WWSC

WALLENBERG WOOD SCIENCE CENTER

Wood nanotechnology – new materials from trees

Annual report 2021

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Fore more information about the research projects within WWSC, please visit www.wwsc.se.

Wallenberg Wood Science Center

Wallenberg Wood Science Center (WWSC) was first launched in 2009 as a collaboration between KTH Royal Institute of Technology (KTH) and Chalmers University of Technology (Chalmers), eventually also with participating researchers from Stockholm University (SU), Luleå Technical University (LTU) and Umeå University (UmU). 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 the funding organizations is for 10 years, ending in 2028. Currently (November 2021), the center engages ~70 faculty members/researchers, ~25 postdocs and ~50 PhD students at six Swedish universities (KTH, Chalmers, LiU, SU, UmU, and LTU).

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 provides molecular and nonstructural control. 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. Research activities in WWSC spans 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 (Prof Lisbeth Olsson, Chalmers)
Program 2: Biobased polymers and modelling (Prof Eva Malmström, KTH)
Program 3: Fibers and fiber nanotechnology (Prof Lars Wågberg, KTH)
Program 4: Composites for energy and electronics (Prof Mats Fahlman, LiU, has replaced Prof Magnus Berggren, LiU)
Program 5: Biocomposites and wood materials (Prof Lars Berglund, KTH)

WWSC 2021

2021 was another year significantly affected by the roaring pandemic which put a lot of restrictions on everyday life. Activities within WWSC were maintained at a high level even though essentially all physical meetings were somehow affected. The workshop held in June, with focus on sustainability aspects of relevance for WWSC, was organized as a virtual workshop with large participation and engagement from center members and invited virtual guests. In November, we were fortunate to be able to organize the winter workshop as a physical meeting which gathered more than 130 participants. The meeting was mainly focused on research conducted by WWSC members, with only a few invited guests. One session was allocated to discussing bibliometrics, publication strategy and merits of publishing.

During the spring, the Knut and Alice Wallenberg Foundation announced a change in their funding scheme and invited WWSC to submit an application for the time period 2023–2028. The application was submitted early November and by the end of November, WWSC received the very satisfying decision that the application was granted and that the budget was extended from 40 MSEK/yr to more than 63 MSEK/yr, including two generous recruitment packages per partner university.

The research conducted during 2021 brought about fundamental findings as is described in the forthcoming program descriptions. Below please find a mini-overview of the research focus in each of the WWSC programs.

Program 1 Wood components and materials biorefinery	The scientific work in Program 1 aims at providing deep insights into structural and processing characteristics of wood and bark components, the main focus being on complexity of their molecular, nano- and macroscale interactions pertaining to their recalcitrance during decoupling and valorization in general. Moreover, structural changes upon processing; whether pre-treatments, separations or fractionation and functionalization, are poorly described and pose additional challenges on the design of biorefining concepts.
Program 2 Biopolymers and modelling	Program 2 is focusing on biopolymers which can be isolated from wood (except (nano)cellulose which is covered by Program 3), and on bio-based polymers attainable by polymerization of low molar mass extractibles or degradation/fractionation products by sustainable methods. The research in Program 2 aims at gaining fundamental understanding on why biopolymers are sensitive to humidity or water which may hamper their potential applicability in various material applications, to design new sustainable materials from bio-based raw materials using as benign chemistry as possible and green chemistry principles, and to elucidate the fate of cellulose- (biopolymer-) based materials at the end-of-life.

Program 3

Fibers and fiber nanotechnology

The focus areas in Program 3 have been the liberation of the fibrils in the fiber wall of cellulose-rich fibers, chemical modification of these fibrils, and the development of filaments and fibril-based materials with a controlled structural organization of the fibrils.

Program 4

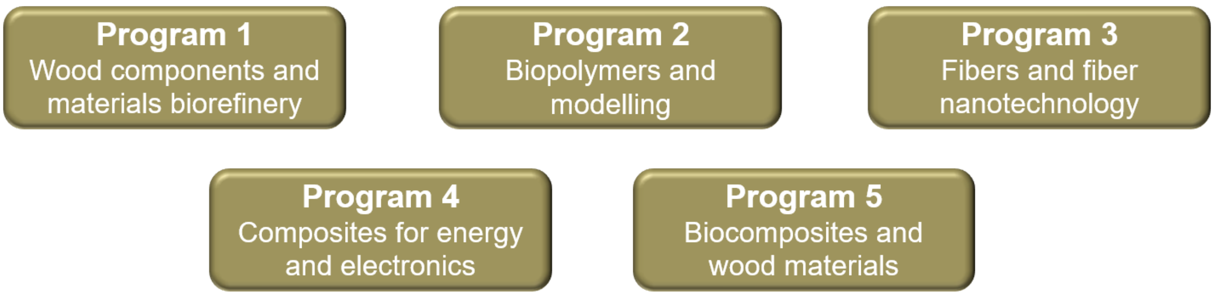
Composites for energy and electronics

Combining forest-based fibers and bulk systems with functional compounds provide unique material amalgamations for a wide range of energy, electronic, photonic and electrical applications. In Program 4, 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 in order to obtain 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.

Program 5

Biocomposites and wood materials

Program 5 is focused on nanostructural control in various types of biocomposite materials. Two major cellulosic substrates are investigated – wood by itself or nanocellulose in the form of cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC). The program is covering three areas; i) wood and nanocellulose substrates for functional biocomposites, ii) aspects of nanocellulose biocomposites, and iii) functional biocomposites for electronics, energy, photonics and mechanical functions



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

Active PIs

Chalmers: Prof Lisbeth Olsson Program 1 responsible, Assoc Prof Johan Larsbrink, Prof Anette Larsson, Prof Lars Evenäs, Prof Hans Theliander, Assoc Prof Merima Hasani, Prof Eva Olsson, Prof Gunnar Westman
KTH: Prof Monica Ek, Assoc Prof Martin Lawoko, Assoc Prof Francisco Vilaplana, Assoc Prof Olena Sevastyanova, Assoc Prof Lauren McKee
LiU: Prof Xavier Crispin, Dr Viktor Gueskine

Overview of the activities within the program

The scientific work in Program 1 aims at providing a deep insight into structural and processing characteristics of wood and bark components, the main focus being on complexity of their molecular, nano- and macroscale interactions pertaining to their calcitrance during decoupling and valorization in general. Moreover, their structural changes upon processing, whether pre-treatments, separations or fractionation and functionalization, are poorly described and pose additional challenge on design of biorefining concepts.

In Program 1, efforts are made on elucidation of native structural motifs of wood focused on deciphering native lignin and hemicellulose structure in relation to their properties, mutual interactions, and interactions within the cell wall. In 1.4.1 covalent bonds between hemicelluloses and lignin within the so-called lignin-carbohydrate complexes have been confirmed by combining novel sample preparation with advanced 2D NMR. For the first time the existence of lignin-xylan ester linkages was demonstrated. In parallel, structural investigations of hemicelluloses in terms of interactions and processability have revealed the impact of genetical modification of lignin pathways on their extractability (1.4.1a). On the other hand, studies of a model system with extracellular lignin production within 1.4.1b, aiming at an improved insight in lignin biosynthesis, pointed out an increased production of extracellular lignin in the presence of xylan. Moreover, combined chromatographic/mass spectrometric and computational approaches in 1.4.2 have demonstrated a spontaneous adsorption of xylan onto hydrated cellulose surfaces. A conformational analysis suggested coating of cellulose fibrils by a rigid and ordered xylan layer functioning as a transition towards more disordered polysaccharide and lignin domains.

Simultaneously, efforts are made on understanding chemical aspects of the wood tissue decoupling along with the accompanying mass transport phenomena. In 1.4.1a, a consolidated biorefinery concept for a simultaneous production of homogeneous lignin with hemicellulose and cellulose-rich fraction was developed. In 1.4.3., the focus was on extracting lignin from Norway spruce bark via a organosolv route. 1.1.2a studied lignin transport through porous model membranes in diffusion cells and could show a strong pH dependency and a size fractionation with larger fractions being more prone to degrade and dissociate. A new addition to the wood tissue decoupling efforts in Program 1 is a work addressing the recalcitrant primary cell-wall residues in cellulose substrates. (1.1.3), where the focus is on isolating these motifs and developing analytics capable of assessing their characteristics.

Selective decoupling of wood tissue is one of the main objectives of Program 1. In that respect, development of enzymatic methods is of special importance. Enzyme discovery work comprises glucuronoyl esterases (potentially targeting lignin-pectin linkages) in 1.3.1a, cutinases (releasing suberin-derived fatty acids and aiding degradation of plastics) in 1.3.2 and LPMOs (degrading oxidative enzymes) in 1.3.1 b, all of them requiring improved fundamental knowledge with regard to biodiversity and structure-function relationship. Characterization of cutinases has been directed towards improved understanding of their activity on bark (facilitated by a new labelling method to localize suberin-rich motifs by CLSM). LPMOs were studied for their applicability on functionalization of CNC for production of hierarchical materials: sulphated CNCs could indeed be oxidized by LPMOs with the crystalline structure retained.

Further functionalization and fractionation of the obtained wood components provide an important adaptation to desired applications. Carbohydrate binding modules (CBMs) have been investigated for their ability to cross-link decorated polysaccharides and induce formation of polysaccharide gels along with mechanistic gelation studies (1.3.1c.) The use of CBMs attached to active enzymes for this purpose was also demonstrated. In addition, work on galactose oxidases, capable of converting the O6 hydroxyl groups of galactose to aldehydes and, thus, potentially, capable of oxidizing wood polysaccharides focused on detailed investigation of this enzyme family and their activity (1.3.3.). Oxidizing activity towards galactose and other alcohols have been shown in initial activity screens.

Attractive biomedical properties of acetone-extracted crude kraft lignin were pointed out in 1.2.1, where lignin nanoparticles prepared from high-molecular-weight fractions were obtained as insoluble residues from acetone extraction. These nanoparticles, with versatile surface functionalities, inhibited the proliferation of hepatocellular carcinoma cells in a dose-dependent manner (carbohydrates on the surface seems to affect the cell interactions).

Down-stream separation of the components is challenging due to heterogeneity of the generated streams and usually comprises strong needs for fractionation and eventually also dewatering. Development of a fluid dynamic gauging technique for *in situ* monitoring of the fouling behavior (1.1.1a) enabled detailed studies of membrane filtration of wood components in aqueous solutions, model studies indicating formation of a highly resilient layer close to the membrane surface. On the other hand, the high energy demand of the traditional dewatering steps was challenged by promoting filtration through employment of an external electric field in 1.1.1b. This electro-assisted filtration was demonstrated to be a promising method for dewatering suspensions of negatively charged fibrillated cellulose with the dewatering rate proportional to the applied electric field.

Characterization as an integral, indispensable part of all the biorefinery efforts in Program 1, comprises an important focus on the development of microscopy methods for investigation of the enzyme-wood component interactions in 1.3.2 b, as well as a focus on rotor-synchronized solid-state NMR (1.1.2b) for biopolymer orientation analysis, alongside with improved structural analysis through high-resolution/high-field NMR. A new addition to this work is development of a spectrophotometer operating in the terahertz region of the electromagnetic spectrum (1.5.2) providing a complementary technique to analyze H-bonding and conformational changes in polysaccharide building blocks and materials.

Program 1 researchers work strongly collaboratively both within the program and the center on addressing e.g. dewatering mechanisms (Theliander and Wohlert), suberin valorization (Olsson and McKee), NMR structural investigations (Evenäs, Westman, Nypelö) and rheology of cellulose solutions (Hasani and Kadár), to mention a few examples.

WWSC Program 2: Bio-based polymers and modelling

Active PIs

KTH: Prof Eva Malmström Program 2 responsible, Prof Monica Ek, Prof István Furó, Prof Minna Hakkarainen, Prof Mats Johansson, Assoc Prof Martin Lawoko, Assoc Prof Lauren McKee, Assoc Prof Karin Odelius, Dr Linda Fogelström, Assoc Prof Per-Olof Syrén, Assoc Prof Francisco Vilaplana, Assoc Prof Jakob Wohlert
Chalmers: Prof Anette Larsson
Linköping University: Prof Mats Fahlman

Overview of the activities within the program

Program 2 is focusing on biopolymers which can be isolated from wood, except (nano)cellulose which is covered by Program 3, and on bio-based polymers attainable by polymerization of low molar mass extractibles or degradation/fractionation products by sustainable methods, all in collaboration with Program 1. Program 2 aims at:

- gaining fundamental understanding on why biopolymers are sensitive to humidity or water which may hamper their potential applicability in various material applications,

- designing new sustainable materials from bio-based raw materials using as benign chemistry as possible and green chemistry principles,

- elucidating the fate of cellulose- (biopolymer-) 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 biomaterial 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.

The interest for lignin has skyrocketed over the last decades as it is a large source of biogenic aromatic carbon. Since long, WWSC has refined wood fibres to retrieve lignin and has developed characterization expertise, modification pathways and curing chemistries to turn it into thermoset applications, mainly in thin films. Recently, Johansson, Hakkarainen and co-workers have shown that microwave-assisted fractionation is an efficient technique and faster than traditional solvent fractionation. Futher, fundamental investigations aiming to deepen the understanding of structure-property relationships between the initial technical lignin structure and the final thermoset performance have been performed.

Different fractions of LignoBoost kraft lignin (KL) and advanced cathode interface materials such as PDIN, PDINN and PFN-Br have been explored as superior electron-extracting contacts in (hybrid) organic solar cells in a collaboration between Fahlman, Ek, Johansson, Kroon and Lawoko. The branched architecture of KLs offers uniformly distributed phenol-groups on a backbone with excellent bonding capacity and an interphase-layer with good pi-pi stacking (advantageous for charge transport).

During 2020, Hakkarainen and co-workers initiated the investigation on the complex interplay between structure, environment, and degradation of biopolymers by using cellulose acetate as a model. It was demonstrated that deacetylation and degradation of cellulose acetate can be triggered by UVA-light after addition of small amounts of carbon dots, produced by hydrothermal carbonization and oxidation of cellulose. More recently, a set of vanillin-derived polyesters with systematically varied composition of aromatic/aliphatic units and functional groups has been prepared and characterized and will subsequently be investigated with respect to enzymatic degradation by Syrén and co-workers.

Odelius and Wohlert have also addressed sustainability issues by using PLA as a model material. Chemical recycling to monomer (CRM) has been demonstrated with high conversion and selectivity. The concept will be further developed in the future to encompass thermoplastic elastomers and PLA-biocomposites.

Odelius and co-workers have initiated the synthesis of wood-based thermoplastics starting from a specifically designed bis-vanillin monomer in the strive to accomplish materials with high glass transition temperature. Step-growth polymerization was utilized to create polymers with glass transition temperatures and modulus defined by small changes in their chemical structure. The polymers were also demonstrated to be chemically recyclable.

Malmström, Johansson and co-workers demonstrated the allylation of ferulic acid and some derivatives. Ferulic acid is an unsaturated hydroxycinnamic acid originating from lignin. All compounds were readily photo-chemically cured with trimethylolpropane tris(3-mercaptopropionate) (TRIS) into crosslinked thin films in the presence of a photoinitiator to demonstrate the potential of bio-based binder-resin components. The thermal/mechanical properties could be tailored by adjusting the composition of the resins.

Since the start of WWSC 2.0, well-defined cationically charged core-shell nanoparticles obtained through reversible addition-fragmentations chain transfer (RAFT)-mediated polymerisation-induced self-assembly (PISA) in water have been designed and synthesized by Malmström and co-workers targeting surface engineering in bio(nano)composites. The synthetic procedure by which the NPs is made is robust, allowing for a fantastic freedom in choice of building blocks and thereby allows for the synthesis of a plethora of compounds with tailorable properties. The general scope of the projects undertaken during 2021 was to understand the interactions between (nano)cellulose and NPs and response to changes in pH or temperature.

Malmström and Fogelström are exploring the use of hemicelluloses in wood adhesive applications inspired by the role of hemicelluloses in nature; to provide adhesion to cellulose surfaces. During 2021, the adhesive activities have spanned broadly; from replacing parts of vinyl acetate with bio-based counterparts in an effort to reduce the negative impact from fossil-based resources to various approaches of lignin-containing wood adhesive by radical polymerization. In the lab, a fully bio-based adhesive with its main constituent from prehydrolysis of wood can be obtained with satisfactory tensile strength and water resistance for both veneers and particleboard and without any addition of formaldehyde.

WWSC Program 3: Fibres and fibre nanotechnology

Active PIs

KTH: Prof Lars Wågberg Program 3 responsible, Adj Prof Tomas Larsson (RISE Bioeconomy), Assoc Prof Torbjörn Pettersson, Prof Daniel Söderberg, Prof Michael Malkoch, Assoc Prof Max Hamedi, Prof Fredrik Lundell
Chalmers: Assoc Prof Merima Hasani, Prof Gunnar Westman
LiU: Prof Igor Zozoulenko, Prof Xavier Crispin
SU: Prof Aji Mathew, Prof Lennart Bergström

Overview of the activities within the program

Focus areas in Program 3 have been the liberation of the fibrils in the fibre wall of cellulose-rich fibres, chemical modification of these fibrils and the development of filaments and fibril-based materials with a controlled structural organisation of the fibrils.

To be able to liberate the fibrils within the fibre wall it is naturally important to clarify and quantify the interactions between fibrils and fibril aggregates. This has been performed both by studying the interaction between model cellulose materials using high resolution measurement techniques, such as GISAXS, AFM and contact adhesion testing and by studying the aging of CNF materials. Results from these investigations show that the physical interactions at the interphases are of large importance both for the making and the breaking of the cellulose-rich materials. It has also been demonstrated that the molecular and supramolecular rearrangements during water removal has a more profound influence on the cellulose-cellulose interactions than previously established. The work with subjecting cellulose-rich fibres and modified cellulose-rich fibres to extreme pressures to determine if this is a possible route to arrive at altered fibre properties has also continued during 2021. The work has been concentrated on the equipment available at KTH allowing for pressures up to 2 GPa and with dynamic pressure pulsed using the large-scale mechanical testing rig at Solid Mechanics. The results indicate an increased crystallinity and specific surface area, as well as changes in bound water content and surface morphology as the pressure over the fibre assembly is increased.

The work with chemical modification of fibres has been developed in different projects. New types of dendrimers with antibacterial properties has been developed and a similar chemistry was then used to functionalise fibres. This opens for totally new ways of tailoring fibres for new applications. In another project the use of the sulphate groups introduced during treatment of the fibres with sulphuric acid has been used for further functionalization of the fibres using diketenes and azetidinium salts. These investigations were performed with cellulose nanocrystals as a model for the cellulose fibres and the influence of the chemical modification on the on the self-organization organisation of the functionalized crystals was then evaluated to estimate how different basic interactions would influence the interactions between the modified surfaces. The work with functionalization of dissolved cellulose in alkaline media has also continued where the influence of the state of cellulose dissolution and cellulose interactions on the reactivity of the cellulose was evaluated. A new type of new quaternary ammonium hydroxide base for dissolving cellulose has also been developed. The work with the concept of preparing interpenetrated networks of cellulose fibrils and water-soluble polymers has also shown the need for having a covalent crosslinking between the fibrils in order to gain the full benefit of both networks. Model studies using oxidized CNFs have also allowed for the development of a network model for describing the rheological properties of the covalently crosslinked fibrillar systems.

Fundamental studies of the colloidal interactions between CNFs and CNFs and other materials have also been performed during the year. High resolution rheological investigations and mathematical modelling has shown that as the dilute gels are loaded the fibrils starts to slide against each other and as the load is stopped the interaction between the fibrils is recovered. This work has also increased the awareness of the huge influence of the aspect ratio of the colloidal chemical properties on the CNFs. By using very high aspect ratios of the CNFs it is possible to form stable gels at weight concentrations as low as 0.02 %. The co-assembly of montmorillonite (MMT) and CNC has also been studied in a project at Stockholm University using time-resolved small-angle X-ray scattering (SAXS) to probe the assembly over a wide concentration range in aqueous levitating droplets. Among other results it was demonstrated that the MMT promoted and increased the gelation of the CNCs. These findings were partly used as an inspiration to prepare composite filaments of CNF and a specially prepared, amphoteric, hyperbranched polyelectrolyte with crosslinkable functionalities. By carefully mixing the polyelectrolyte with CNFs before the preparation of the filaments it was possible to prepare filaments with a significantly improved toughness and wet integrity. A deepened understanding of the organization of the CNFs also demands an increased understanding of the movement of high aspect ratio CNFs in dispersion and the work regarding coarse-grain modelling of low-concentration nanofibrillar dispersion has been continued during 2021. Efforts have been made to allow for using high-performance computing clusters for running advanced simulations of sufficiently many rods/fibrils for the investigation of different critical dispersion parameters (stiffness, surface interaction, concentration, and morphology). The self-organization of CNCs into nanostructured, anisotropic foams also showed that by a careful control of the nanostructure it was possible to form super-insulating foams from the CNCs. The foam wall nanoporosity and, to a lesser extent, the orientation of the CNC particles and alignment of the columnar macropores, was also found to influence the insulation performance of the foams.

In our activities to prepare interactive fibrous materials it has been found that by combining cellulose fibers and UV-interactive zinc oxide it has been possible to prepare new functional and sustainable materials. By growing ZnO on cellulose-rich fibres and using a simple papermaking procedure it is possible to form a stable semiconducting paper, and photo-capacitors can then simply be fabricated by screen printing carbon paste as electrode patterns on this paper. In addition to the superior photoconductive properties, ZnO nanowire paper acts as an efficient photocatalyst. It was shown that by dipping the photoconductive paper into water it was possible to produce hydrogen peroxide by a photoreduction of the dissolved oxygen from air under sunlight irradiation.

Earlier work has shown that piezo-electric properties can be induced to nanocellulose films by a poling of nanopapers. Recent progress has shown that this is associated with a electrohydrolysis of the water in the film which leads to an exposure of the films to high pHs. This is suggested to lead to a hydrolysis of less ordered glucan segments of the CNFs which in turn locks the degraded nanofibrils in an oriented position due to the high electric field perpendicular to the gold electrodes used for poling of the nanosheet. This will in turn induce piezoelectric properties to the sheets.

The multiscale theoretical modelling capacity developed by professor Igor Zozoulenko and his team at LiU, has continued to be a very important, common denominator for many of the projects in program 3. The association of CNCs under different conditions has been successfully modelled and the movement of anionic nanolatexes in dispersions of CNFs at different concentrations has shown how the thin, slender CNFs will oppose the movements of latexes in different concentration regimes. In other projects the theoretical modelling has assisted in the understanding of the influence of moisture on the thermal conductivity of CNF-based foams. Our efforts in this area will indeed continue during 2022 and the combination of high-resolution measurement techniques and multiscale modelling has improved the scientific quality of our joint publications.

WWSC Program 4: Composites for energy and electronics

Active PIs

LiU: Prof Mats Fahlman Program 4 responsible, Prof Magnus Berggren, Assoc Prof Simone Fabiano, Prof Magnus Jonsson, Assoc Prof Renee Kroon, Prof Igor Zozoulenko
Chalmers: Assoc Prof Merima Hasani, Prof Aleksander Matic, Prof Christian Müller, Assoc Prof Tiina Nypelö

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 Program 4, 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 in order to obtain 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 results of WWSC-Program 4 in 2021 are summarized below.

Cellulose-based metamaterials where the visible properties of cellulose are tuned via its microstructure were developed. We formed reflective (porous) and transparent (homogenous) cellulose films, which both remained non-absorptive in the visible. We then used those materials systems to demonstrate (and compare) solar-reflective and solar-transparent radiative coolers only based on cellulose. We further addressed the challenge of not only providing white (reflective) or transparent systems, but also coloured. Most recent coloured radiative cooling systems generated colours by absorption, which counteracts the cooling via solar-induced heating. To avoid that, we instead generate colour by selective reflective/transmission, using cellulose nanocrystals self-assembled into chiral photonic films. We made films of different colours in reflection and showed that they remain low-absorptive in the whole visible range. They all provided high thermal emissivity and demonstrated radiative cooling.

Furthermore, infrared electrochromic paper consisting of a porous cellulose layer sandwiched between two electrochromic conducting polymer films was developed. The cellulose simultaneously can act as strong thermal emitter and electrolyte-containing separator to facilitate redox-switching. We demonstrated electrochemically tuning of the infrared reflection and emissivity by tens of percent, enabling us to regulate the thermal emission from the devices, and thereby their ability for radiative cooling.

A new conjugated polymer, PCAT-K, was designed with the aim of creating recyclable electroactive cellulose coatings. The developed water-soluble conjugated polymer can be reversibly crosslinked via acid-base chemistry, and the hydrogen bonding that it imparts reinforces the electroactive coating and offers improved interaction with cellulose substrates. We were hence able to demonstrate that PCAT-K can be easily fixated onto and recovered from cellulose substrates via simple acid-base chemistry.

We have synthesized lignin-derived hard carbons, for use in Na-ion batteries, and characterized the complex structure using a combination of x-ray and Raman spectroscopies to reveal the correlation between local structure and electrochemical performance. We also explored the possibility of creating a solid polymer electrolyte from a bio-based polymer (hydroxyethyl cellulose) with the aim to replace the aqueous electrolyte in rechargeable zinc batteries.

Organic electrochemical transistors (OECTs) hold promises for developing a variety of high-performance (bio-)electronic devices/circuits. While OECTs based on p-type semiconductors have achieved tremendous progress, n-type OECTs suffer from low performance hampering the development of power-efficient electronics. We demonstrated that finetuning the molecular weight of BBL enables the development of n-type OECTs with record-high geometry-normalized transconductance, electron mobility × volumetric capacitance, fast temporal response, and low threshold voltage. We also demonstrated OECT-based complementary inverters with record-high voltage gains and ultralow power consumption. These devices can be printed using a polymeric quaternary ammonium salt of hydroxyethyl cellulose as the solid-state electrolyte materials, thus yielding low-power/high-gain flexible complementary circuits based on printed OECTs which are among the best <1 V complementary inverters reported to date. We also developed a direct-write additive manufacturing process for OECTs fabrication. We created 3D printable inks for conducting (graphene oxide + carbon nanotubes), semiconducting (PEDOT), insulating/electrolyte (PSSNa) and substrate (NFC) layers to create fully printed OECTs. We developed a cross-linkable cellulose formulation for the substrate enabling the formation of a hydrogel that is easy to 3D print and delaminate, yielding free-standing OECTs possessing long-term plasticity (~ 1 hour).

A cellulose yarn containing chitosan was developed as the positive charge of chitin was hypothesised to improve the binding the negatively charged PSS in PEDOT:PSS. An improvement in the washability of the conducting chitosan/cellulose yarn was however not observed. In another project, regenerated cellulose yarn was spray-coated with BBL:PEI to produce n-type conducting yarns. Ongoing work focuses on improvement of the electrical conductivity as well as mechanical characterization, followed by the fabrication of textile thermoelectric devices.

Composites of the conjugated polymer p($g_4$2T-T) and various nanocellulose components, CNC, MFC or CNF were developed. The mechanical properties of the composite films indicate considerable reinforcement with a tensile modulus of up to 150 MPa in case of p($g_4$2T-T) reinforced with 10 wt% CNF. Ongoing work focuses on the characterization of the mechanical and electrical properties as a function of nanocellulose content, as well as electron microscopy to determine the distribution of the nanocellulose.

We explore how the molecular weight heterogeneity of lignin modulate lignin and lignin blend film morphology and configuration, seeking to establish control of lignin blend phase separation and film configurations which are important for *e.g.* control of adhesion, friction, and micro-organisms' affinity to surfaces. Ongoing work addresses phase separation with respect to composition, molecular weight, and polydispersity.

WWSC Program 5: Biocomposites and wood materials

Active PIs

KTH: Prof Lars Berglund Program 5 responsible, Prof Mikael Hedenqvist, Assoc Prof Richard Olsson, Prof Qi Zhou, Assist Prof Yuanuan Li, Dr Peter Olsén
LiU: Assoc Prof Klas Tybrandt, Assoc Prof Eleni Stavrinidou, Assoc Prof Isak Engquist, Prof Xavier Crispin
Chalmers: Prof Paul Gatenholm, Assoc Prof Roland Kádár, Assoc Prof Tiina Nypelö
LTU: Prof Kristiina Oksman, Assoc Prof Shiyu Geng
UmU: Prof Jyri-Pekka Mikkola

Overview of the activities within the program

This program is focused on nanostructural control in various types of biocomposite materials. Two major cellulosic substrates are investigated - wood by itself or nanocellulose in the form of cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC). The program is covering three areas:

1. Wood and nanocellulose substrates for functional biocomposites
2. Processing aspects of nanocellulose biocomposites
3. Functional biocomposites for electronics, energy, photonics and mechanical functions

Nanocellulose materials is a very large international research field including nanocelluloses from a wide variety of plant resources. Important problem areas include those addressing sustainable development issues, interesting chemistry with specific functionalities in mind and scientific problems related to applications. Nypelö at Chalmers (periodate oxidation) and Zhou at KTH (enzymatic nanocellulose oxidation) are both working on new types of nanocellulose.

Wood prepared by top-down chemical treatment is a new nanostructured substrate, enabling many nanotechnology developments. Li and Zhou at KTH are leading two groups developing new ways to control wood substrate nanostructure. Zhou is collaborating with Engquist at LiU on supercapacitors and other devices based on wood, extending the use of wood substrates into the device area. Li is doing mineralization and is also filling the lumen pore space with CNF fibrils to increase specific surface area for new functionalities.

Processing investigations of nanocellulose bicomposites is carried out at Chalmers by Gatenholm (3D-printing for biomedical applications), Kadar (rheo-optical studies) and by Oksman at LTU (melt-processing). Kadar, Oksman, Berglund and Zhou are collaborating in a separate program on biocomposites, where processing aspects are emphasized.

Tybrandt (soft robotics), Stavrinidou (living plant electronics) and Crispin (thermoelectric effects) are working on aspects of organic electronics applied to wood and cellulosic structures. Collaboration with researchers at KTH, Chalmers and Umeå Plant Science Center (Stavrinidou) is essential for these activities.

Biocomposites inspired by plant cuticles (Hedenqvist) for barriers, hybrids between cellulose and mineralized ZnO (Olsson) and between cellulose and platelets (nacre-inspired) are examples of bioinspired composites investigated. Transparent wood (Berglund) does not exist in nature although many sea animals are hydrated gels of high optical transmittance.

WWSC Academy

Persons involved

Paul Gatenholm, professor, Chalmers

Objectives and PhD student training concept

The WWSC Academy is a very important part of the WWSC Program 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 main goal is to provide graduate level, fundamental education within wood materials and science for all WWSC PhD students (32 students graduated in 2018, 30+ students graduated in 2014/15 and 40+students are enrolled since 2019). 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 the fundamentals of Wood Science and Technology but also knowledge of the Forest and the Forest Industry. All schools are combined with site visits.
- All PhD students have to present their research as pitch- and poster presentations twice a year during the WWSC annual workshops. The best presentations receive awards.

2021 activities

During 2021 we organized two Graduate Schools, both virtual. The topic of the Winter School 2021 was: Characterization of Hierarchical Order in Solid and Liquid Wood Derived Systems. The main purpose of this School was to serve as an introduction to the scattering techniques and their use for characterization of hierarchical order in solid and liquid wood-derived systems. The School offered excellent lectures given by experts in the field and virtual visits to ForMAX and MAX IV and Tetra Pak. During the course, PhD students had group exercises which included choice of scattering facility, writing of research proposal according to the appropriate template and presentation. In total, 54 PhD students participated; 46 from WWSC Academy and 8 from Treesearch. The PhD students came from; Chalmers (12), KTH (26), LiU (7), SU (3), LTU (2), UmU (2), and KaU (1).

The topic of the Summer School 2021 was: Biocomposites; Relationship between Processing, Structure and Properties. Among the knowledge objectives were; know the raw materials used in biocomposites, basic concepts for natural fiber biocomposites and nanocomposites, basics of composite micromechanics, principles of processing using thermoset and thermoplastic polymers and cellulose nanomaterials and processing: orientation of latest research developments and scientific challenges and applications. The PhD students learned about important parameters for biocomposites microstructural characterization, mechanical testing, data reduction and analysis of results. This was achieved by group exercises and virtual lab demonstrations. In addition, virtual study visits were carried out at Tetra Pak, RISE SICOMP, ABB, Podcomp and Stora Enso. In total, 51 PhD students participated. The PhD students came from; Chalmers (13), KTH (23), LiU (7), SU (1), LTU (2), UmU (1), MMK (1), MIU (1), SLU (1) and Valmet (1).

Figure1. In 2021 WWSC Academy organized two Graduate School. The Winter School gave an introduction into advanced scattering techniques and the Summer School provided advanced virtual laboratories for processing and evaluation of properties of biocomposites.

Both Schools included extensive project work which ended with group presentations. There were great interactions between PhD students which resulted in very high quality of presentations.

Graduated WWSC PhD students during 2021

Name	University	WWSC Project – thesis title
Johannes Gladisch	LiU	Investigating volume change and ion transport in conjugated polymers
Thai Bui	UmU	Development of nitrogen-containing materials for capture and catalytic conversion of carbon dioxide to value-added chemicals
Pierre Munier	SU	Assembly and alignment in cellulose nanomaterial-based composite dispersions and thermally insulating foams
Varvara Apostolopoulou-Kalkavoura	SU	Thermal Conductivity of Hygroscopic Foams Based on Cellulose Nanomaterials

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