WWSC
WALLENBERG WOOD SCIENCE CENTER

# Wood nanotechnology - new materials from trees



## Annual report 2019

KTH VETENSKAP OCH KONST · CHALMERS · LiU LINKÖPINGS UNIVERSITET · TREESEARCH · Knut och Alice Wallenbergs Stiftelse

# Table of contents

# Wood nanotechnology - new materials from trees

In January 2019, the Wallenberg Wood Science Center entered a new 4-year phase, as the WWSC 2.0 center started. The center is now formed between KTH Royal Institute of Technology, Chalmers University of Technology and Linköping University. The annual funding of 72 MSEK is shared between Knut and Alice Wallenberg (KAW) foundation (40 MSEK), universities (22 MSEK) and industry (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.

The term "wood nanotechnology" actually originates with the WWSC center. The meaning of nanotechnologies for wood and wood components is broad and in a somewhat fluid state, since this area of research is very young. Researchers aim to develop scientific understanding and techniques for manipulation and control of wood-based molecules and nanoparticles at small scale. In combination with other functional polymers, active compounds and nanocomponents, new materials and devices can be assembled, investigated for basic understanding and explored for new functionalities.

Although existing forest products in industry can benefit from research efforts towards gradual improvement and optimization, such activities are unusual in WWSC 2.0. Instead, the Wallenberg Wood Science Center has a longer-term perspective within "New materials from trees", with a research school for PhD-candidate training, and the goal to maintain its position as one of the leading international research centers. Scientific activities have two main objectives; the first is on fundamental understanding of wood tissue, wood fibers, cellulose, hemicelluloses, lignin and related components, including bio-based polymers. This includes extraction, disintegration, purification processes and their mechanisms, characterization of biomolecules, nanocelluloses, 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. The ultimate purpose of this type of nanotechnology is to extend the range of properties for wood-based materials, and provide materials with new functions. Historical technology development shows that early scientific breakthroughs (eg cellulose nanofibrils) can inspire industrial development into commercial technologies (eg microfibrillated cellulose applications in packaging, coatings, films, personal care etc).

The KAW foundation uses bibliography as one evaluation criterion for WWSC. In addition, assessments from the scientific advisory board (SAB, see page 23) is part of the evaluation. This combination is helpful as a driver for research quality. Bibliography measures means that journal impact factors (a quality measure for research journals) and number of citations for WWSC publications are important. Within the theme "New materials from trees" publications in more general scientific journals are therefore attractive. The teams in WWSC are therefore multidisciplinary and composed of researchers from various fields. International collaboration is required in order to solve challenging problems and there is a strong network of researchers all over the world, contributing to WWSC projects and publications. Method development is important, and recent progress is noted in the use of synchrotron light sources for x-ray studies, neutron scattering, NMR but also theoretical modeling including molecular dynamics simulation.

During 2019, two workshops of three days each were organized where research presentations were mixed with project discussions and planning activities for the center. The center primarily has members from KTH, Chalmers and LiU, although selected researchers from SU, LTU and UmU also contribute. There are about 50 PhD-students, 25 postdocs and 60 senior researchers in the center. In addition to the 72 MSEK in annual funding, WWSC researchers bring in at least another 70 MSEK in additional funding, from other research agencies such as the EU, ERC, Vinnova, industry, SSF, Formas and VR. There is also additional KAW funding through other centers and programs for Academy Fellows, and KAW Scholars.

The main idea of WWSC 2.0 is captured in the title. Researchers can focus on larger ideas contributing towards fundamental understanding, and towards the forest products of the future where nanotechnology will be an ingredient. Although the center is organized in different programs and subjects, the center operates in a highly integrated manner. It means that disintegration of wood tissue into components or novel templates is carried out in many different projects; and fundamental efforts on wood science understanding are integrated with new materials efforts.

WWSC is divided into five programs, which are highly integrated:

1) Wood components – extraction and characterization

2) Biobased polymers and modelling

3) Functional fibers and fiber systems

4) Composites for energy and electronics

5) Biocomposites and wood materials

In Program 1 *Wood components*, various approaches towards a materials biorefinery vision are included, where wood constituents are separated from wood tissue for use in new bio-based materials and chemicals, rather than pulping only. Several approaches are combined, such as mild steam explosion, membrane and chromatographic separation, enzymatic treatment and leaching, ionic-liquid extraction, and fractionation together with chemical pulping. The engineering-science goals are related to generation of new ideas and explorative investigations. 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.

The topics in Program 2 *Biobased polymers and modelling* are dominated by a polymer chemistry viewpoint, where new polymers are synthesized from biobased building blocks, or wood biopolymers and cellulose are modified by various approaches. These polymers can either be components in material systems such as paper and polymer matrix biocomposites, but they can also be used in coatings, adhesives and films and as ingredients various material systems. Although biocomposites and other fiber systems can be straight-forward applications for new polymers, the main scientific goal is directed towards fundamental challenges with wood biopolymers. In contrast with synthetic polymers, the biological polymers have much more heterogeneous structure at molecular level. This creates variability in properties and characteristics, which need to be addressed in order for bio-based materials to have a larger impact in society. Another scientific challenge is that biobased molecules tend to be more difficult to react or modify chemically, since the reactivity of functional groups varies more than in synthetic molecules.

Programs 3 *Functional fibers and fiber systems* and 5 *Biocomposites and wood materials* are not so different in terms of objectives, but the research teams are different. In both programs, wood and cellulose-based materials are in focus although fundamental aspects of wood components are included. Examples of materials include nanocellulose films, composites, aerogels, hydrogels, inorganic hybrids and wood biopolymer films, fiber materials and materials from delignified wood. It is fair to say that nanocellulose has dominated this research field for the past 10 years. Within WWSC, this is now broadened to include wood-pulp fibers and solid wood. The idea is that processing will be much easier if the fiber or veneer structure is preserved, although the nanostructure of the wood cell wall provides specific functionality, in line with the spirit of wood nanotechnology. Fundamental studies of fibrils, colloids, fiber swelling, material nanostructure etc are combined with exploration of new material concepts. Furthermore, lignin-based materials are increasing in scientific importance, which is interesting in a society where lignin is primarily used as an energy source obtained from the bleached Kraft process for wood-fiber pulping.

Program *4 Composites for energy and electronics* is directed towards functional materials and devices. These functions include electric, electronic and photonic properties. Templates include nanocellulose, fibers and wood veneer, as well as the materials mentioned in the previous section. 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.

Stockholm, June 2019

Lars Berglund
Director WWSC
Professor KTH Biocomposites

# Activity highlights

During 2019, close to 100 scientific journal articles were published by WWSC-researchers. For this reason, a short section like the present one can only cover part of the program. One of the challenges addressed in WWSC, is to separate the different wood biopolymers. Hemicelluloses and lignin are intimately mixed in the wood cell wall and very difficult to separate. One mechanism responsible for lignin-hemicellulose association is the formation of lignin-carbohydrate complexes (LCC). In international collaboration, Dr Lawoko at KTH is summarizing current LCC knowledge and presenting progress from WWSC (Giummarella et al). A related study is presented by Dr Larsbrink, who is building his research program at Chalmers. Specific enzymes are shown to cleave chemical linkages between lignin and xylan (Mazurkewich et al). This is interesting, since enzymatic processing of biomass could be a route towards more pure fractions of lignin and hemicelluloses.

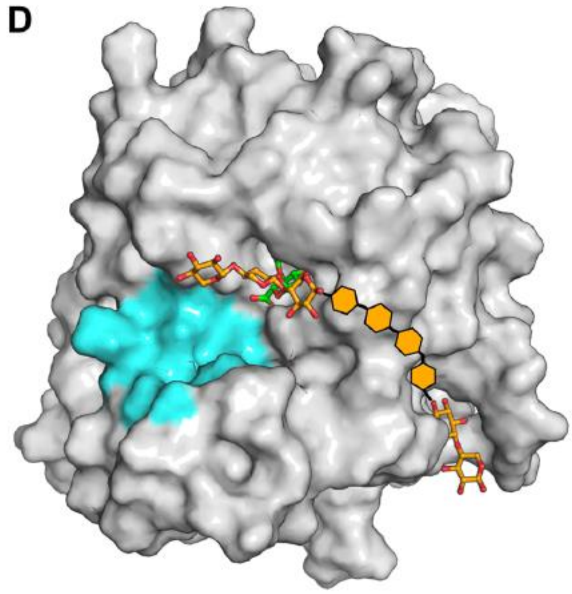


*Figure 1. Proposed mechanism for how a specific enzyme (grey image) can interact with lignin in a lignin-carbohydrate complex (Mazurkewich et al). The bluish region has this function in the enzyme model.*

On the chemical engineering side, Dr Theliander at Chalmers and his team have deepened investigations of mechanisms for Kraft lignin precipitation (Sewring et al), and his colleague Dr Rasmuson with coworkers have modeled diffusion in wood (Kvist el al), which has been pretreated by steam explosion to facilitate separation of wood components. The solubility of wood biopolymers in water is important not only for lignin precipitation, but also for understanding hemicelluloses. Dr Wågberg at KTH with a team from multiple disciplines have shown that the solubility of hemicelluloses in water is actually quite poor (Kishani et al). This has consequences for existing industrial processes, but also for any use of hemicelluloses in new materials, where water-based processing is often desirable.

Polymer chemistry is an important discipline for WWSC. In an interesting, high-risk project, a combined chemical and enzymatic approach is applied to pinene (Stamm et al), an important terpene present in pine. Dr Syrén and Dr Malmström at KTH are involved, and this is an effort to find new wood-based building blocks for biopolymers. Malmström is also designing polymers in water-based systems, for the use in cellulose nanomaterials (Engström et al).

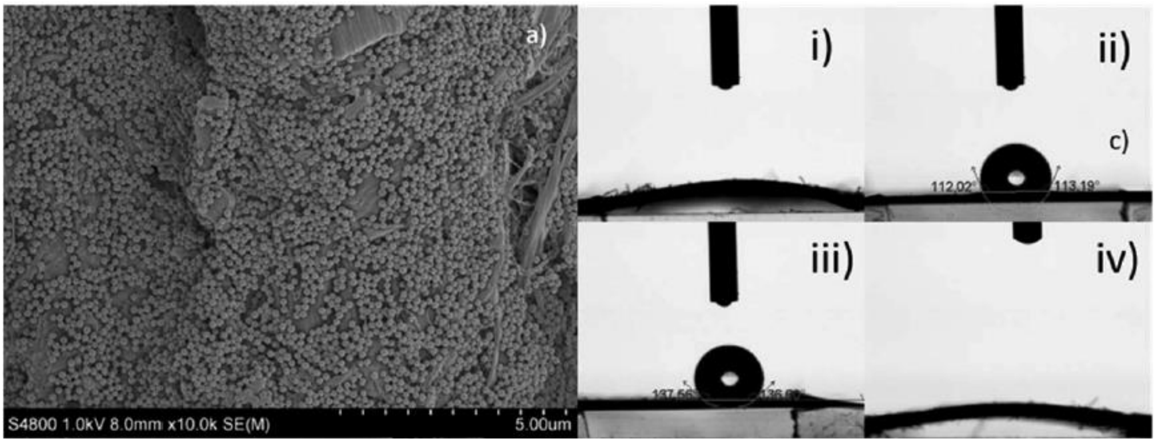


*Figure 2. Small latex particles of polymers synthesized in water, of potential use as a cellulose biocomposite polymer matrix (left). Wetting behavior against cellulose for different polymer compositions (copolymers), making it possible to tailor adhesion, (Engström et al).*

In a center like WWSC, many unexpected results are presented. Dr Gatenholm at Chalmers has worked for many years on 3D-printed structures, and recently managed to draw analogies with wood biosynthesis (Markstedt et al). Many interesting suggestions are proposed, and this printing technology not only provides possibilities for arbitrarily shaped structures, but also for materials from novel combinations of wood components. At Stockholm University, Dr Bergström has realized an idea of utilizing traditional dyes in a cellulose nanotechnology context (Limaye et al). Mechanisms are clarified by MD computer models and simulation studies by team members from WWSC.

One of the more interesting multidisciplinary results from WWSC, is the spinning process for filaments based on nanocellulose. Drs Söderberg, Lundell and Wågberg at KTH have collaborated across the boundaries of fluid mechanics and cellulose colloids. The most recent contribution is the study by Nittal et al. In this context, the increasing and more qualified use of synchrotron x-ray techniques in WWSC is notable, for the purpose of understanding fine scale structures in nanomaterials (for example Brett et al, Medina et al).

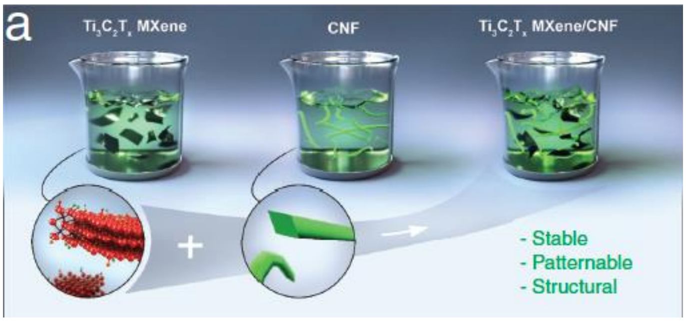


*Figure 3. Colloidal mixtures of nanocellulose and MXene 2D components in water, for filtering, drying and use in materials and devices (Tian et al).*

Dr Hamedi, previously LiU, now KTH, has been very successful in leading work on composites between nanocellulose and 2D platelets from MXene (Tian et al), a study which already is well-cited. These films have multiple functions, including exceptional capacitance. In Linköping (LiU), the large team with Dr Berggren is a strategically important addition to WWSC, with strong functional materials competence and focus on organic electronics. For example, Bamgbopa et al have clarified mechanisms involved in conducting polymer-redox biopolymer supercapacitors. The most commonly used conducting polymer, both in research and in industry, is PDOT-PSS, which means that its interaction with wood components is of critical importance in the program. Belaineh et al at LiU have investigated how the structural organization of PDOT-PSS can be controlled on cellulose.

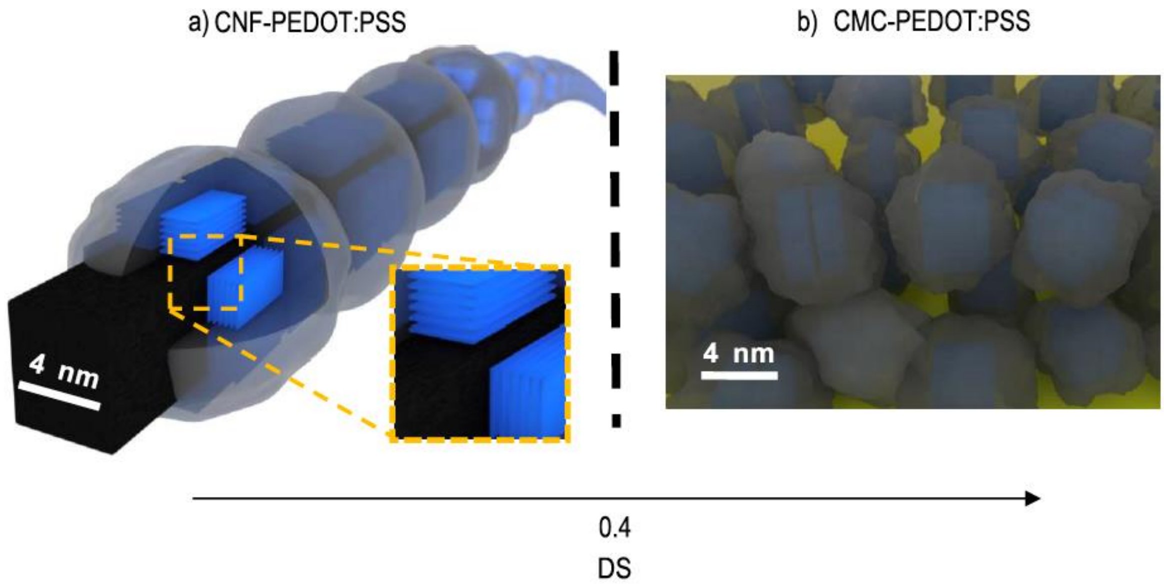


*Figure 4. Schematic model of how the conductive polymer blend PEDOT:PSS in the investigation appears to be organized on cellulose nanofibrils (Belaineh et al). The right image shows the organization of CMC with the conductive polymer.*

The nanostructure of cellulose fibrils can be exploited in many different types of materials. Three final examples from nanocellulose, pulp fibers and wood are added to the list: Cellulose nanofibrils (CNF) is nowadays a difficult area for original contributions, but Dr Zhou and colleagues at KTH have managed to use a new type of oxidizing enzyme (LPMO) to create CNFs which are colloidally stable due to this oxidation (Koskela et al), without the use of chemicals. Yang et al have made strong, transparent biocomposites by preserving the cellulose nanostructure in pulp fibers; a nanostructure which is often compromised in industrial fibers. Montanari et al managed to provide heat storage function in transparent wood for use in buildings, also by manipulating the wood cell wall nanostructure.

In conclusion, the WWSC 2.0 center is in full operation with multidisciplinary teams from different universities. The researchers, along with PhD-students, are actively addressing important engineering science hurdles, resulting in a strengthened competence platform, laboratory development, and a steady stream of publications and examined PhD:s. In a longer-term perspective, this will facilitate introduction of more eco-friendly materials in society as well as corresponding industrial development.

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

## Active PIs

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

KTH: Professor Monica Ek, Associate professor Martin Lawoko, Associate professor Francisco Vilaplana

Linköping University: Professor Xavier Crispin, Dr Viktor Gueskine

## Overview of the activities within the program

In program 1, our main target is to provide insights to details of wood processing, by providing deeper understanding of the chemical and structural properties of wood polymers in native and processed state. 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. The strong component interaction and small-scale complexity, however, 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. Here, we aim for a deeper understanding of those to allow a knowledge-based foundation for mild and sustainable tailor-made pretreatment and fractionation methods, that can be combined into different biorefinery concepts. An added raw material for study in WWSC 2.0 is bark. So far, the fractionation methods for separating molecules in bark has been established and detailed characterization of the streams have started (1.4.3)

In wood biorefinery, complex streams are generated, putting high demands on down-stream processing. Membrane filtration is commonly applied, this energy demanding step would benefit significantly from optimization. Here, we developed a fluid dynamic gauging (FDG) device that allow detailed studies of the membrane filtration process. The understanding of fouling during membrane filtration of different wood components is studied (1.1.1 a). Filtration is also a key towards dewatering of pulp streams, this energy consuming unit operation is poorly described, why a modelling approach combined with experimental verification has been started (1.1.1 b).

Mass transport and its limitation is of key importance in separation and fractionation. An increased understanding of the mass transport and its limitation can build a foundation for deeper understanding of different phenomena connected to separation and fractionation. To enable deeper studies of mass transfer, diffusion cells has been set up and are used to characterize and study diffusion, in the first round of lignin molecules (1.2.1 a).

Enzymes may play an important role in wood decomposition as they can act very precisely and specifically on targeted chemical bonds. During 2019, we have further investigated the role of enzymes in degradation of the chemical bond between lignin and carbohydrates (1.3.1 a). Also, in suberin, found in the skin of plants, including the tree bark, lignin-carbohydrate like chemical bonds are present (1.3.2). Suberin is composed of medium to long-chain fatty acids linked to polyaromatic, lignin-liked domains via ester linkages. A group of enzymes, esterases, is studied in molecular detail to explore their function in wood decomposition. Lytic polysaccharide monooxygenases (LPMOs), are one class of enzymes active in biomass degrading. LPMOs are oxidative enzymes and in addition to its critical role in efficient biomass saccharification, it can act on cellulose and hemicellulose to create molecular attractive groups for further tailoring of the wood polymers to give them specific properties. In 1.3.1.b we are exploring LPMOs to understand their diversity in catalytic ability and how they can be used in wood biorefinery.

Lignin is a heterogenous aromatic polymer, that is poorly understood, why its controlled processing and valorization is hampered. The lignification process in spruce cell cultures is studied to provide deeper fundamental understanding of lignin polymerization and thereby gaining insights to native lignin (1.4.1b). Processing of native lignin by ball milling is studied to understand how processing influence it the lignin structure. Technical lignins are highly heterogeneous in structure, functionality and molecular weight. Such properties make them I less attractive as polymer precursors for material synthesis. In WWSC 1.0, we developed a green solvent sequence to refine technical lignins to relatively more homogeneous fractions (1.4.1 a), efforts that now have been further developed. In valorization of lignin, the high content of polyphenol moieties in lignin enables the oxidative and reductive interconversions of intact biopolymer on electrochemical interfaces. The various derivatives of 1,2-benzenediol attached to the polymer backbone render the redox character of lignin (1.2.2) which makes them attractive in organic electronics.

A major effort in program 1 is to gain deeper insights to what actually happens with the biomass as a consequence of different unit operations, which requires insight to chemical and structural changes. Therefore, we also work towards detailed understanding of the wood polymers. Along those lines, NMR is applied to characterize and determine heterogeneity, domain sizes, molecular orientation and other anistropic features of cellulose in in wood derived materials (1.2.1 b). Furthermore, the molecular structure of wood hemicelluloses and their cell wall interactions, will be deciphered b integrating advanced analytical and molecular dynamic approaches (1.4.2).

Extended collaboration inside and between the different programs is of large importance to exercise the interdisciplinarity that the center offers. One example of this kind of collaboration is the study of the interaction between cellulose particles in a filter cake with help of modelling – a collaboration between Hans Theliander (project 1.1.2) and Jakob Wohlert, KTH (active in program 2). Another example of a collaboration is between program 1 and 2, where an overall aim is to make use of enzymatic released suberin in building novel biopolymer. Collaboration in the complex characterization of suberin, its extraction and the valorization in biopolymers (Lisbeth Olsson and Lauren McKee is the PIs in this collaboration). On the lignin side in the lignin biorefinery concept driven in 1.4.1 (by Martin Lawoko), heterogenous lignin is starting point for thermosets that were fabricated, in collaboration with Program 2 (Prof. Mats Johansson) and Program 5 (Prof. Lars Berglund).

# 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 that can be isolated from forest products, except (nano)cellulose, and on bio-based polymers that can be obtained by polymerization of low molar mass extractives or degradation products by sustainable methods, all in collaboration with Program 1. Program 2 also aims at understanding why biopolymers are sensitive to water/humidity, which often circumvent 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 will be assessed in collaboration with Programs 3 - 5.

The effects of water in cellulosic biomaterial are ubiquitous but the molecular origins of those effects remain obscure. Wohlert, Furó and coworkers aim at elucidating these by combining nuclear magnetic resonance (NMR) on the experimental side and molecular dynamics simulations (MD) on the interpretational side.

In Program 2, Johansson and Lawoko utilize well-defined fractions from Program 1 for thin film applications. Various lignin-fractions were allylated and cured with thiol-ene chemistry. The resulting thermoset films were thoroughly characterized and the results demonstrate the potential for lignin as a raw material for high performance thermoset polymers. Advanced characterization techniques (synchrotron-based SAXS and WAXS) provided structural information on how lignin organizes within a thin film.

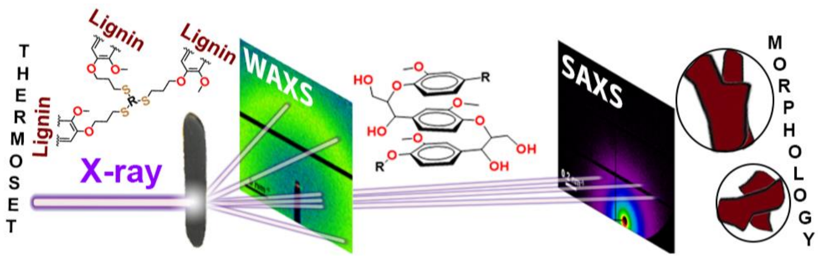


*Illustration reprinted from Johansson et al. ACS Appl. Polym. Mater. 2020, 2, 2, 668–676*

Syrén and collaborators have explored α-pinene, a terpene abundant in turpentine from pine, as an interesting starting material for bio-based materials. They demonstrated that α-pinene could be upgrade into a lactone amenable for ring-opening polymerization which was subsequently polymerized into polyesters harboring rings as backbone motifs. Further, sobrerol, a metabolite of α-pinene, could be acylated with acrylates, yielding potent monomers for radical polymerization. The generated sobreryl methacrylate (SobMA) resulted in high-molecular weight polymers, both by conventional free radical polymerization, as well as via horseradish peroxidase-mediated radical polymerization (enzymatic polymerization). Syrén and coworkers have successfully demonstrated the potential of a-pinene as valuable starting material for bio-based plastics.

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 and also to obtain novel bio-based plastics. So far, sobrerol, a metabolite from a-pinene has been methacrylated to result in a hydrophobic monomer and various sugar-derivatives have been produced to render hydrophilic monomers. The synthesized monomers will be evaluated for the production of colloidal nanoparticles and the corresponding materials will be thoroughly characterized.

Mckee and collaborator have established a reproducible suberin-extraction protocol based on previous activities within program 1. They have demonstrated that it is possible to thermally polymerize suberin into a black elastic material that is currently under further investigation. They have also produced epoxidase enzymes from bacteria and poplar. The bacterial enzyme has been well characterized, and is currently applied to suberin monomers with the intention to increase the abundance of epoxy groups.

Green thermoplastic elastomers (GreenTPEs), is based on bio-based starting materials and the elasticity relies on phase separation between soft and hard chain segments instead on chemical crosslinks. δ-Lactones are naturally abundant and can be used as soft segments in GreenTPEs and have been researched by Odelius and Hakkarainen. They have also demonstrated chemical recycling of the resulting material.

Hakkarainen and co-worker undertook a project aiming to understand how modification of biopolymers affects their degradability in different environments. Several test environments have been set up to simulate degradation in sea- or lake water under accelerated conditions. A common commercial cellulose derivative, cellulose acetate with a degree of acetylation approximately 40%, was selected as model compound. Overall, Hakkarainen and co-worker aim at precise molecular level characterization of molecular weight, chemical and physical structures/properties, and correlation of the observed changes to the specific environmental conditions.

Fahlman entered Program 2 in October 2019 with the ambitious and challenging overall aim to fabricate (nearly) all-forest-based optoelectronic devices (organic photovoltaics, OPV, and organic light emitting diodes, OLEDs) based on compounds provided from P1-2 and commercial sources.

Program 2 is a new addition to WWSC and program activities are still in their cradle. Program 2-internal collaborations have started on a small scale and are further formulated for the future. PI’s in program 2 collaborate with PI's 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 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, Docent Daniel Söderberg, Professor Michael Malkoch, Docent 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

One of the major aims of program 3 is to use the extensive knowledge collected for nanocelluloses and to apply this competence to delignified wood-based fibres where the fibrils have been separated while maintaining the fibre form since these macroscopic entities are much easier to process in subsequent applications, CNFs in fibre form. In order to be able to reach this bold target it is necessary to establish which inherent forces, inside the fibre wall, that are needed to be overcome to separate the fibrils fully and to develop new fibre processing techniques beyond the current state of the art. Two different projects have therefore been devoted to these two scientific questions and the aim is to use a combination of our competence in cellulose adhesion and the in-depth competence we have on flows, in and around wet fibres.

An exceptionally expanded fibre wall will also allow for the development of new materials and devices by combining our competence in fibre technology, advanced polymer synthesis and new interactive devices. In one of our projects the aim is therefore to form new materials by creating interpenetrating polymer and nanofibrillar networks by polymerising polymers inside the expanded fibrillar networks, inside the fibre wall, in order to create unique structures with outstanding mechanical and water holding capacity. In another project the intention is to create Gas Diffusion Electrodes by polymerizing conducting polymers within the fibre wall and to produce a final electrode through a papermaking type of process. Finally, we are also devoting a project to identify totally new ways of functionalizing the interior of the fibre wall by advanced polymer chemistry and toposelective modifications by tuning the chosen cellulose modification and polymerization chemistries. We are also going to combine our knowledge about fibril and fibre modification with applications to form new fibre-based devices and in a co-operation between LiU and KTH a new project has been initiated for using modified fibres in photocatalysis. Finally, in this initial part, we are investigating how the fibres can be molecularly dissolved and chemically modified to create precise chemical modification of the dissolved cellulose to allow for the preparation of new functional cellulose materials after a suitable regeneration procedure.

In the first phase of WWSC we were able to show how the liberated cellulose nanofibrils (CNFs) could be combined into filaments with exceptionally good mechanical properties by combining our knowledge in the colloid chemical properties of CNFs and our expertise in the control of the flow of highly anisotropic cellulose-rich nanoparticles. This work also showed the necessity to further deepen our knowledge about the colloidal chemistry of this nanomaterial where general theories such as the DLVO theory is not sufficient to describe the behaviour of different types of nanocelluloses. Apart from experimental evaluations of the colloidal chemical properties of the CNF it is necessary to create a new theoretical foundation for this experimental system and therefore a close co-operation between the modelling expertise at LiU and the colloidal chemical evaluations at KTH has been established. A similar co-operation has also been initiated between Chalmers and LiU where the influence of a careful chemical modification of CNCs on the interactions between the nanocellulose particles is also modelled at LiU. At SU the work of characterizing the nano-structure of nanocellulose based colloidal systems with high resolution scattering techniques at very high solids contents and the change of the structure with time is continuing. This knowledge is naturally very important for determining how the nano-systems are consolidating as the water is finally removed from NC dispersions. Our earlier work also showed that it is necessary to further develop our fundamental insight on how the NCs are oriented in different types of flow and how advanced polymer chemistry can be used to create new types of biologically and biochemically interactive filaments. New projects are therefore initiated where we are combining our expertise in advanced two-phase flow systems, advanced polymer chemistry and biointeractive polymers and nano-components.

The collected knowledge about the properties of expanded fibre walls, colloidal chemical behaviour of nanocelluloses and how to combine different interactive components with new types of fibres, filaments and functionalised cellulose and other nanomaterials will then be used in three new projects aimed at forming the scientific base for new materials and devices. At SU the structure and chemical composition of novel superinsulation foams will be investigated. In another project at SU new types of 3D-printed filters will be prepared where the properties of NCs will be tuned to be used in compositions that are fitted for a 3D printing process. Finally, the piezoelectric properties of NC-based films will be investigated where the effect of a high electric field on the morphology and phase properties, as detected with AFM, will be studied in detail in order to evaluate possible piezoelectric applications of cellulose.

# WWSC Program 4: Composites for energy and electronics

## Active PIs

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

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

KTH: -

## Overview of the activities within the program

The scientific pathways of Program 4 (P4) aims at exploring electric, electronic and photonic functions in and on biomaterial systems from the forest. Functions are introduced into and onto cellulose and lignin-based materials from a vast array of protocols, including complexing of materials at the nano- and/or macro-scales, via blending, synthesis, molecular assembly, self-organization etc. Further, cellulose and lignin materials are also being converted into functional materials using for instance carbonization and chemical treatments. The functional biomaterials are then further refined into inks, substrates, fibres, coatings and components to enable manufacturing of electronic and photonic devices and systems. Especially, large-scale and low-cost manufacturing process steps are considered to enable giant scale and eco-friendly technology for future applications in energy, healthcare, commerce and digital communication.

One common theme of this P4 relates to introducing conductivity and dynamic photonic properties, at different hierarchical and organization levels, ranging from the single (nano)fibre level to the macroscopic level of *e.g.* the top surface of a paper substrate. The potential applications of those systems include electrical energy storage (batteries and capacitors), electronics, digital applications, radiative cooling and large-area electrochromism. The electro- and photonic-active materials, introduced into the forest biopolymer systems include a wide range of different materials, such as PEDOT:PSS (p-type organic conductor), silver nanowires, carbonized CNF, $MnO_2$, LiS, BBL (n-type organic conductor), p($g_4$2T-T) (p-type organic conductor), and $SiO_2$ microparticles. Scientific and engineering efforts have been devoted to properly complexing these materials with the forest biopolymers in order to enable both desired manufacturing routes and specification for targeted applications.

For electrical energy harvesting systems, i.e. batteries and supercapacitors, energy density and power density together define the prime and crucial parameters and specifications. To optimize these two parameters, efforts have been devoted to achieve highest possible electronic conductivity, large area for charge compensation between electronic charges and electrolyte components and porosity to allow for intermixing of electrolyte and conductor. Together, these efforts aim at optimizing the densities of energy and power for targeted applications.

For electronic applications, various strategies to achieve high conductivity has been conducted including complexing organic conductors with other organic conductors and also with inorganic conductors and semiconductors. A novel organic-organic printing ink was developed exhibiting stable and high conductivity possible to print onto paper. In another effort, a regenerated yarn was developed including and inorganic-organic conducting composites finally exhibiting an optimized conductivity of 190 S/cm. In a third effort, CNF paper substrates has been explored to enable patterned conductivity as a base substrate for electronic applications.

Further research aims at studying these materials from a fundamental point of view, including spectroscopy, microscopy and electronic/photonic parameterization of components, using the competences of KTH, Chalmers and LiU. This work will serve as the foundation to build more advanced devices, systems, demonstrators and even prototypes using large-volume production and integration techniques.

# 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, Researcher Yuanyuan Li

LiU: Associate professor Isak Engquist, Professor Xavier Crispin, Assistant professor Eleni Stavrinidou, Associate professor Klas Tybrandt

Chalmers: Professor Paul Gatenholm, Assistant professor Tiina Nypelö, Associate professor Roland Kadar

LTU: Professor Kristiina Oksman, Associate senior lecturer Shiyu Geng

## Overview of activities within the program

Activities are primarily on preparation or processing of solid biocomposites and wood-based materials, with controlled structures for the purpose of extended property range and new functions. The scientific focus is on structure-property relationships as well as exploitation of wood 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 areas of applications, previously only considered for classical functional materials.

Nanocelluloses are classical building blocks for wood-based nanomaterials, and lignins, hemicelluloses and other biobased molecules are used in new materials. The present program is extending nanocelluloses as structural components to include wood "templates" 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 bottom-up nanocellulose structures.

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. The scientific focus is on preparation of controlled nanostructures, 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 for geometrically complex biomedical applications is investigated with the purpose to combine nanoscale characteristics and intrinsic properties of cellulose with bioactive components. In the context of biocomposites processing, melt-compounding of thermoplastic composites is performed in order to improve performance and the eco-friendly profile of the materials. This activity is coordinated with fundamental rheology studies of thermoplastic melts mixed with wood fibers. The materials are of great interest as replacement for petroleum-based thermoplastics.

Bioinspired gas barrier films based on novel nanocomposites are investigated for the purpose of packaging materials. A related concept in the form of inorganic/cellulose hybrid composites is studied, both using 2D nanoplatelet reinforcement and nanoparticle precipitation on nanocellulose scaffolds from salt solution. The scaffolds can be viewed as strong gels based on cellulose nanofibrils, and such gels are also investigated for medical radiotherapy applications. More fundamental studies are underway, investigating small-scale friction and wear phenomena on wood biopolymer surfaces in different environments.

Finally, 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. Wood templates, holocellulose fibers and new nanocelluloses are used with a focus on structure-property relationships.

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 runs between Programs 1, 2 and 5.

# WWSC Academy, research school

## Persons involved

Paul Gatenholm, professor, Chalmers


*WWSC and Treesearch PhD students and instructors participating in WWSC Summer School, August 25-31, 2019, outside Örnsköldsvik.*

## Objectives and PhD student training concept

The WWSC Academy is very important part of WWSC Program and aims to contribute to fostering a new generation of scientists who will transform the world towards circular bio-economy based on forest resources. The goals is 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 graduate education carried out at respective University. It is a complement.
- All WWSC PhD students **have to** attend series of **Summer and Winter Graduate Schools** designed to provide **basics of Wood Science and Technology but also knowledge of Forest and Forest Industry.** All schools are combined with site visit.
- All PhD students **have to** present their research as pitch and posters in June and in November/December during WWSC annual conferences. The best presentation receives Award.

## 2019 activities

During beginning of 2019 PhD students were recruited and we waited with the first school until August 25-31. Kick off meeting took place on June 11, 2019, during WWSC annual conference and students held their first poster-pitch and poster presentations which were very impressive. At the end of 2019 we had 42 PhD students enrolled; 26 at KTH, 10 at Chalmers and 6 at Linköping University. We combined the first two schools in one long week starting already on

Sunday August 25 in Umeå and ending on Saturday, August 31 in Örnsköldsvik. Those two schools provided introduction to Wood Biotechnology with site visit to Umeå Plant Science Center, planting spruce in Holmens Plant Nursery in Gideå and concentrated course in Biorefinery: From Wood Chips to Material Components with site visit to Biorefinery cluster in Örnsköldsvik/Domsjö. During lectures given by scientists from UPSC the basics of forest biotechnology were provided including cellulose biosynthesis, wood formation and forest genomics. The site visit with short sessions in small groups provided great inside into research at UPSC. The second course included basics of forest biorefinery. In order to enhance the learning process, the PhD students were divided in six teams and worked with exam projects with the theme: Maximizing utilization of wood raw material while producing special products. The schools ended with project presentations which held very high quality. Team building and social interactions with each other and the instructors are other very important elements of fostering new generation of WWSC researchers.

*Prof. Ove Nilsson introduces students to basics of tree growth, and PhD students planting spruce in Gideå.*


*Site visit at Biorefinery cluster in Örnsköldsvik.*

All PhD students attended the WWSC annual winter conference and presented poster pitch and poster on November 27, 2019.

## Graduated WWSC PhD students during 2019

| Name | University | WWSC Project – thesis title |
|---|---|---|
| Jennie Berglund | KTH | Wood Hemicelluloses - Fundamental Insights on Biological and Technical Properties |
| Joakim Engström | KTH | Tailored adhesion of PISA-latexes for cellulose modification and new materials |
| Tahani Kaldéus | KTH | Surface modification approaches of cellulose nanofibrils and their effect on dispersibility |
| Nitesh Mittal | KTH | Nanostructured Biopolymeric Materials – Hydrodynamic Assembly, Mechanical Properties and Bio-Functionalities |
| Tobias Benselfelt | KTH | Design of Cellulose-based Materials by Supramolecular Assemblies |
| Lilian Medina | KTH | High Clay Content Cellulose Nanocomposites for Mechanical Performance and Fire Retardancy |
| Tobias Ingverud | KTH | Exploring crosslinked networks of polymers and hybrid cellulose materials |
| Pernilla Karlsson | KTH | Swelling of Cellulose Fibrillar Matrices and Gels |
| Saina Kishani | KTH | On the Solubility of Wood Hemicelluloses in Water and its Influence on the Adsorption at Cellulose/Water Interfaces |
| Patric Kvist | Chalmers | Diffusion of large molecules in steam-exploded wood |
| Tor Sewring | Chalmers | Precipitation of Kraft Lignin from Aqueous Solutions |
| Xuan Yang | KTH | Eco-friendly Holocellulose Materials for Mechanical Performance and Optical Transmittance |
| Valentina Guccini | SU | Nanocellulose: Energy Applications and Self-Assembly |
| Thomas Paulraj | KTH | Plant cell-inspired microcontainers: Fabrication, Characterization and Applications |

# WWSC Scientific Advisory Board

**Prof. Harry Brumer**
The University of British Columbia, CA
Fundamental and applied carbohydrate enzymology.

**Prof. Dr. Ingo Burgert**,
ETH Zürich, Switzerland
Nanostructural and micromechanical characterisation of wood and fibre composites and their modification in order to optimise material properties.

**Prof. Robert Pelton**
McMaster Uni., CA
Polymer colloids, water soluble polymers, interfacial engineering, flocculation, adhesion, cellulose, and pulp and paper technology.

**Prof. Natalie Stingelin**
Georgia Tech., USA
Organic functional materials, including organic electronics; multifunctional inorganic/organic hybrids; smart, advanced optical systems based on organic matter; and bioelectronics.

# WWSC Board

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