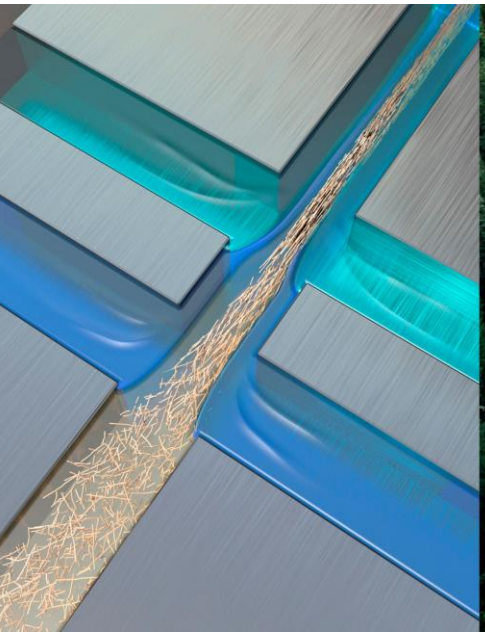
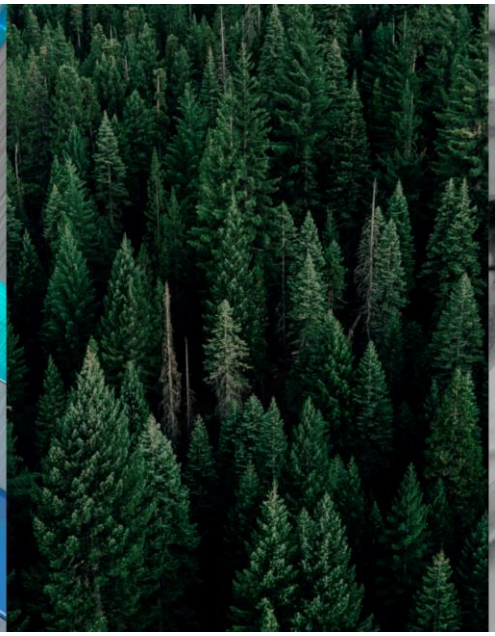
WWSC

WALLENBERG WOOD SCIENCE CENTER

Wood nanotechnology – new materials from trees


Annual report 2020

KTH VETENSKAP OCH KONST

CHALMERS

LINKÖPINGS UNIVERSITET

TREESEARCH

Knut och Alice Wallenbergs Stiftelse

Table of contents

Wallenberg Wood Science Center

Wallenberg Wood Science Center (WWSC) was first launched in 2008 as a collaboration between KTH Royal Institute of Technology (KTH) and Chalmers University of Technology (Chalmers) with participating researchers also from Stockholm University, Luleå Technical University and Umeå University. The first ten years of center activities resulted in ~60 PhDs, 600 publications, and more than 10,000 citations. The second phase of WWSC was launched in January 2019 and now also includes Linköping University (LiU).

The annual funding of 72 MSEK is shared between Knut and Alice Wallenberg (KAW) Foundation (40 MSEK), universities (22 MSEK) and industry via Treesearch (10 MSEK). The research goals are set in a long-term perspective, and the center agreement signed by funding organizations is for 10 years, ending in 2028. Currently, the center engages ~70 faculty members/researchers, ~25 postdocs and ~50 PhD students.

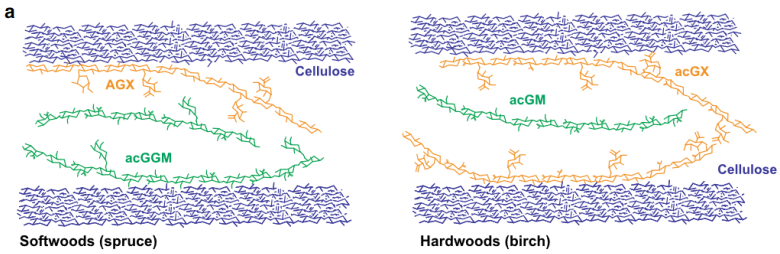
The research in the center has a focus on new materials from trees. The aim of WWSC is to create knowledge and build competence that has the potential to form the basis for an innovative future value creation from forest raw materials by developing methods and processes that provide molecular and nonstructural control. The scientific activities have two main objectives; the first is on fundamental understanding of wood tissue, wood fibers, cellulose, hemicelluloses, lignin, and related components, including biobased polymers. This includes extraction, disintegration, purification processes and their mechanisms, characterization of biomolecules, nanocellloses, fibers, colloids etc, as well as novel modification routes and biopolymer synthesis. The second objective is new material concepts, where the wood material components (fibrils, fibers, wood veneer, lignin polymers etc) are combined with other constituents and assembled into materials and devices. Research activities in WWSC span broadly from extraction/fractionation of biopolymers and other constituents in wood to the utilization of wood polymers and other constituents in advanced nanotechnological devices.

To capture and nurture the full breadth of the activities in WWSC, the center is organized into five highly integrated programs which are led by experienced researchers in each field (program responsible in brackets).
Program 1: Wood components – extraction, characterization and properties (professor Lisbeth Olsson, Chalmers)
Program 2: Biobased polymers and modelling (professor Eva Malmström, KTH)
Program 3: Fibers and fiber nanotechnology (professor Lars Wågberg, KTH)
Program 4: Composites for energy and electronics (professor Magnus Berggren, LiU)
Program 5: Biocomposites and wood materials (professor Lars Berglund, KTH)

Research in WWSC

Program 1: Wood components – extraction, characterization and properties

To efficiently utilize the components in wood, sophisticated and effective methods are required to separate the individual components from the complex hierarchical structure in wood, so exquisitely formed by Nature. To make full use of the potential of the various components provided by wood, their fractionation and isolation need to be further detailed and understood on a molecular level. From a more fundamental perspective, focus is on understanding various separation mechanisms, but also on the development of new characterization methods for lignins, hemicelluloses and other components.

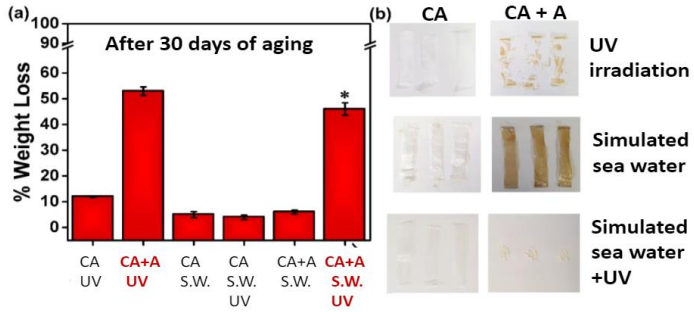


Schematic illustration of the polymeric network in a model BC-H system mimicking the secondary cell walls of softwoods and hardwoods prior to lignification. Ref: Vilaplana et al. Nature Communications 2020, 11, 4692

Program 2: Biobased polymers and modelling

This program is focusing on biopolymers which can be isolated from forest products (except (nano)cellulose) and on biobased polymers attainable by polymerization of low molar mass extractibles or degradation/fractionation products by sustainable methods.

The program also aims at a molecular understanding on the origin of why biopolymers are sensitive to water/humidity and at elucidating the fate of biopolymer- and cellulose-based materials at the end-of-life.



Degradation of cellulose acetate (CA) investigated by Yadav and Hakkarainen at KTH.

Program 3: Functional fibers and fiber systems

The use of biobased nanomaterials allows bottom-up engineering but the use of nanocellulose is also very demanding as it involves large amounts of solvents. It is hence necessary to explore new routes that adds to the overall understanding of nanocellulose and how to create controlled self-assembly of nanomaterials. To alleviate this challenge the activities in Program 3 have been focused partly on cellulose-rich fibers, where the fibrils have been made available inside the fiber wall for further modification while keeping the macroscopic dimensions of the fibers, and partly on different self-assembly methods where the problem with solvent handling can be carefully managed based on a fundamental understanding of the colloidal chemical properties of the nanocelluloses.

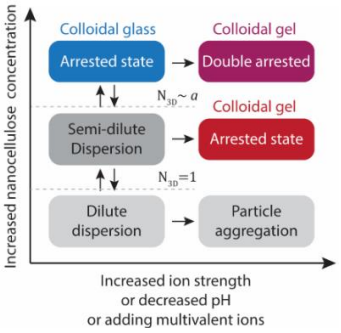
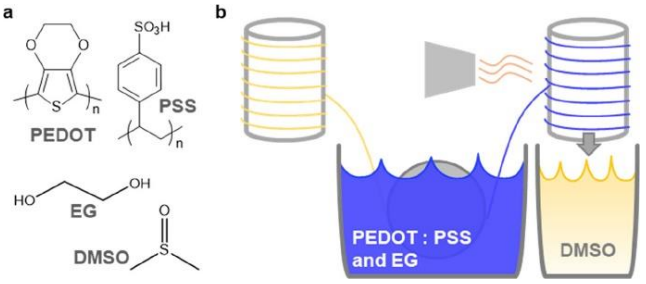


Illustration from thesis by Nordenström, M. (KTH 2020). Supervisor L. Wågberg.

Program 4: Composites for energy and electronics

The topics in this program are directed towards functional materials and devices. These functions include electric, electronic and photonic properties. Templates include nanocellulose, fibers and wood veneer, as well as other components available within WWSC. The methods to functionalize wood-based materials include blending, synthesis, molecular assembly, self-organization, carbonization and various chemical functionalization routes, and this is carried out at different length scales depending on the purpose. These materials are then refined into inks, substrates, fibers, coatings, and components for manufacturing of electronic and photonic devices and systems. Large-scale and low-cost manufacturing process steps are of particular interest to enable eco-friendly technologies for applications in energy, healthcare, commerce and digital communication.

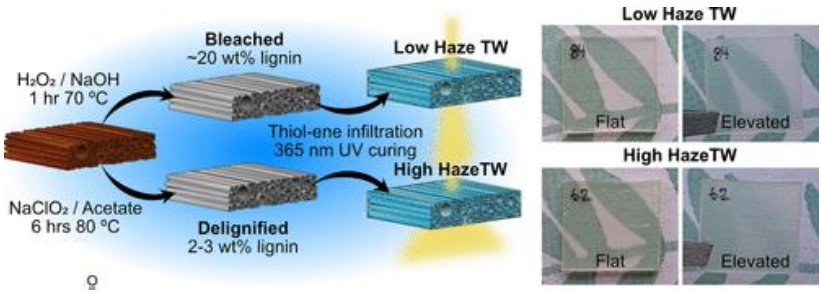


a) Chemical structures of PEDOT:PSS, EG, and DMSO. (b) Schematic of the yarn-dyeing process: the pristine yarn travels through the dye bath and is then dried by a heating gun and collected. Afterward, the coated yarn is post-treated with DMSO. (Ref: Müller, Hamedi et al. ACS Appl. Mater. Interfaces 2020,12, 56403-56412.

Program 5: Biocomposites and wood materials

Program 5 is extending nanocelluloses as structural components to wood “templates” based on modified wood. Initial wood modification can create nanoporosity, remove light absorbents, carbonize for electrical conductivity, etc. Functional-materials activities include soft robotics for sensors and actuators, wood-template electronics, wood photonics, and ionic thermoelectric supercapacitors, which combine energy harvesting and storage with controlled discharge.

The exceptional mechanical properties of oriented cellulose structures, even living plants, are combined with functionalization for ionic and electrical conductivity, active mechanical excitation, photonics, etc. Complex nanocomposite materials are created to obtain desired functions or improve device performance. Structural biocomposites, new fiber materials, and interface phenomena are investigated for materials with functionalities such as optical transmittance and photonics applications, eco-friendly characteristics, and moisture durability.



Transparent wood biocomposites by fast UV-Curing for reduced light-scattering through wood/thiol-ene interface design. Ref: Berglund, Johansson et al. ACS Appl. Mater. Interfaces 2020, 12, 41, 46914-46922.

WWSC 2020

2020 has been a very special year, dominated by the pandemic Covid-19. Maybe the scientific community has been mostly hampered by the complete travel- and physical-meeting bans that have been in place since the second quarter of 2020. Despite the very different working conditions, WWSC rapidly adapted to the new circumstances and managed to maintain research undertakings and center activities at a high level.

WWSC Academy quickly transformed all teaching activities to an online format with the support of highly engaged leaders (Gatenholm and Westman, Chalmers) and ambitious teachers (many). More than 50 PhD students participated in WWSC Academy during the year. WWSC in collaboration with Treesearch organized a highly appreciated webinar series with 13 webinars, streamed over Youtube, that has attracted more than 6,000 views (April 2021). Both the summer and the winter workshop were also transformed into an online format via Zoom but still attracted roughly as many participants as the conventional workshops that have been organized previous years.

The actual output in terms of scientific publications is lower during 2020 than in 2019; however, that is most likely reflecting that many of the PhD students within the center are early in their PhD education and thus, not as productive regarding publications as closer to graduation. Nonetheless, research tasks and challenges are actively addressed with a high degree of ambition and energy.

WWSC Program 1: Wood components – extraction, characterization and properties

Active PIs

Chalmers: Professor Lisbeth Olsson – Program 1 responsible, Professor Lars Evenäs, Associate professor Johan Larsbrink, Professor Anette Larsson, Assistant professor Tuve Mattsson, Professor Hans Theliander

KTH: Professor Monica Ek, Associate professor Martin Lawoko, Dr Lauren McKee, Dr Olena Sevastyanova, Associate professor Francisco Vilaplana

Linköping University: Professor Xavier Crispin, Dr Viktor Gueskine

Overview of the activities within the program

The heterogeneity in the molecular structure of the wood components and the complex nature of their interactions at the nano- and macroscales are fundamental for their structural function in cell walls. However, the strong interaction between wood components and small-scale complexity also contributes to the recalcitrance of lignocellulosic biomass towards degradation and fractionation into wood polymers. Molecular and structural changes take place after different pretreatment- and fractionation steps, and these are poorly described and understood. Key to accelerate our knowledge is the development of more and more sophisticated analytical methods. In program 1, we aim for a deeper understanding to allow a knowledge-based foundation for mild and sustainable tailor-made pretreatment and fractionation methods, that can be combined into different biorefinery concepts. Development of a bark biorefinery concept (1.4.3) led to a methodology to produce nanocellulose from cellulose oxalate powder in a solvent-free process. The thermal stability of this nanocellulose composed of a mixture of rod-like nanocrystals and nanofibrils was promising.

Membrane separation processes play an important role in the wood-fractionation process. Membrane fouling is a challenge that is particularly difficult when biorefinery streams are to be separated. A method based on fluid-dynamic gauging was developed to characterize in situ the shift in fouling behavior during membrane ultrafiltration of steam explosion (STEX) liquors (Project 1.1.1 a). This method allowed insight in the dynamics of the fouling process and how that is influenced by the filtration conditions and filter material. For dewatering of cellulose nanofibrils using electroenhanced filtration, modelling combined with experimental work revealed that both an electrical field and a mechanical pressure is required for efficient dewatering (project 1.1.1b). This work led to an understanding of how the electrical field influence the wettability of the nanocellulose on a molecular scale.

To understand the mechanisms of the decomposition and fractionation process, increased understanding of mass transfer events in the wood structure is necessary. A diffusion cell was developed to study the transport of lignin fragments through the fiber walls (1.1.2a). Here, the effect of pH and solubility of lignin fragments and the diffusion rate in a diffusion cell was studied. Importantly, both the molecular weight and the association of lignin fragments influenced the diffusion rate. To further understand the diffusion and mass transfer, more detailed characterization of the solution in the different chambers will take place by NMR.

The role of enzymes in wood decomposition and in tailoring wood components is attractive due to their specificity and reaction at mild conditions. In the program, special interest is given to esterases that act on bonds between hemicellulose/long chain fatty acids and lignin (1.3.1.a and 1.3.2) and oxygenases (LPMO) that oxidatively cleave cellulose and hemicelluloses (1.3.1 b). X-ray crystallography was used to in detail understand the structure-function relationship of enzymes (1.3.1a). Glucuronoyl esterases were studied in details and mutational studies of key amino acid residues is unravelling molecular determinants for their action on cleaving lignin-carbohydrate bonds. Yet another group of esterases, cutinases/suberinases were studied for their ability to release suberin-derived fatty acids (1.3.2). The biodiversity of this underexplored enzyme group was approached by a screening of 3000+ CAZY entries, leading to a phylogenetic tree on 180 genes, where ten enzymes covering this tree was cloned, expressed and characterized. From identification in a genomic and transcriptomic study of Thielavia terrestris, the role and activity of multitude LPMOs were investigated in detail (1.3.1b). The activity of six different cloned and expressed LPMOs were studied on different hemicellulose and cellulose substrates.

The molecular structure of wood hemicellulose and their interaction with cellulose and lignin in the plant cell wall was studied in detail (1.4.2). A battery of mild extraction methods, analytics and computational methods formed the basis for detailed studies of the plant cell wall. Taken together, the approach accelerated our understanding of the role of hemicellulose to plant cell wall properties and function.

Lignin is an underexplored biopolymer and much remain to understand of its chemical composition and molecular properties. In the program, we explored technical lignins and designed a library of lignin nanoparticles using both spruce and eucalyptus kraft lignin (1.2.1). A methodology to produce the lignin nanoparticles with defined shape and size were developed. Using NMR for characterization, it was concluded that the lignin nanoparticles consist of oxygen-rich surface and non-oxygenated aliphatic core. Another application is lignin-based electrodes (1.2.2). In order to optimize the composition and the protocol of fabrication of the electrodes, the electrochemical performance of three lignin derivatives was investigated. Lignosulfonate, partially desulfonated lignosulfonate, and fully desulfonated lignin, in a composite with carbon was investigated. Partial desulfonation was found to ensure better stability of the composite in aqueous media, simultaneously favoring its water processability and facilitating the ionic access to the entire bulk of the electrodes.

Furthermore, a process concept for extraction of lignins of high quality was developed, where, importantly, condensation reactions were avoided (1.4.1a). Processing of lignin will to the same extent account for the heterogeneity observed in lignin preparations. A battery of characterization methods (SEC, XRD, 1D and 2D NMR) was applied to ball-milled wood and it was concluded that supramolecular and molecular events led to the observed heterogeneity (1.4.1b).

Characterization of different wood-derived structures and the heterogeneity of the material is very important. During 2020, a project on NMR (using rotor-synchronized solid-state NMR) for studying heterogeneity of biomass was started (1.1.2b). Methods to increase the sensitivity of the analysis several magnitudes are developed, taking advantage of dynamic nuclear polarization (recent installed instrumentation at the Swedish NMR center in Gothenburg is used).

WWSC Program 2: Bio-based polymers and modelling

Active PIs

KTH: Professor Eva Malmström – Program 2 responsible, Professor István Furó, Professor Minna Hakkarainen, Professor Mats Johansson, Associate professor Martin Lawoko, Associate professor Lauren McKee, Associate professor Karin Odelius, Associate professor Per-Olof Syrén, Associate professor Francisco Vilaplana, Docent Jakob Wohlert

Chalmers: -

Linköping University: Professor Mats Fahlman

Overview of the activities within the program

Program 2 is focusing on biopolymers which can be isolated from forest products, except (nano)cellulose which is covered by Program 3, and on biobased polymers attainable by polymerization of low molar mass extractibles or degradation/fractionation products by sustainable methods, all in collaboration with Program 1. Program 2 also aims at understanding why biopolymers are sensitive to water/humidity which may hamper their potential applicability in various material applications, and at elucidating the fate of biopolymer- and cellulose-based materials at the end-of-life. The rationale for the design of novel materials and the potential material applications are explored in collaborations with Programs 3–5.

The effects of water in cellulosic biomaterials are ubiquitous but the molecular origins of those effects remain obscure. A central question is the effect of hydration on both micro- and macrostructure, as well as on segmental dynamics. Wohlert, Furó and co-workers aim at using atomistic molecular dynamics simulations and compare with experimental results from, e.g., scattering (X-rays, neutrons) and spectroscopic (NMR) measurements.

Lignin is one of three abundant biopolymers in wood and substantial efforts are devoted to remove it during pulping. Traditionally, lignin-rich side-streams have been utilized for energy recovery but with the development of the biorefinery concept, lignin has rendered significant interest as it is one of very few biobased sources of aromatic compounds. In Program 2, Johansson and Lawoko utilize well-defined fractions from Program 1 for thermosetting thin-film applications. Utilizing advanced characterization techniques (synchrotron-based SAXS and WAXS) on the materials has given fundamentally new insights on the understanding of lignin structures from a material perspective.

Terpenes are readily abundant biobased compounds of the generic formula $(C_5H_8)_n$. There is a plethora of terpenes; α-pinene can be isolated from turpentine retrieved from pine trees or betulin from birch bark. Fahlman et al. have fabricated organic bulk heterojunction solar cells using betulin-containing co-polymers supplied from Ek et al. (Program 1). The betulin-based polymer was used as a filler material to dilute the organic semiconductor with the purpose of increasing the power conversion efficiency and enhance the life-time of the devices. Positive effects were observed. Even though some terpenes contain double bonds, their inherent reactivity is often too low to allow for direct utilization as monomers in polymer synthesis. However, they can be upgraded to more reactive compounds that may prove useful for the synthesis of bio-renewable bio-based materials. Syrén and collaborators have explored α-pinene as an interesting starting material for biobased materials by transforming it into more reactive starting materials for both (meth)acrylate polymers and polyesters.

McKee and co-worker have explored suberin from birch bark. Suberin comprises a network of long chain fatty acids, aromatic compounds, and glycerol. A simple biorefinery approach to isolate suberin monomers and other valuable compounds from birch bark was developed. Fully biobased, highly flexible materials were produced directly from suberin monomers.

Malmström and Fogelström are exploring the use of hemicelluloses in wood adhesive applications inspired by the role of hemicelluloses in nature; adhering to cellulose surfaces. However, the high water solubility brings about challenges. Research is also conducted on how to valorize lignin (from Program 1) in wood adhesives.

Malmström, Vilaplana and co-workers are aiming to design wood-based hydrophilic and hydrophobic monomers suitable for polymerization-induced self-assembly to accomplish colloidal nanoparticles that can be used to stabilize bio(nano)fibers in a composite matrix, to obtain novel bio-based plastics and for nanostructuring of surfaces. So far, sobrerol, a metabolite from α-pinene, has been methacrylated to result in a hydrophobic monomer and various biobased compounds have been produced to render hydrophilic monomers. The monomers are evaluated in the production of colloidal nanoparticles and the corresponding materials will be thoroughly characterized.

Thermoplastic elastomers (TPEs) are a group of polymeric materials with elastomeric properties, yet they are not chemically crosslinked. Instead their elasticity arises from immiscibility between structural segments (soft and hard segments) within the polymeric chain. Compared with conventional elastomers, they have the benefit of being processable and mechanically recyclable, analogous to common thermoplastics; however, they are disadvantaged by a strong dependence of fossil-based starting materials and insufficient material properties. Odelius and co-workers have recently presented a route to expand the structure of the soft segment in the TPEs by introducing the naturally derived δ-lactones. The same group also developed a chemical recycling route which allows for recovery of more than 90 % of pure lactide within 2 hours when using PLA as a model polyester.

Hakkarainen and co-worker undertook a project aiming at elucidating the complicated interplay between structure, environment and degradation of biopolymers by using cellulose acetate (CA) as a model. The degradation processes of CA at molecular level in different aqueous environments, e.g., in real and simulated sea water and lake water were investigated, as well as the photodegradability triggered by UV-light. At high degrees of acetylation, the open environment degradability was limited, as expected. A simple bio-based additive was developed and was blended with CA without deteriorating the material properties. It was found to significantly accelerate the degradability of CA under UV-A radiation in air or in simulated sea water (90 % of UV from sun is UV-A).

PIs in program 2 collaborate with PIs in program 1; Lauren McKee and Lisbeth Olsson collaborate on the complex characterization of suberin, its extraction and valorization into biopolymers, Mats Johansson and Martin Lawoko are investigating the use of lignin in thermoset thin film applications, Jakob Wohlert and Hans Theliander study the interactions between cellulose particles in a filter cake supported by modelling. Program 2 is still looking to develop more collaborations to span more broadly over the entire WWSC.

WWSC Program 3: Fibres and fibre nanotechnology

Active PIs

KTH: Professor Lars Wågberg – Program 3 responsible, Adjunct professor Tomas Larsson, (KTH and RISE Bioeconomy), Associate professor Torbjörn Pettersson, Professor Daniel Söderberg, Professor Michael Malkoch, Associate professor Max Hamedi, Professor Fredrik Lundell

Chalmers: Associate professor Merima Hasani, Professor Gunnar Westman

Linköping University: Professor Igor Zozoulenko, Associate professor Eric Glowacki, Researcher Mikhail Vagin, Professor Xavier Crispin

Stockholm University: Professor Aji Mathew, Professor Lennart Bergström

Overview of the activities within the program

The development of the knowledge in the nanocellulose area has been, and is, impressive and opens many new possibilities for preparation of materials and devices. The use of biobased nanomaterials opens for a bottom-up engineering with a totally new toolbox, but the use of nanocellulose is also very demanding since it involves the handling of huge amounts of solvents which in turn leads to very high costs for up-scaling. It is hence necessary to explore new routes where the gain in nanocellulose knowledge can be used to create controlled self-assembly of nanomaterials. To alleviate this problem the activities in Program 3 have been focused partly on cellulose-rich fibers where the fibrils have been made available inside the fiber wall for further modification, while keeping the macroscopic dimensions of the fibers and partly on different self-assembly methods where the problem with solvent handling can be carefully managed based on a fundamental understanding of the colloidal chemical properties of the nanocelluloses. These latter activities have also been combined with the development of theoretical models for the self-assembly processes of the nanomaterials and for the development of our understanding of the relationships between supramolecular structures and macroscopic properties.

In our activities to study the liberation of the fibrils inside the fiber we have two main activities focusing on studying the structure of the fiber wall under extreme pressures using the Large-Volume Press at the P63 beamline at DESY in Hamburg and WAXS analysis of the structure of the fiber wall and a fundamental study of the adhesion between cellulose nanofibrils under different heat and temperature treatments. The results show that extreme pressures will change the nanostructure in the fiber wall and the aging studies of the fibril assemblies show that fibrils will associate irreversibly at increased temperatures and extended times, and the degree of irreversibility is dependent on the detailed molecular composition of the fibrils. In two other project we are studying how the fibrillar structure in the fiber wall can be tailored using dendritic materials and interpenetrating polymer networks to generate fibrillar structures with novel chemical and mechanical functionalities. Initially these projects have been performed with fibrils but the aim is indeed to apply these technologies to fibrous assemblies. In two following projects the fundamental solubility properties of cellulose under alkaline conditions and surface modification of the nanocellulose structures with sulphuric-acid hydrolysis and different counterions are studied to show how these modification techniques can be used to alter the macroscopic properties on the cellulose-based materials. New combinations of

cellulose fibers and active components have then been investigated in three different projects to create photocatalytic and photoactive natural materials, biophotovoltaic system by integration of IR-absorbing and conducting composites based on conducting cellulose fibers and piezoelectric cellulose materials. All these projects are of a very fundamental character and the activities have all been focused on catalytic processes of the systems, the photoactivity induced by combining the cellulose with different interactive chemistries and piezoelectric poling of cellulose nanocrystals.

In project 3.2 the fundamental colloidal chemical properties of the nanocellulose is investigated in order to quantify the factors controlling the interaction between the fibrils to allow for a controlled self-assembly of the nanofibrils into Volume-spanning Arrested States (VASs) and the assembly of nanocelluloses and other nanomaterials. Carefully prepared VASs show that bodies with elastic properties can be achieved at solids concentrations around and below 0.5 g/L. This knowledge base is then used to prepare filaments from CNFs and filaments from CNFs and carefully tailored dendritic polyelectrolytes. In order to allow for a controlled preparation of ultrastrong filaments the fundamental flow properties of nanocellulose are investigated both theoretically and experimentally with x-ray scattering techniques in addition to the colloidal chemical characterization of the CNFs. The self-assembly of cellulose nanofibrils and chitin in a PLA (polylactic acid) matrix was then used to 3D-print filaments and filters with a controlled structure. In another project in project 3.2 the self-assembly of CNCs and MMT (montmorillonite) were studied in acoustically levitating and slowly evaporating droplets using time-resolved small-angle X-ray scattering (SAXS). The structure analysis provided information on the evolution of interparticle distances and assembly or aggregation processes over a very broad range of volume fractions, as well as qualitative insights on the relative role of CNC and MNT on the global assembly of bi-component dispersions. The macroscopic properties of superinslulating foams have also been related to the nanostructure of the foams and its development of the moisture uptake of the foams. These properties have also been modelled using molecular simulations. Self-assemblies of CNFs and 2D MXene nanoflakes using the layer-by-layer self-assembly were prepared on different substrates in the range from planar silicon wafer, glass slides, to 1D cellulose filaments, to 3D nanocellulose aerogels. The functional multilayers endowed the different substrates with multi-functionality of high conductivity and electrochemical energy storage capability.

Many of the different activities in program 3 were joined together by the molecular dynamics simulation competence at LiU in the group of Igor Zuzoulenko and these efforts were able to support and extend the experimental developments and conclusions in the different projects. This development will also be an important common denominator for the future developments of program 3 and these efforts at LiU will also be combined with other simulation efforts at KTH.

WWSC Program 4: Composites for energy and electronics

Active PIs

Linköping University: Professor Magnus Berggren – Program 4 responsible, Senior lecturer Renee Kroon, Associate Professor Isak Engquist, Senior lecturer Simone Fabiano, LiU, Senior lecturer Magnus Jonsson

Chalmers: Professor Christian Müller, Professor Peter Enoksson, Professor Alexander Matic, Professor Hans Theliander

KTH: -

Overview of the activities within the program

Combining forest-based fibers and bulk systems with functional compounds provide us with unique material amalgamations for a wide range of energy, electronic, photonic and electrical applications. In P4, we try to explore and advance along this pathway, in a broad sense, by introducing p-type conducting polymers (e.g. PEDOT:PSS), n-type conducting polymers (BBL) carbon(ized) materials (e.g. graphite oxides), silicon dioxide microparticles and metallic materials to introduce various active properties on the material level. In addition, we explore a wide range of engineering techniques and production protocols (spinning, 2D/3D printing and coating protocols) to manufacture fibers, scaffolds and substrates then targeting a specific device or system needed for dedicated applications. The developments are carried out in the spirit of large-scale applications, low-costs, easy production and device setups, sustainability and favorable life-cycle protocols. The results of WWSC-Program 4 can be summarized as follows:

- Conducting cellulose yarns targeting electrode materials for energy storage, actuators and transistors, (Chalmers: Müller, Olsson, LiU: Fabiano, Stavrinidou, KTH: Hamedi)
- Fibre-electrodes for supercapacitors and batteries (Chalmers: Matic, Enoksson, Theliander, Engquist, Berggren)
- Logic circuits, memories and conducting circuits on and in paper (LiU: Fabiano, Engquist, Berggren)
- IR-Electrochromic papers expressing control over heat reflectivity and emissivity (LiU: Jonsson, Berggren)
- Water-soluble conductors for versatile paper/cellulose-based electronics (LiU: Kroon)

WWSC Program 5: Biocomposites and wood materials

Active PIs

KTH: Professor Lars Berglund – Program 5 responsible, Professor Qi Zhou, Professor Mikael Hedenqvist, Associate professor Richard Olsson, Assistant professor Yuanyuan Li

Linköping University: Associate professor Isak Engquist, Professor Xavier Crispin, Associate professor Eleni Stavrinidou, Associate professor Klas Tybrandt

Chalmers: Professor Paul Gatenholm, Associate professor Tiina Nypelö, Associate professor Roland Kádár

Luleå Technical University: Professor Kristiina Oksman, Associate senior lecturer Shiyu Geng

Umeå University: Jyri-Pekka Mikkola

Overview of the activities within the program

This program has on one hand fundamental activities on material components, primarily cellulose and delignified wood substrates and on the other hand activities on biocomposites and functional cellulosic materials and devices. The focus is on structure-property relationships as well as exploitation of material characteristics in new ways. Wood offers a unique combination of structures at nano, meso and microscales, and can in addition be shaped into large structures, even on the meter scale. The addition of functional additives in the form of active molecules, nanoparticles, functional polymers etc widens the wood nanomaterial scope to new applications, previously only considered for classical functional materials.

The present program is extending nanocelluloses as structural components to include wood substrates based on delignified and modified wood. Initial wood modification can aim towards increased specific surface area, removal of light absorbents, carbonization for increased electrical conductivity etc. Delignified wood can also serve as a hierarchical aerogel or hydrogel with a higher degree of order than in nanocellulose structures prepared by bottom-up fabrication.

Functional materials activities include soft robotics for sensors and actuators, wood template electronics, wood photonics and ionic thermoelectric supercapacitors which combine energy harvesting and storage with controlled discharge. The exceptional mechanical properties of oriented cellulose structures, even living plants, are combined with functionalization for ionic and electrical conductivity, active mechanical excitation, photonics etc. Complex nanocomposite materials are created, where tailoring and optimization of structures are carried out to obtain desired functions or improve device performance. Carbonized wood is used for water splitting where the catalysts are integrated in the structure. Soft actuators make use of nanocellulose aerogels as basic building blocks. Wood electrodes for energy storage is another example, where wood is modified by a conducting polymer for conductivity of electrons, and by lignin sulfonation for ion conductivity. The main scientific focus is on preparation of controlled nanostructures and understanding structural effects on performance, although many activities are explorative in nature. The reason is that devices or functions are often highly complex, with limited possibilities for theoretical predictions. Systematic studies

are then performed to elucidate structure-property relationships, which provides better understanding and a unique competence platform.

3D-printing of nanocellulose dispersions is used in several geometrically complex biomedical applications, where also electrical conductivity is imparted. In the context of biocomposites processing, recycling of thermoplastic composites is performed in order to extend the service life. This activity is related to fundamental rheology studies of nanocellulose dispersions, where the orientation state can be quantified during rheology measurements by optical microscopy (birefringence). CNC coatings are also studied and subjected to chemical modification.

Gas barrier films inspired by plant cuticles and also nacre-mimetic nanocomposites of high mechanical properties are investigated. Inorganic/cellulose hybrid composites is studied, both using 2D-nanoplatelet reinforcement and nanoparticle precipitation on nanocellulose scaffolds from zinc oxide salt solution. In general, nanparticle dispersion is the key problem addressed in these investigations, since this is a prerequisite in order to realize the potential of nanocomposites.

Structural biocomposites, new fiber materials and interface phenomena are investigated for materials with additional functionalities such as optical transmittance and photonics applications, eco-friendly characteristics and moisture durability. The need to estimate cumulative energy demand, carbon dioxide emissions and water-depletion potential for new material concepts is becoming increasingly important. As an example, it may be more eco-friendly to use wood substrates which are processed by top-down modification rather than using nanocellulose. Nanocellulose is based on chemical pulp, which is mechanically disintegrated, and then assembled into a new material by a bottom-up approach, which requires more energy than the top-down approach.

Program 5 works collaboratively (other programs, international partners) in multidisciplinary materials-science efforts ranging from plant biology, polymer synthesis, cellulose science, molecular-dynamics simulations, engineering physics devices and functional materials, to composite materials, wood chemistry, nanotechnology etc. Collaboration examples include thermoplastic biocomposites jointly investigated by Chalmers, KTH and LTU, devices-functional materials in Program 4 and 5 by LiU and KTH (wood templates), and lignin collaboration is on-going between Programs 1, 2 and 5.

WWSC Academy – research school

Persons involved

Paul Gatenholm, professor, Chalmers

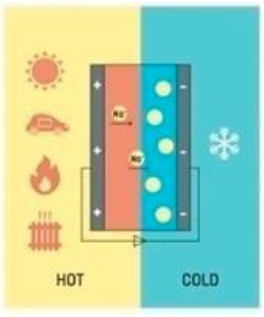
Objectives and PhD student training concept

The WWSC Academy is a very important part of WWSC and aims to contribute to fostering a new generation of scientists who will transform the world towards a circular bio-economy based on forest resources. The goals are:

- To provide graduate level, **basic** education within wood materials and science for all WWSC PhD students (32 students graduated in 2018, 30+ students graduated in 2014/15). The WWSC Academy is not replacing the graduate education carried out at the respective universities. It is a complement.
- All WWSC PhD students **have to** attend the series of **Summer and Winter Graduate Schools** designed to provide **basics of Wood Science and Technology but also knowledge of the Forest and Forest Industry.** All schools are combined with site visits.
- All PhD students **have to** present their research with a pitch- and a poster presentation during the WWSC Workshops in June and in November/December. The best presentations receive awards.

2020 activities

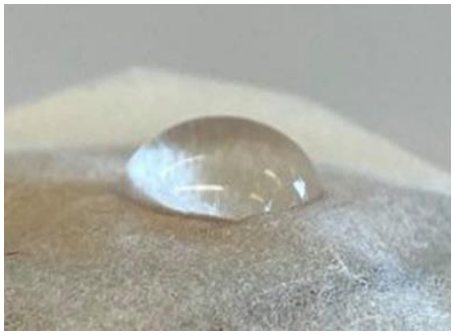
WWSC Academy Winter School in collaboration with Treesearch was organized March 30–April 3, 2020: **"From Forest to Organic Electronics, Energy Storage and Electronic Plants"**. The course which was initially planned to be "internat" was converted to internet due to the COVID-19 pandemic. The course included 27 hours of lectures and projects covering relevant subtopics: lignocellulosic surfaces, wetting, adhesion, printability, design, supercapacitors, batteries, fuel cells, solar cells, wearable/thermoelectric devices based on forest materials and proposal for bioelectronic systems to monitor the forest.





The teachers and administrative support quickly converted the lectures and all information to fit the virtual platform and the PhD students actively participated in the projects showing great ability to collaborate and communicate in the virtual environment. The course gathered 57 students; 47 PhD students from WWSC Academy and 10 from Treesearch, and was extremely appreciated by students, as reflected in the course evaluation.

WWSC Academy Summer School in collaboration with Treesearch was organized August 24–28, 2020: **"Surface and colloidal properties of wood-based fibers and nanofibrils"**. The Summer School, which was also held online, covered the following topics; fundamentals of surface-active agents, surfactants and polymers in solution, mixed surfactant-polymer systems and implications in lignocellulosic processes and utilization in materials design. 50 PhD students participated (9 from Treesearch).

The most important part of the course was the exam projects covering surface and colloidal properties of wood-based fibers and nanofibrils. The PhD students made very advanced presentations.

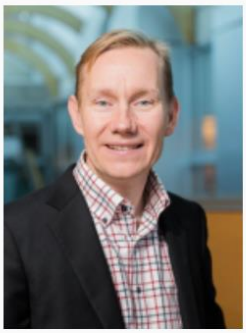
Project 1. Water-repellent fibers (paper). Hydrophobation (sizing) is widely used for surface modification of fibers.
Project 2. Wet-strong paper. Describe use of paper chemicals to improve wet strength of paper.
Project 3. Liquid packaging board. Tuning chemistry for final product properties.
Project 4. Fluff pulp and hygienic products.
Project 5. Paper made by foam-forming process.
Project 6. Nanocelluloses in industrial products.

All WWSC PhD students attended the WWSC Workshop November 26-27, 2020, online and presented a poster pitch and poster. For the poster session we used the virtual platform "Wonder".

Graduated WWSC PhD students during 2020

Name	University	WWSC Project – thesis title
Marcus Jawerth	KTH	Thermoset resins using technical lignin as a base constituent
Hyeyun Kim	KTH	Wood-Based Nanocellulose In Lithium Ion Batteries and Electrochemical Coatings
Joanna Wojtasz-Mucha	Chalmers	Pre-extraction of wood component – Mild hydrothermal methods for a future materials biorefinery
Malin Nordenström	KTH	Colloidal interactions and arrested dynamics of cellulose nanofibrils
Calvin Brett	KTH	Neutron and X-ray Surface Scattering Reveals the Morphology of Soft Matter Thin Films
Karin Sjövold (Sahlin)	Chalmers	Chemical Modification of Cellulose Nanocrystals: Creating a Novel Toolbox Utilising the Overlooked Sulphate Surface Groups

WWSC Scientific Advisory Board



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