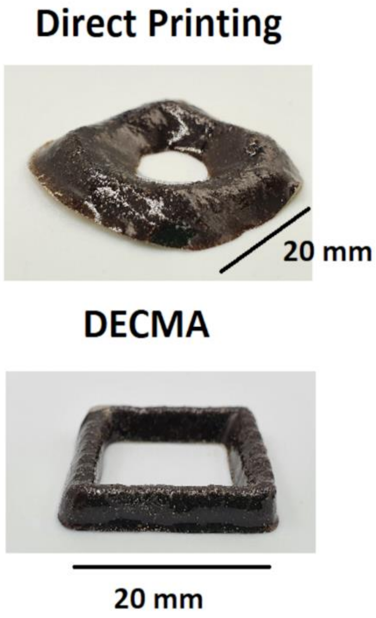
We developed a 3D printing process based on thermoset biocomposites following Delayed Extrusion of Cold Masterbatch (DECMA) approach. First, a masterbatch was produced by mixing a bio-based resin (bioepoxy) and a biofiller (sawdust and/or lignin), which were partially cured at room temperature until reaching an apparent viscosity suitable for extrusion (≈10^5 mPa*s at 10 s^{-1}). Following, the system was cooled down (5-10 °C) to delay subsequent hardening, prior to 3D printing. Clogging, which is a typical challenge when handling thermosets, was prevented during paste extrusion after the given holding period. The printability of the biocomposite paste was systematically investigated and the merits of the delayed extrusion, DECMA, were assessed. Our approach afforded cost-effective, shear-thinning dopes with high bio-based content (in the range of 58% and 71%). The -biobased 3D printed materials demonstrated good machinability by computer numerical control. Overall, the benefits of the introduced DECMA method are shown for processing biobased materials and for on-demand solidification during additive manufacturing.





Melt processing of cellulosic fibres with only water as plasticiser

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Upon heating, native cellulose fibres degrade before softening or melting. This is a well-known limitation to the development of cellulosic thermoplastics as a sustainable alternative to fossil fuel-derived thermoplastic polymers. In biocomposites, cellulosic fibres have been successfully employed as strength additives within polymer matrices.[1] Non-fibre derivatives such as cellulose acetate can be melt processed, although only within a narrow processing range and with the aid of plasticisers.[2,3] Here we present cellulosic fibres that were partially modified to impart thermoplastic characteristics, while preserving their morphology as fibres. We demonstrate melt processing of these modified fibres, by twin-screw extrusion as representative of conventional polymer processing methods, using only water as plasticiser. Figure 1 is a schematic overview of the procedure.

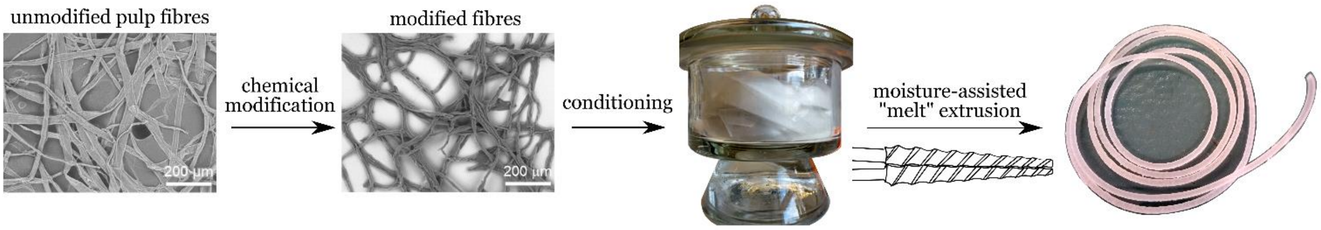

Figure 1. Protocol beginning with chemical modification of regular beaten pulp fibres by partial conversion to dialcohol cellulose (modified fibres). The modified fibres are then conditioned under controlled atmosphere to exploit water as plasticiser. The conditioned fibres are then processed by twin-screw extrusion via a circular die.

Conventional cellulose pulp fibres (beaten kraft pulp) were partially modified to dialcohol cellulose by partial oxidation with sodium metaperiodate follow by total reduction with sodium borohydride.[4] These modified fibres, which are known to be highly ductile and soften upon heating,[5] were melt processed for 11 min (6 min for feeding and 5 min of additional recirculation) at a controlled moisture content of 25 or 63 wt% and processing temperature of 70 or 100 °C. Melt processing was carried out using a commercial lab-scale twin-screw extruder of 5 cm^3 capacity. The extruded materials were characterised by SEM, X-ray diffraction analysis, thermal analysis and tensile testing. Our results establish that water is an adequate plasticiser for melt processing of dialcohol-modified cellulosic fibres, at relatively high degree of modification, without the addition of a synthetic polymer. Although shearing, during twin-screw extrusion, damages the fibres, resulting in moderate losses in tensile strength and elasticity, exceptional ductility is preserved and may even be enhanced.

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Cellulose nanofibers/lignin particles/tragacanth gum nanocomposite hydrogels for biomedical applications

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The plethora of environmental concerns faced today is demanding the development of new biodegradable materials from renewable resources. In this regard, natural polymers are promising resources for the design of new materials owing to their ecologically correct and renewable nature. Cellulose is an abundant, biodegradable, non-toxic, and low-cost biopolymer, already widely used to produce bio-based materials. Cellulose fibers when disintegrated result in cellulose nanofibrils (CNF) that have water-binding capacity and produce stable hydrogels[1]. Lignin is also a bio-renewable polymer that has attracted interest in recent years for its antimicrobial, antioxidant, and UV-shielding properties conferred by the presence of aromatic compounds in its structure[2]. Lignin can be converted into hydrophilic spherical nanoparticles (LNP) with well-defined surface structure. This is an approach to overcome lignin heterogeneity and low solubility in water and explore new applications. Gum tragacanth (TG) is a highly branched polysaccharide extracted as a dry exudation from the stems and branches of *Astragalus gummifer* trees. It is also environmentally friendly, biocompatible, and has good rheological properties[3], however, the potential applications of TG have not been fully investigated.

All these characteristics make CNF, LNP, and TG attractive for material design, applicable in a variety of technological fields, for instance, biomedical materials as drug carriers, wound dressings, and tissue engineering scaffolding. These polymers have a wide range of functionalities in their chemical structures such as hydroxyl and carboxyl groups and great potential to produce hydrogels with high water retention capacity[4,5]. Hydrogels can be engineered in tunable microstructure, and consequently tunable mechanical properties and degradation rate to mimic the tissue environment. Hydrogel scaffolds can promote the regulation of cellular functions, therefore, improving tissue growth.

In this study, CNF, LNP, and TG were used to prepare multicomponent hydrogels for 3D printing scaffolds with biocompatible properties for biomedical application. The results of our work showed that the rheological behavior was improved with the addition of TG to the hydrogel composition. A similar result was observed for the scaffold's swelling capacity and degradation rate, the properties were improved with the increase of the TG content in the hydrogels. The values of Young's compressive modules for hydrogels made it possible to classify them as soft gels at the level between skin and muscle tissues. The combination of properties of these materials makes plant-based hydrogels attractive to design materials with the potential to improve patients' lives through regenerative medicine.

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Bio-based lactones – Exploring their free-radical polymerization and polymer properties

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The replacement of fossil-based materials with bio-based alternatives is highly relevant due to environmental concerns and limited resources. Bio-based building blocks result in new materials with sometimes unprecedented properties rendering them an interesting subject to study.

The lactones α-methylene-γ-butyrolactone and the structurally similar α-methylene-γ-valerolactone are two of these building blocks that can be derived from the bio-based itaconic acid and levulinic acid, respectively. Itaconic acid is a promising platform chemical that is produced by the fermentation of carbohydrates and it was listed by the U.S. Department of Energy as one of the top-value added chemicals from biomass. In this study, the free-radical polymerization of these two lactones into homopolymers or together with fossil-based (meth)acrylate monomers, methyl acrylate and methyl methacrylate in different ratios, was explored. 2,2′-Azobisisobutyronitrile or lauroyl peroxide were used as initiators to investigate their effect on the polymerization behaviors. Polymerizations were monitored by monomer conversion, and the final polymers were characterized with respect to molecular weight, composition, glass transition temperature and thermal degradation.

The incorporation of the monomers in the copolymers was significantly affected by the differences in reactivity ratios, resulting in a substantial compositional drift in some cases as reflected in the thermal properties of the copolymers. Increasing the thermal stability and obtaining varying T_g by mixing monomers at different ratios make lactones promising building blocks, that can be used to synthesize bio-based or partially bio-based polymers with properties tailored for their final application.

Hemicellulose cross-linked nanocellulose as immobilization matrix for photosynthetic cell factories

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Cell factories from photosynthetic microorganisms have been widely researched as an alternative to petroleum-based feedstock in the production of sustainable fuels and chemicals. Immobilization of photosynthetic organisms is a promising approach that could be used to overcome the challenges of suspension cultures limiting industrial scale utilization of this technique. It is crucial that the matrix material used to immobilize the photosynthetic cells has sufficient wet mechanical properties in addition to being biologically compatible with the cells. Recently, the use of PVA-cross-linked TEMPO-oxidized cellulose nanofiber (TCNF) matrices with high wet strength has been reported as a superior alternative to conventional alginate-based solutions.[1,2] Here, we investigated the use of mixed-linkage glucan (MLG), a hemicellulose found in grassy plants as a structural cross-linker, as a natural cellulose-based alternative to PVA. Previously, MLG has been shown to create strong hydrogels with TCNF.[3] The performance of MLG cross-linked TCNF matrices was investigated using rheological measurements and biological activity monitoring. TCNF-MLG matrices are shown to have even less variation in wet strength with and without cells than TCNF-PVA. Additionally, the cell viability in TCNF-MLG is shown to be supported up to 47 days. The results demonstrate the feasibility of an all-cellulose based matrix for novel photosynthetic immobilized cell factories.

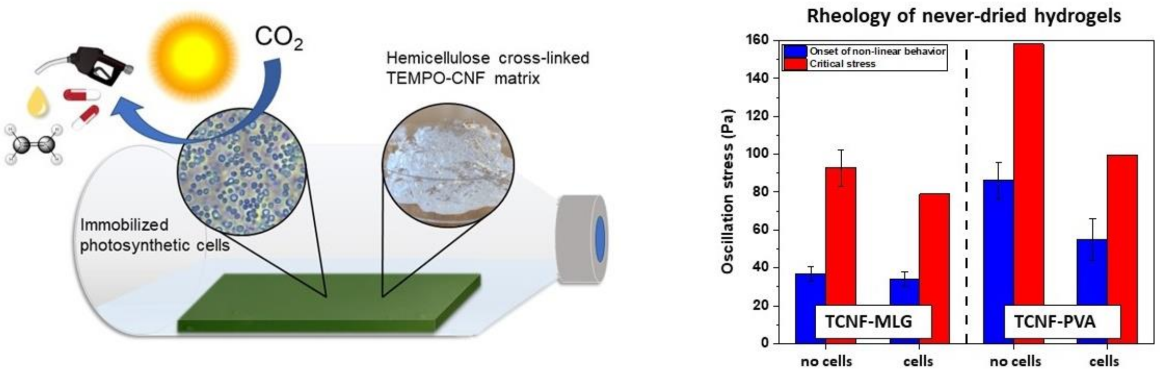

Figure 1. (A) Conceptual representation of photosynthetic cells immobilized in MLG-cross-linked TCNF, and (B) the onset of non-linear behavior and critical stress (yield point) values of never-dried TCNF-MLG and TCNF-PVA hydrogel films with and without immobilized cyanobacterial cells.

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Nanocellulose-based immobilization matrices for photosynthetic cell factories

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Immobilization of photosynthetic microbes can greatly improve the efficiency of cell factories designed for sustainable chemicals production. Here, we introduce a mechanically durable cell factory matrix architecture with ethylene-producing cyanobacteria entrapped within a matrix of never-dried TEMPO-oxidized cellulose nanofibers (TCNF) cross-linked with polyvinyl alcohol (PVA). Studied via rheology, the rigid nanofiber network combined with strong PVA crosslink enables the formation of a strong self-standing hydrogel structure that outperforms conventional matrix structures based on polymeric Ca^{2+}-alginate. Moreover, the hygroscopic and porous nanofiber network protects the cells from the surrounding environment, illustrated via long-term cell viability. Finally, the novel TCNF matrix remains stable in submerged conditions with high concentrations of $NaHCO_3$ supplement, resulting in efficient ethylene production and prolonged operational capacity of the immobilized cells. In contrast, alginate-based matrices fail under the same conditions and leak the cells into the surrounding medium. These results demonstrate the potential of cell immobilization using a versatile TCNF-based matrix, paving way towards a novel solid-state cell factory concept for efficient and sustainable bioproduction of valuable chemicals.

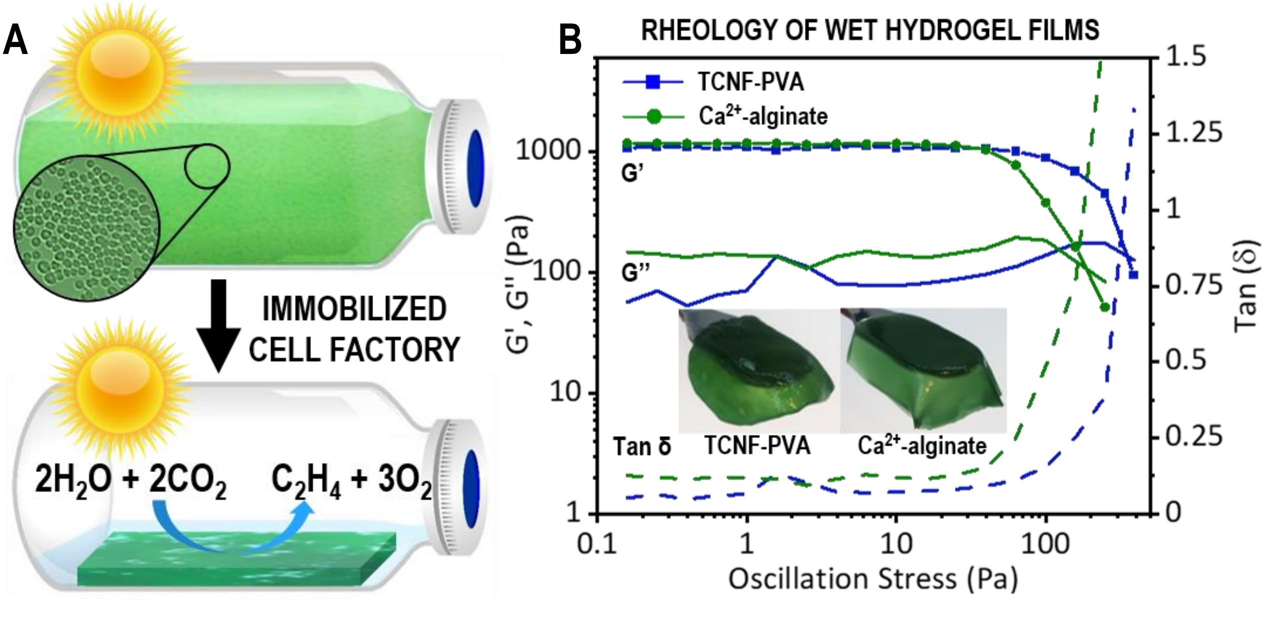

Figure 1. A) Conceptual approach of immobilized cell factory for biocatalytic ethylene production, and B) rheological properties of wet TCNF and alginate –based hydrogel films with immobilized cyanobacterial cells.

Cellulose nanocrystal-based bio-nanocomposite matrix for cell immobilization with continued photosynthetic activity

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Cellulose-based biopolymer films and hydrogels have a surge in demand due to their outstanding optical, thermal, and mechanical properties. [1] Biocompatibility, low toxicity, porous nature, and self-standing network formation are some of the properties that make cellulose nanocrystals (CNC) a great candidate for cell immobilization systems.[2] Inspired by the plant cell wall, different polysaccharides have been proposed to be introduced to the CNC suspension to form an amorphous network for self-standing native hydrogels. Cellulose nanocrystals (CNC) based matrix with polysaccharides are designed to form dense films and viscous hydrogels to confine microbial cells while sustaining vital activity such as photosynthesis. In this work, rheological analysis of hydrogels containing different polysaccharides such as xylan, pectin, carboxymethyl cellulose, and mixed-linkage beta-glucans are carried out in order to determine the hydrogel network strength. After immobilization of cells inside the gel network, to determine the change in the rheological properties is crucial in order to find out the best material for the next step. Thus, changes in the network formation with different additives while varying cell and additive concentrations are tested and correlations have been presented. Optimized self-standing architecture for cell viability while allowing gas and light transfer are vital criteria to be met for a promising biocomposite with potential uses in drug carrier systems and artificial photosynthesis. We present new cellulose-based biocompatible hydrogels, its design and investigation of rheological properties for future bio-systems.

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Friday, August 20

NPD

Session: Functional polymers / sustainable polymers

Electrically Conducting Elastomeric Fibers with High Stretchability and Stability

Sepideh Zokaei[1], Mariavittoria Craighero[1], Claudia Cea[2], Lucas M. Kneissl[1], Renee Kroon[1], Dion Khodagholy[2], Anja Lund[1*] and Christian Müller[1*]

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Stretchable electronic materials hold an intriguing promise to function as imperceptible wearable electronic devices e.g. e-skins and electronic textiles (e-textiles). Conjugated polymers with polar oligoethylene glycol side chains are great candidates for realization of wearable electronics due to having low T_g, hence low stiffness, and high miscibility with polar stretchable polymers. The polar side chains enhance the compatibility with molecular dopants and improve the electrical conductivity and thermal stability of the doped material. This class of conjugated polymers attracts substantial attention for being utilized in organic thermoelectrics, energy storage devices and bioelectronics. Improving the versatility of these polymers, strategies are needed to fine-tune their mechanical stiffness. In this contribution, we report our efforts to blend a polar polythiophene with polyurethane to fabricate elastomeric and stretchable blend fibers through a versatile, reproducible, and scalable wet-spinning process followed by chemical doping.

The blend fibers display a record combination of mechanical stretchability and electrical properties as they are stretchable up to 480% even after chemical doping with iron (III) p-toluenesulfonate (FeTos) and exhibit an electrical conductivity of up to 7.4 S cm^{-1}. The fibers keep being conductive during elongation until fiber fracture and show outstanding long-term stability at ambient conditions. Cyclic stretching of the doped fibers up to 50% strain, at least 400 strain cycles, revealed their high cyclic stability and ability to retain electrical conductivity.

Nonionic antimicrobial hyperbranched polyesters with indole or isatin functionalities

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Antimicrobial polymers (AMPs) have received growing attention due to their enhanced antimicrobial effects, low toxicity and low leaching potential compared to small molecular antimicrobials.[1] Today most AMPs are ionic and may have low miscibility with non-ionic plastics. Our group have been working on biobased nonionic AMPs.[2] In this work, two nonionic hyperbranched polyesters (HBPs) with indole or isatin functionality were synthesized.[3] The molecular structures and thermal properties of the obtained HBPs were characterized by GPC, NMR, FTIR, TGA and DSC analyses. Antimicrobial disk diffusion assay revealed that these HBPs were more effective against 8 human pathogenic bacteria than the small molecules with indole or isatin groups. DSC results suggested that up to 20 wt % indole-based HBP can form miscible blends with polyhydroxybutyrate or polycaprolactone, which was likely due to the favourable hydrogen bonding between N-H moiety of indole and the C=O of polyesters. Preliminary enzymatic degradation studies indicated that the incorporation of indole into HBPs as well as small molecules facilitated their enzymatic degradation with PETase from *Ideonella sakaiensis*, while isatin exerted complex or negative impact. Finally, MTT assay with a mammalian cell line showed negligible cytotoxicity of the obtained HBPs.

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Synthesis and Lca of vanillin-based spirocyclic diol toward fiber and packaging applications

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Lignin is promising bio-based resource to produce bioplastics. It can be cracked to yield various aromatic structures like vanillin, vanillic acid, syringaldehyde etc. with different functionalities for making monomers for polymer synthesis. [1,2] In our work, we have synthesized a rigid diol monomer using vanillin, pentaerythritol and ethylene carbonate (Fig. 1A).[1] The greenhouse gas emission measured using a preliminary life cycle assessment (LCA) showed that the new spiro-diol **V** are significantly lower environmental impact than that of bio-based 1,3-propanediol. This fully bio-based spiro-diol **V** was then used for synthesizing copolyesters with dimethyl terephthalate and 1,6-hexanediol by melt polycondensation. A series of semicrystalline and amorphous polyesters with up to 30% incorporation of spiro-diol **V** were obtained. Incorporation of spiro-diol **V** in copolyesters improved the glass transition temperatures (T_g up to 64 °C) and thermal stability. Dynamic mechanical analysis indicated that the copolyesters showed storage moduli comparable to a commercial high-performance polyester Akestra™ with a similar spirocyclic diol (Fig. 1B). Moreover, when 1,6-hexanediol in the copolyesters was replaced by a more rigid neopentyl glycol, further enhancement in thermal and mechanical properties was observed. Additionally, it improved oxygen barrier properties of copolyesters.

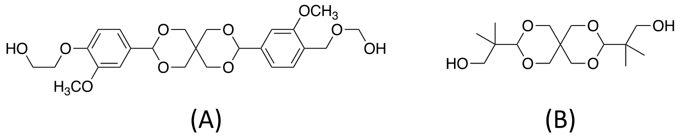

Figure 1. Structure of (A) vanillin-based spiro-diol **V** we synthesized and (B) a spirocyclic diol used to synthesize commercial polyester Akestra™ by Perstorp AB.

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Valorization of lignin for coating applications

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Within the coating industry, approximately 90% of epoxies utilized for heavy-duty coatings originate from bisphenol A diglycidyl ether (BADGE) due to its excellent mechanical properties, solvent resistance and anti-corrosive protection.[1] However, in a world where sustainability is key for future generations, its toxicity and petrochemical source is starting to become a problem and green alternatives to BADGE are required to sustain the increasing demand for heavy-duty coatings. Lignin is an abundant raw material that could be attractive for coatings. It is a by-product from the pulp and paper industry, which in structure compares to the aromatic nature of BADGE, where it consists of large condensed structures of phenolics, which in nature gives structure to plant cell walls. By exploiting the potential for chemical modification of lignin, a greener alternative to petrochemical raw materials within the heavy-duty coating industry can be obtained for a more sustainable future.

In this study, we demonstrate how chemical modification of lignin with green epoxy functionalized components can be utilized for substitution of petrochemical derived BADGE. Initially, chemical modification of lignin with a variety of green moieties was synthesized to investigate compatibility with BADGE for partial substitution and change in polarity, the latter leading to compatibility with solvents utilized in the coating industry. Subsequently, green epoxy modified moieties of lignin was synthesized (Figure 1), cured in various compositions, and their physiochemical properties investigated. Through chemical modification, valorization of lignin could be achieved and in the future potentially substitute the need for petrochemical raw materials within the coating industry.

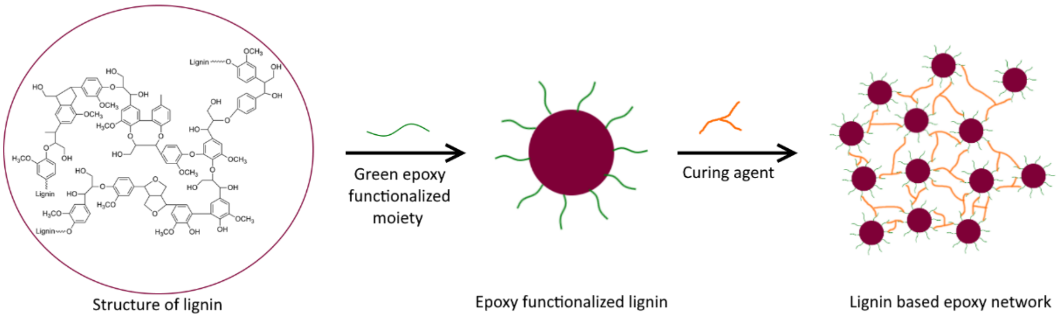

Figure 1. Valorization of lignin through chemical modification as a green alternative to BADGE

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Friday, August 20

NPD

Session: Polymer composites & processing

Synergic effect of water in reactive melt crosslinking of thermoplastic/thermoset poly(ε-caprolactone)/cellulose nanocrystals biocomposites

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To improve the performance of biodegradable polyesters, such as poly(ε-caprolactone) (PCL), cellulose nanocrystals (CNC) can be incorporated as renewable reinforcement to produce novel sustainable biocomposites. Despite CNC's inherent relatively high mechanical properties (specific Young's modulus 85 J/g[1]), it is challenging to achieve the expected reinforcement because of poor CNC dispersibility and interfacial adhesion with a more hydrophobic polyester matrix. Wet-feeding of cellulose water suspensions has been reported as a successful strategy to increase dispersion in PCL melt processed biocomposites, therefore enhancing their mechanical performance[2]. In this work, a one-step reactive melt process was designed by wet-feeding of PCL/CNC (90/10 wt.%) coupled with peroxide-initiated crosslinking (Figure 1), a widely applied technique for thermoplastics rheological improvement. The objective was to evaluate a potential synergy between CNC wet-feeding and the use of water as a low-viscous medium to boost radical reactions[3], with the final aim of improving PCL thermomechanical and rheological properties. Structural analyses of the reacted biocomposites revealed a gel content of 38 % (at 1 wt. % peroxide), in which around 70 % of the initial CNC weight was irreversibly incorporated. Increase of both complex viscosity and melt elasticity with increasing crosslinking degree were recorded by dynamic shear rheology, together with more pronounced shear thinning behavior. Increased melt elasticity was also observed in creep tests at 120 °C, as the synergy between PCL crosslinking and CNC dispersion led to high creep resistance and recovery. Moreover, the crosslinked biocomposite acquired a heat-shrink character, indicating a thermoplastic/thermoset behavior, suggesting heat-triggered shape-memory potential.

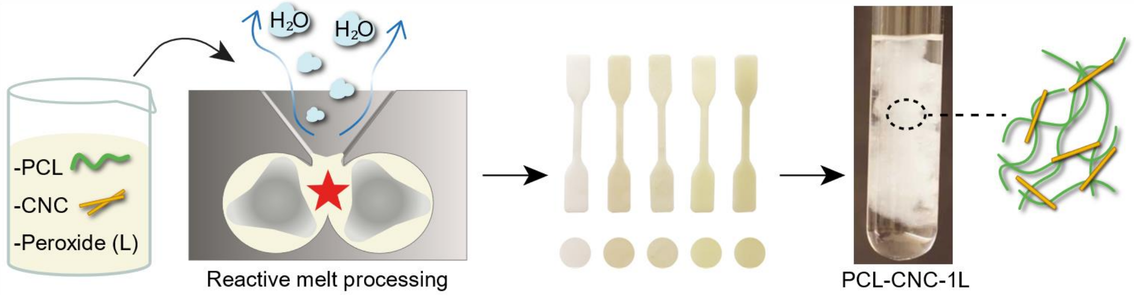

Figure 1. Scheme of reactive melt processing, with test specimens and photo of gel floating in dichloromethane.

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Highly Oriented Electrospun Conductive Nanofibers of Biodegradable Polymers-Revealing the Electrical Percolation Thresholds

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An electrospinning process with a special rotating collector electrode is used to generate highly oriented electrospun conductive fiber composites (ECFCs) of biodegradable polymers. Polyethylene oxide (PEO), polycaprolactone (PCL) and polylactic acid (PLA) are blended with intrinsically conductive polymers (ICPs)-fillers of Poly (3,4- ethylenedioxythiophene) (PEDOT) and polyaniline (PANi). As the proportion of filler increases, the number of “conductive pathways” grows, and consequently the conductivity of the ECFCs also increases. A procedure is developed for calculating the volume fraction (φ) of filler, density and conductivity of electrospun nanofibers. The conductivity as a function of filler fraction is shown and described by using a McLachlan equation for the first time to reveal the electrical percolation threshold (φ_c) of nanofibers[1]. During the annealing process, a build up of additional conductive channels within ECFCs is responsible for increasing inter and intra-chain conductivities among fillers and matrices. Therefore, annealed ECFCs transport charge more efficiently due to an increase in continuous pathways, which lead to superior electrical conductivity and lowering the percolation threshold. Moreover, a time-temperature effect on percolation thresholds of ECFCs is evident. The compatibility between filler and matrix and the inherent conductivity of filler and molar mass of matrix are among significant factors for determining φ_c. The fiber diameter and conductivity of ECFCs are both tunable. The comparative study shows that these highly oriented electrospun conductive nanofibers have great potential in various biomedical applications.

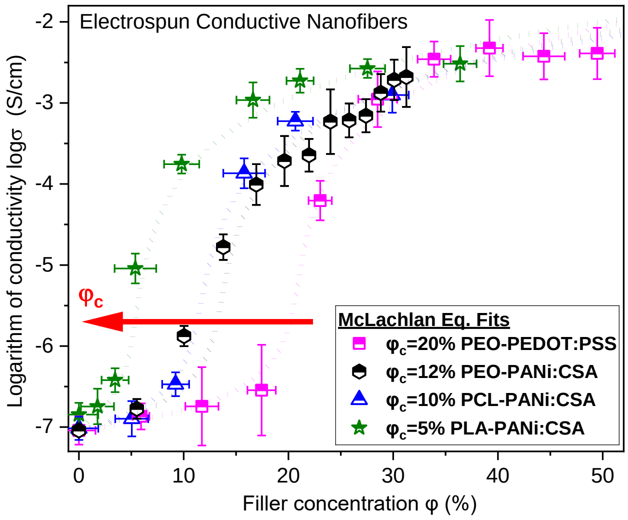

Figure 1. Logarithm of conductivity (*log σ*) versus percentage volume fraction (*φ %*) of filler (PEDOT & PANi) for un-annealed ECFCs of PEO, PCL and PLA.

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Processing and properties of polyethylene plastics packaging waste

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Plastic recycling has gained significant attention in society for decades motived by an increasing amount of plastic waste. Here material recycling of post-consumer plastic packaging waste is of great importance, but this also constitutes several complexities and challenges. The whole process involves the steps of waste collection, sorting into different fraction of polymers, shredding/grinding, washing, melt processing and granulation. Moreover, homogeneity, purity and cleanliness of the resulted material are important factors for having recycled material to perform consistency, by that to compete with virgin material in an economic sense.

This study illustrates an overview of variation in the composition of sorted plastic packaging waste which is performed in a collaboration with a plastic packaging waste sorting facility in Sweden. The fractions of interest were low-density polyethylene (LDPE), rejected fractions of LDPE-sorting line, and high-density polyethylene (HDPE). First, the samples were collected in successive days over five weeks, then sampling at least 100 pieces. The polymer fractions were identified by the type of polymer using handheld near-infrared spectroscopy (NIR) analyzer to have overall composition analysis. The confidence within the sampling routine were determined with a guidance of standard CEN/TS 16010 and the results are evaluated considering different confidence intervals.

Additionally, preliminary extrusion trials were performed with LDPE fraction as received, without washing or other pre-treatments. The idea was to study the behavior of unwashed plastic waste in terms of thermal and mechanical performance. Extrusions were performed by twin-screw extruder with several temperature profiles. Then injection molding was performed to produce samples. Differential scanning calorimetry analysis were performed to characterize the thermal behavior. The further work will involve, composition analysis, properties of compounds that produced using selected parameters, washing study and its effect on the resulted product and finally degradation assessment of the compounds. The aim is to illustrate influence of different processing parameters on the resulting performance of the recycled material.

Thursday, August 19

NRC & NPD

Session: Posters

Studying the loosening effect of secreted, non-hydrolytic fungal proteins on cell wall polysaccharides

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Background: Expansins, originally reported in plants, are non-enzymatic proteins that promote cell enlargement and stress relaxation in plant cell walls, presumably through disruption of non-covalent interactions between carbohydrate polymers[1]. To date, the existence of expansin homologs in bacteria has been extensively reported. Genome surveys indicate that a few fungi have canonical expansins, and also more distantly related proteins named swollenin, cerato-platanin, EXPN, and loosenin (LOOS1)[2], that have been called expansin-like[3]. Previous genomic analysis of *P. carnosa* identified 13 genes as distantly related to plant expansins[4] and further phylogenetic analysis determined that 12 of those proteins are loosenin-like proteins, rather than expansin-like proteins, and named the proteins as LOOL1 to 12 (LOOsenin-Like)[5].

Materials and Methods: The possible loosening effect of 4 LOOLs on cellulose (CNF) and chitin (ChNF) nanofiber gels was studied using oscillatory shear measurements under amplitude sweep mode (strain range from 10^{-1} to 100 % at constant frequency 1 1/s) and frequency sweep mode (angular frequencies from 100 to 1 1/s at constant strain 1 %). 'Gel strength' was defined according to Yang et al. (1986): the yield point σ_γ is the maximum elastic stress ($G'\gamma$) the gel can endure, calculated by $\sigma_\gamma = \max(G'\gamma)$, where G' is the storage modulus and γ is the strain[6].

Results: The treatment of CNF and ChNF with increasing concentration of LOOLs results in lower yield strain values compared to the control samples, which indicates that the presence of LOOLs within the polysaccharide fibrillar network induces significant changes of the internal structure, possibly by progressive breakdown of the entangled fibril network.

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Rheological characterization of non-dairy alternatives to milk.

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The viscosity of daily consumed beverages is one parameter used to describe its qualities. However, popular words like “good viscosity”, “mouthfeel” and other sensory ratings seems rather subjective to understand key sensory profiles of the products. Milk and non-dairy alternatives are normally consumed cold.

The viscosity of a selection milk and some non-dairy alternatives were measured at 5 °C. The tests employed in rotation were shear rate sweeps including low shear rates and hysteresis tests to detect thixotropic behavior. The results were fitted to the Herschel-Bulkley model. Conventional start-up tests were also performed.

Amplitude sweeps were performed in oscillation to determine stiffness, strength and limiting strain if the fluids formed a structure.

The results show variations in rheological behavior and show that some of the products exhibited non-Newtonian behavior either being pseudoplastic or thixotropic. Some of the milk alternatives had a much higher viscosity than milk. Most products behaved like viscoelastic liquids. None of the products exhibited yield properties.

Rheological methods for characterization of liquid soaps and detergents

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In this introductory study, several rheological methods were used to investigate and characterize the texture and viscosity of some commercially available liquid soaps and detergents. Viscosity and rheology play a crucial role in the performance of these products both as household products and as cleaning agents in various industries. For the food industry it is important to have knowledge about these products behavior in the factory; for example, during automatic CIP-wash of pipelines and process equipment. Rheological measurement equipment like a high - performance rheometer is important for the industry that require quick and reliable methods for characterization and control of shear conditions and viscosity regarding different mixing, pumping and temperature regimes.

The tests employed in rotation were shear rate sweeps including low shear rates and hysteresis tests to detect thixotropic behavior. The results were fitted to the Herschel-Bulkley model. Conventional start-up tests were also performed.

Amplitude sweeps were performed in oscillation to determine stiffness, strength and limiting strain if the fluids formed a structure.

The results exhibit variations in rheological behavior and show that some of the products show signs of a yield stress, some were Newtonian while other were pseudoplastic. Some of the products also revealed clear thixotropic behavior.

Gelation of acid milk gel with and without addition of iota-carrageenan (IC) investigated from macroscopic to microscopic and molecular levels.

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This work investigated the formation of acid milk gel with and without the addition of IC at 30°C, using bulk rheology and syringe compression test at the macroscopic level, passive particle tracking at the microscopic level and pulsed field gradient (PFG)-NMR with poly(ethylene oxide) (PEO) at the molecular level. IC induced the early formation of the gel network as demonstrated by the progressive G′ and G″ increase (where G′ > G″) in the macroscopic measurement. When repeatedly compressed at the developing stage, the formed gel network in the IC sample reassociated into non-native colloidal structures unable to contain the serum phase, suggesting the importance of hydrophobic interactions. The increased PEO diffusion at 30 min in PFG-NMR reflected the emerging casein-casein network and its extensive rearrangement occurring at the molecular level regardless of IC addition. This corresponded with the mean square displacement of the probe particles with IC, indicating that IC altered the length scale of the extensive network rearrangements occurring only at the molecular level without IC to be detected at the microscopic level in the sample with IC. The size-dependent particle behaviors demonstrated a high degree of IC-induced network heterogeneity that continued to develop even at later incubation stage, on contrary to the drastic compaction of the network in the sample without IC.

Figure 1. Graphical abstract.

Compression of plant seeds assuming soft spheres

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To measure the mechanical properties of samples in the size of a couple of millimetres, such as bilberry seeds is challenging. The compression and force measurement of such seeds is possible, however, due to the irregular shape and the contact area changes during compression the tensile strength and modulus are challenging to calculate and thus, the properties cannot be compared to other materials. In this study we investigated the mechanical properties of bilberry seeds (*Vaccinium myrtillus*) using an Instron testing machine. The seeds had a size of 0.7 – 1.5 mm with a slight convex shape. To estimate the tensile strength and the modulus we have adopted and used a model from Lin et al.[1] for incompressible spheres. The assumption in the model is that the volume does not change, but the lateral surface changes and is assumed to be spherical, see Figure 1. Points M and M’ are the sphere centres without and with compression, is the penetration depth, and *a* is the contact surface radius. The contact area, A, can be estimated as follows:

		(1)

The radius of the compressed particle, , can be calculated as

		(2)

The estimated Young’s modulus of wet bilberry seeds was in the range of 50 MPa, which is about ten times higher compared to carrot or potato.[2]

Figure 1. Left: bilberry seed before compression under a probe of 2.37 mm diameter; right: sketch of the compression of a sphere.

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Wet-granular rheology to measure cuttings-bed strength

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Cuttings-beds formation while drilling wellbores is a common problematic, especially if they are highly deviated or horizontal and efficient removal of the cuttings is of utmost importance during drilling operations [1]. Removal of the drilled-cuttings is done through the drilling fluid flow, but when the wellbore is inclined or horizontal, they tend to settle and form cuttings-beds, which can cause several problem such as, increased torque and drag, pipe sticking or pipe breakage, among others. The consolidation strength of these cuttings-bed has been an unknown, and studies on cuttings-bed removal usually approach the method on the final result: effective cuttings-bed removal. In this study, the focus is to understand the cuttings-bed strength and the stress required to erode it. Performing granular rheology to the cuttings wetted with different fluids has shown to be an effective approach to describe the strength formation of the beds [2]. We have analysed simulated cuttings-beds' shear strength using quartz particles saturated with water and a water-based drilling fluid, using a rheometer powder shear cell. Assuming solid behaviour of the cuttings-beds, it is possible to analyse through the Mohr-Coulomb failure envelope the cuttings-beds' shear strength and particle cohesion. The results show that the interstitial fluid significantly impact the shear strength of the bed.

Figure 1. Mohr-Coulomb envelope for drilled cuttings wetted by water and water-based drilling fluid.

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Viscoelastic Behaviors of Self-Healing Hydrogel Containing Chitosan and Cellulose Nanocrystal for Wound Healing

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There is a big challenge on healing of the wounds due to some issues like long healing time, large size and irregular shape, pain and reinjury at wound dressing changes, as well as scarring. To facilitate wound healing, hydrogels are promising materials as wound dressings since they absorb and retain the wound exudate and sustain an ideal moist environment for healing while protecting the wound. Self-healing injectable hydrogels are outstanding candidates to overcome the wound healing problems thanks to their ability to be injected quickly and directly to the large and irregular wounds and even to the certain areas with difficult access. Recently, hydrogels based on Schiff Base linkages have received significant attention in the formation of self-healing hydrogels owing to the ability to recover their structures and functions after damages. Because of the growing environmental trends to switch from synthetic petroleum-based polymers toward macromolecules obtained from renewable and sustainable sources, as well as the potential of naturally occurring polymers in biomedical and pharmaceutical applications, hydrogels made out of natural polymers, such as chitosan and cellulose, have attracted much attention in the past few decades.

Because of the excellent merged properties of chitosan (biocompatibility and antimicrobial activity) and CNC (good barrier, thermal, mechanical, and high aspect ratio) in chitosan/CNC nanocomposite, the main aim of this research is chemical grafting of dialdehyde-CNC to carboxymethyl chitosan (CMC) through Schiff-base linkages using diamine as a cross-linker (Figure 1) for preparing self-healing hydrogel. The hydrogel's viscoelastic behaviors, mechanical strength, and self-healing efficiency were optimized by adjusting the degree of aldehyde of modified CNC and the molar ratio of the amine group of CMC and diamine.

Figure 1. Schematic illustration of dialdehyde-CNC/CMC hydrogel through Schiff-base linkages (left); the extrusive hydrogel was used as ink to write "A!" smoothly (right, top) and strain-sweep at a fixed frequency of 10 rad·s^{-1} (right, bottom)

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3D printing of plant-based hydrogels: a rheology study

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Several research studies revealed that a shear-thinning hydrogel ink, which exhibits a viscoelastic response to applied pressure, can be extruded from a nozzle to directly deposit the gel to fabricate a 3D object [1]. Therefore, the rheological performances of all inks were studied. Figure 1a illustrates viscosity-shear rate curves, where the viscosity curves were smooth with no mutation, indicating that the inks were stable enough [2]. The viscosity of all inks was within the reported range suitable for the extrusion of hydrogels, which may afford excellent shape fidelity when printing. Furthermore, all inks revealed a similar shear-thinning behavior, wherein the viscosity dropped approximately two orders of magnitude as the shear rate increased from 0.01 to 100 s^{-1} [3].

To guarantee the successful direct writing of the ink, in addition to shear-thinning behavior, the ink should be flow through the nozzle under the applied pressure. In other words, the yield stress (τ_y) of the ink should be lower than the maximum shear stress generated within the nozzle (τ_{max}) [4,5]. To obtain τ_y of the inks, the stress sweep test was done at a fixed frequency of 10 rad.s^{-1} (Figure 1b). The maximum shear stress (τ_{max}) at the nozzle wall was 252 Pa, which was higher than the yield stress of all samples, suggesting that all inks could be printed.

Figure 1. (a) Viscosity curves versus shear rate (), (b) shear stress-sweep at 25 °C. The solid and blank symbols indicate G′, and G″, respectively.

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Highly Filled Biocomposite: Modelling, Processing, and Characterization

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Biocomposites play a critical role in the context of overarching societal efforts to increase the use of renewable materials. In particular, the use of biocomposites based on wood fibers as sustainable materials can lead to an impactful reduction in the consumption of plastic materials and subsequently, much less carbon footprint. A current drive for polymer biocomposites is to maximize the use of renewable content in mass production systems. A major challenge therein is to understand the flow field - polymeric matrix/filler, filler-filler interactions, including boundary conditions, in order to design custom processing solutions that enable the manufacturing of parts with desirable performance. In this work, the rheology and processing of commercial highly filled wood fibers-based biocomposites (DuraSense®, StoraEnso) are analyzed from experimental and numerical points of view. The wood fiber biocomposites investigated are based on polypropylene and contain up to 40% wood fiber reinforcement. Their rheological properties are explored using rotational rheometry subject to simple shear, capillary rheometer, and inline measurements in single screw extrusion. Slippage study on these materials has been implemented by the Mooney method. In the extrusion process, pressure values of two different dies (Slit and Film die) at the entrance and middle of the dies have been obtained by our two pressure transducers. Further, the experimental findings are compared with numerical simulations. Finite element method simulations are performed using generalized Newtonian and viscoelastic constitutive models, both in the absence and coupled with extensions of the dilute suspension theory for concentrated suspensions (Folgar-Tucker). The goal of our experiments is to establish a correlation between the rotational rheometry, capillary rheometer, extrusion process, and numerical simulations. It is the first step towards the implementation of material functions in numerical models for optimization and modeling of processing flows of highly filled polymer bicomposites.

Enhanced mechanical strength in supramolecular gels induced by salts/ions

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Stimuli responsive low molecular weight gelators (LMWGs)[1] are excellent class of soft materials where the gelation properties can be switched on/off by an external stimulus[2] such as light, redox, pH and salts/ions.[3] The overall self-assembly of the LMWGs depends on the combination of various non-bonding interactions such as hydrogen-bonding, π-π stacking, ion/dipole interaction and van der Waals interaction. However, the dynamic nature of these noncovalent interactions makes it difficult to understand the role of specific interaction in the self-assembly process. Our group has shown that the functional group modification of an existing gelator will enable us to elucidate the role of the specific interactions,[4,5] which was achieved by comparing the gel strength of bis(pyridyl) urea-based gelator to the modified pyridyl *N*–oxide gelator. We are now analysing the effect on bis(pyridyl)-bis(urea) based compounds with two different linkers, namely hexylene and butylene as the parent compounds. The structural modification was achieved by modifying the bis(pyridyl urea) compounds to the corresponding bis(pyridyl-*N*-oxide urea), and the solid-sate interactions of these gelators were identified by single-crystal X-ray diffraction. The modification of the pyridyl groups to the corresponding pyridyl-*N*-oxide resulted in hydrogelation, which was confirmed by inversion test and the gel stability was evaluated by rheological measurements such as oscillatory-amplitude and -frequency sweep experiments. The effect of salts/ions on the mechanical strength of the gel network was analysed by rheology. The addition of salts/ions disrupts the self-assembly of the gelator by altering the non-bonding interactions, which can result constructively by triggering gelation or destructively by gel dissolution.[3] Interestingly, the addition of potassium salts resulted in enhanced thermal and mechanical strength of the modified *N*-oxide gels, but a reversed phenomenon was observed for the parent gelators. The enhanced gel strength was confirmed by the higher storage modulus (G') in the oscillatory frequency sweep experiments, where the addition of the salts resulted in increase of the G' value. We are now analyzing the mode of interaction of ions/salts in these stimuli responsive materials, which will be correlated to the enhanced mechanical strength.

Figure 1. Inducing gelation in presence of cations such as K$^+$, Ca^{2+}, and Mg^{2+}.

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Recombinant spider silk proteins as a sustainable wet adhesive for cellulose based materials

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Delignifying and densifying wood is a promising processing method for bioengineering novel wood-based materials with superior tensile properties and features like mouldability. After delignification those materials can be stored under wet conditions. These never-dried materials are advantageous since they maintain intact micro- structures; however their fabrication requires wet adhesives.[1] Previous studies show that recombinant spider silk proteins are excellent candidates as adhesive for cellulosic materials.[2] Biological adhesives such as spider silk are well known for their ability to form coacervates, a process called liquid-liquid phase separation.[3] This step is crucial for the adhesive properties of spider silk proteins. Here we utilize an engineered version of *Araneus diadematus* drag-line silk, combined with cellulose binding domains, as a wet adhesive for delignified wood. First results indicate that the engineered protein is well suitable as a sustainable wet adhesive for delignified wood with shear strength values of up to 10 MPa. To maximize the shear strength, it is crucial to understand molecular interactions of the recombinant spider silk/delignified cellulose system. Therefore, mechanical testing was combined with amino-acid analysis to elucidate protein distribution and viscosity measurements to characterize the adhesive. Image analysis of the fracture area allowed to analyse the breaking behaviour of the samples. Our results indicate that the amount of protein-adhesive applied is important only to a certain extent and that it is possible to receive got adhesive strength with relatively small protein amount. The relatively low viscosity of the protein-adhesive allows infiltration but also leads to spreading in the fibre direction. Our hypothesis is that good infiltration is essential to obtain high adhesive strength.

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Effects of trehalose and sucralose on phase separation and decapsulation of eicosapentaenoic acid in biopolymer emuslsions

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In the present study, eicosapentaenoic acid (EPA) was emulsified into whey protein, lambda-carrageenan systems using power ultrasound, and the effects of minutes amounts of trehalose or sucralose, on the stability of these systems were investigated. Time-dependent phase separation in the emulsions was assessed by measuring the volume changes in separated aqueous, lipophilic, and solid layers. Aliquots of the systems were freeze-dried and the glass transition temperature (T_g) of the freeze-dried encapsulated EPA was determined using differential scanning calorimeter (DSC). The freeze-dried samples were stored at various water activity conditions and the release of EPA was measured gravimetrically. The emulsion systems containing trehalose showed further delayed phase separation compared to the one prepared with sucralose. This suggests that trehalose exhibited higher molecular interactions with *lambda*-carrageenan, possibly due the hydrogen bonding. T_g of trehalose- and sucralose-containing systems were 55ºC and 50ºC, respectively. Above a_w value of 0.444, the release of EPA increased with increasing a_w in both systems. A study of the combined effects of water activity and glass transition temperature on the release of EPA is under way to determine the conditions that govern the release of encapsulated EPA.

Insertion of secondary crosslinking strategies in thermogelling hydrogels

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Hydrogel based systems find application in a wide range of different fields.[1] To enhance their stability in aqueous solution chemical crosslinks between the polymer chains can be incorporated.[2] In this work a diblockcopolymer comprising hydrophilic poly(2-methyl-oxazoline) and thermoresponsive poly(2-n-propyl-oxazine) is used for the insertion of functional moieties for chemical crosslinking by post synthesis modification. The used polymer shows thermoresponsive solubility in water, whereby 20 wt% aqueous polymer solution forms physical gel by heating above 20 °C but liquefies when cooling.[3] Placing the hydrogel in aqueous solution results in dissolving the gel. The chemical crosslinking is to be conducted by thiole ene reaction[4], copper-free azide alkyne cycloaddition[5] and reaction of boronic acid with 1,2- and 1,3-dioles[6], respectively. The incorporation of these functional moieties was conducted by post synthesis modification. In other words, after the polymer synthesis the hydrophilic poly(2-methyl-oxazoline) block was partly hydrolyzed in acidic solution and high temperature to obtain secondary amine groups within the hydrophilic block of the polymer. To obtain polymers with well defined degree of hydrolyzation a kinetic study was conducted. The partly hydrolyzed polymer was used to incorporate azide, alkyne, boronic acid and alkene moieties, respectively. The formation of amides can be observed by adding carboxylic acids, which contain the functional moiety for crosslinking, and an activation agent. While modifying the polymer care was taken to the fact that the polymer is still able to form a physical gel. In this study the physicochemical properties of every modified polymer were determined. Afterwards, these modified polymers were used to produce chemical crosslinked hydrogels. The copper-free crosslinking between azide modified polymer and alkyne modified polymer by mixing aqueous solutions of the polymers and placing the mixture in an oven at 37 °C resulted in stable hydrogels after 4 h. In this context stable hydrogels means the hydrogels do not dissolve when placing them in aqueous solutions. Depending on crosslinking time the swelling behavior vary between 1200 % and 300 %. The swelling ability decreases with increasing crosslinking time. Similar results were obtained by crosslinking the ene modified polymer with dithiol. In contrast to the azide alkyne click reaction, a photocatalyst needs to be added. The crosslinking time amounts to only a few minutes of UV irritation. However, the crosslinking of boronic acid modified polymer and the polysaccharide dextrane did not result in any stable hydrogels.

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Cellulose nanofibrils doped with polymer nanoparticles by PISA

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In our quest to shift from a fossil-based to a biobased chemical economy, biomass must be engineered to mimic or surpass the properties of today's fossil-based materials. Cellulose is an interesting raw material for this because of its abundance, renewability and impressive mechanical properties. Biomass can be treated to release cellulose fibers of diameters below 40nm and aspect ratios up to 100, which form entangled networks and highly interesting material properties. These fibers are called cellulose nanofibers (CNF) and assemble into materials with high stiffness, strength, transparency and barrier properties. Thus, they have been suggested for applications such as packaging, flexible electronics substrates and semipermeable membranes [1].

But for CNF materials to be widely adopted in the applications above it is not only the premium on price which needs to be addressed. Compared to plastics, CNF materials are brittle and their mechanical properties tend to be highly dependent on humidity. One method in which to modify the behavior of cellulose materials is the incorporation of hydrophobic polymer in the form of latex. Latexes are colloidally stable dispersions of polymer in water, traditionally stabilized by surface active agents. In the last few decades with the advent of controlled polymerization techniques, new types of surfactant-free, self-stabilising latexes assembled from amphiphilic diblock copolymers can be synthesized via polymerization-induced self-assembly (PISA). These PISA latexes are highly uniform with tunable surface activity and size. Their interaction with cellulosic fibers can thus be engineered to maximise the impact on bulk material properties.

A few seminal studies have indicated that certain PISA latexes at low concentrations can improve the toughness of CNF materials in a synergistic way [2, 3]. SAXS studies have indicated that latex nanoparticles rearrange under stress in the CNF network and provide slip planes to aid plastic deformation [4]. Based on this initial work we propose to study the assembly and plastic deformation mechanisms of CNF materials doped with small amounts of latex nanoparticles synthesized by PISA.

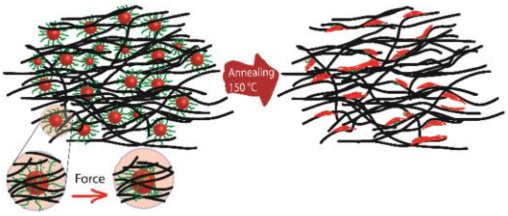

Figure: Schematic of latex nanoparticles in CNF network from [3]

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Analyzing the transmission of visible light through electrospun nanofibrous PCL scaffolds

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In comparison to homogenous films, nanofibrous scaffolds not only reflect and absorb electromagnetic waves but scatter them. The scattering depends to a higher extend on the ratio of the wavelength to the dimension of the scatterer. Therefore, in this study light transmission through nanofibrous scaffolds is evaluated for varying fiber diameter in the nanometer range. Furthermore, the influence of refractive indices of the surrounding medium and scaffold thickness is examined.

PCL scaffolds were produced via electrospinning from the solvent system formic acid/acetic acid in the ratio 7:3. Different PCL concentrations were used with 5 % w/v, 8 % w/v, 10 % w/v, 12 % w/v, 14 % w/v and 16 % w/v. Based on preliminary spinning experiments, scaffolds with varying thickness between 2 µm to 50 µm were fabricated for each concentration. Transmission measurements were conducted using UV/Vis spectroscopy in the range of visible light from 380 nm to 780 nm. Therefore, the scaffolds were fixed in tissue carrier rings and then placed in an adjusted cuvette filled with ethanol or phosphate buffered saline (PBS). With the scaffold fully covered in medium, differences in the refractive indices of the surrounding medium could be evaluated.

By plotting the light transmission of a sample type as function of the scaffold thickness for a fixed wavelength, an exponential decrease in light transmission could be identified and the extinction coefficient could be calculated (Fig. 1). The extinction coefficient was then further analyzed regarding the ratio of reflectance, scattering and absorption depending on the scaffold characteristics and ambient medium. Eventually, based on theoretical considerations a formulation is provided for a better understanding of the underlying mechanism for light transmission through nanofibrous scaffolds.

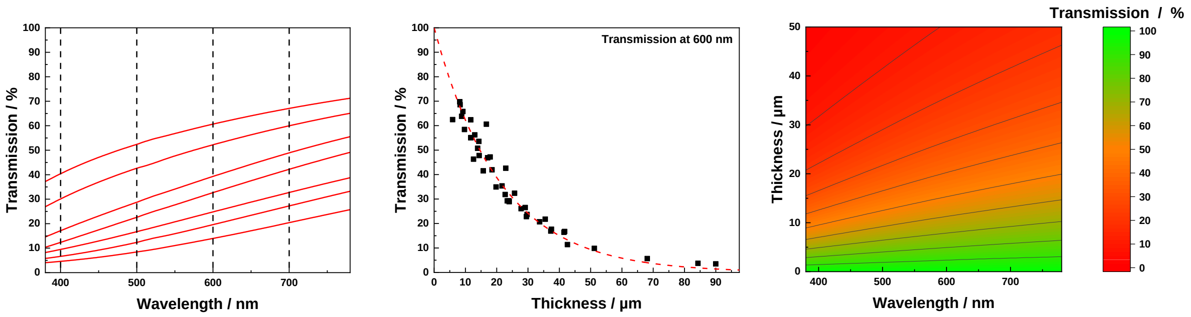

Figure 1. From the individual transmission measurements of several scaffolds (left), transmission vs. thickness curves for discrete wavelengths are plotted (middle) and the data are fitted following the Lambert-Beer Law. Eventually, contour plots can be generated showing the light transmission as a function of wavelength and scaffold thickness.