Colloidal Processing and Alignment of Wood-Based Dispersions and Hybrid Functional Foams

Seyed Ehsan Hadi
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Academic dissertation for the Degree of Doctor of Philosophy in Materials Chemistry at Stockholm University to be publicly defended on Friday 12 April 2024 at 13.00 in Magnéli Hall, Kemiska övningslaboratoriet, Svante Arrhenius väg 16 B.

Abstract

This thesis presents novel methods and approaches for designing, preparing/fabricating, and characterizing wood-based nanomaterials. It investigates how modifications in structure, process variables, and composition can enhance functional properties. It employs advanced characterization techniques to analyze process-structure-property relationships and utilizes innovative colloidal processing approaches such as controlled nanoparticle incorporation, Layer-by-Layer self-assembly, and unidirectional ice-templating to improve the functional properties of wood-based nanomaterials.

A novel approach has been developed to fabricate lightweight, highly porous hybrid foams using iron oxide nanoparticles (IONP) and TEMPO-oxidized cellulose nanofibers (TOCNF). The addition of tannic acid (TA) and the application of a magnetic field-enhanced unidirectional ice-templating technique (MFUIT) enhanced processability, mechanical, and magnetic characteristics of the foams. The hybrid foam containing 87% IONPs exhibited a saturation magnetization of 83.2 emu g$^{-1}$, which is equivalent to 95% of the magnetization value observed in bulk magnetite.

Hybrid, anisotropic foams have been prepared by incorporation of reduced graphene oxide (rGO) onto the macropore-walls of anisotropic TOCNF foams using a liquid-phase Layer-by-Layer self-assembly method. These hierarchical rGO-TOCNF foams exhibit lower radial thermal conductivity ($\lambda_r$) across a wide range of relative humidity compared to control TOCNF foams.

The shear-induced orientations and relaxations of multi-component dispersions containing cellulose nanocrystals (CNC) and montmorillonite nanoplatelets (MNT) have been studied by rheological small-angle X-ray scattering (Rheo-SAXS). The addition of MNT resulted in gelation and changes in flow behavior, shear responses, and relaxation dynamics. Rheo-SAXS measurements showed that CNC and MNT aligned under shear, creating aligned structures that relaxed upon shear removal. Gaining insights into shear-induced orientations and relaxation dynamics can aid in the development of advanced wood-based nanocomposite materials.

Transmission Electron Microscopy (TEM) was employed to characterize lignin oleate nanoparticles (OLNPs) derived from abundant lignin waste. TEM analysis revealed that the OLNPs had a spherical shape and a core-shell structure. Upon drying, the particles tended to agglomerate due to the loss of electrostatic repulsion forces. This agglomeration behavior indirectly supports the hypothesis that oleate chains act as a hydration barrier, preventing water permeation into the particles.

Finally, a comprehensive study showed that TEMPO-oxidized lignocellulose nanofibers (TOLCNF)-based foams made from unbleached pulp can be used to prepare anisotropic, light-weight ice-templated foams with high mechanical strength. TOLCNF foams utilize lignin and hemicellulose to enhance properties while require less energy for production compared to TOCNF-based foams. This study emphasizes the potential for developing sustainable wood-based nanomaterials using TOLCNF.

The results presented in this thesis offer valuable insights for further advancements of wood-based nanomaterials.

Keywords: wood-based nanomaterials, process-structure-property relationships, nanocellulose, lignocellulose nanofibers, rheology, small-angle X-ray scattering, lignin, tannic acid, unidirectional ice-templating, foams, aerogels, sustainability.

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Seyed Ehsan Hadi
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Seyed Ehsan Hadi
To whom believed in me through it all and remained Steadfast by my side through thick and thin, Lows and highs, joy and grieving.
Indeed, one day, we will bend the fabric of reality.

Know the outcome and I will show you the journey.

SEH
Abstract

This thesis presents novel methods and approaches for designing, preparing/fabricating, and characterizing wood-based nanomaterials. It investigates how modifications in structure, process variables, and composition can enhance functional properties. It employs advanced characterization techniques to analyze process-structure-property relationships and utilizes innovative colloidal processing approaches such as controlled nanoparticle incorporation, Layer-by-Layer self-assembly, and unidirectional ice-templating to improve the functional properties of wood-based nanomaterials.

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Finally, a comprehensive study showed that TEMPO-oxidized lignocellulose nanofibers (TOLCNF)-based foams made from unbleached pulp can be used to prepare anisotropic, light-weight ice-templated foams with high mechanical strength. TOLCNF foams utilize lignin and hemicellulose to enhance properties while require less energy for production compared to TOCNF-based foams. This study emphasizes the potential for developing sustainable wood-based nanomaterials using TOLCNF.

The results presented in this thesis offer valuable insights for further advancements of wood-based nanomaterials.

**Keywords:** wood-based nanomaterials, process-structure-property relationships, nanocellulose, lignocellulose nanofibers, rheology, small-angle X-ray scattering, lignin, tannic acid, unidirectional ice-templating, foams, aerogels, sustainability.
Sammanfattning

Denna avhandling presenterar nya metoder och tillvägagångssätt för design, beredning/tillverkning och karakterisering av träbaserade nanomaterial. Den undersöker hur förändringar i struktur, processvariabler och sammansättning kan förbättra funktionella egenskaper. Avancerade karaktäriseringstekniker används för att analysera samband mellan process, struktur och egenskaper, och innovativa kolloidala bearbetningsmetoder såsom kontrollerad nanopartikelinkorporering, lager-på-lager-självmontering och unidirektionell is-templering används för att förbättra de funktionella egenskaperna hos träbaserade nanomaterial.

En ny metod har utvecklats för att tillverka lätta, högporösa hybridskum med järnoxidnanopartiklar (IONP) och TEMPO-oxiderade cellulosanano fibrer (TOCNF). Tillsatsen av tanninsyra (TA) och användningen av en magnetfältförstärkt unidirektionell is-templeringsteknik (MFUIT) förbättrade bearbetningsbarheten, de mekaniska egenskaperna och de magnetiska egenskaperna hos skummen. Hybridskummet med 87 % IONP uppvisade en mättnadsmagnetisering på 83,2 emu g⁻¹, vilket motsvarar 95 % av magnetiseringsvärdet hos bulk magnetit.


Skjuvinducerade orienteringar och relaxationer av multikomponentdispersioner innehållande cellulosananokristaller (CNC) och montmorillonitnanoplattor (MNT) har studerats med hjälp av reologisk röntgenstrukturanalys med små vinklar (Rheo-SAXS). Tillsatsen av MNT resulterade i gelbildning och förändringar i flödesbeteende, skjuvresponser och relaxationsdynamik. Rheo-SAXS-mätningar visade att CNC och MNT linjerades upp under skjuvning, vilket skapade linjerade strukturer som slappnade av efter att skjuvningen avlägsnats. Att få insikt i skjuvinducerade orienteringar och relaxationsdynamik kan hjälpa vid utvecklingen av avancerade träbaserade nanokompositmaterial.

Transmissionselektronmikroskopi (TEM) användes för att karakterisera nanopartiklar av ligninoleat (OLNPs) som härstammar från rikligt förekommande ligninavfäll. TEM-analysen visade att OLNPs hade en sfärisk form och en kärna-skal-struktur. Vid torkning tenderade partiklarna att
agglomerera på grund av förlusten av elektrostatiska repulsionskrafter. Denna agglomerationsbeteende stöder indirekt hypotesen att oleatkedjorna fungerar som en hydratiseringsbarriär, vilket förhindrar vatteninträngning i partiklarna.

En omfattande studie visade att skum baserade på TEMPO-oxiderade lignocellulosa nanofibrer (TOLCNF) tillverkade av obelagd massa kan användas för att förbereda anisotropa, lätta is-templaterade skum med hög mekanisk styrka. TOLCNF-skum utnyttjar lignin och hemicellulosa för att förbättra egenskaper samtidigt som de kräver mindre energi för produktion jämfört med TOCNF-baserade skum. Studien betonar potentialen för att utveckla hållbara träbaserade nanomaterial med hjälp av TOLCNF.

Resultaten som presenteras i denna avhandling erbjuder värdefulla insikter för ytterligare framsteg inom träbaserade nanomaterial.

**Nyckelord:** träbaserade nanomaterial, process-struktur-egenskapsrelationer, nanocellulosa, lignocellulosananofibrer, reologi, småvinkelröntgenstrålningsanalyser, lignin, garvsyra, riktad isstruktureringsstrategi, skum, aerogeler, hållbarhet
List of publications

This thesis is based on the following publications.

I. **Highly Magnetic Hybrid Foams Based on Aligned Tannic Acid-Coated Iron Oxide Nanoparticles and TEMPO-Oxidized Cellulose Nanofibers**


**My contribution:** I conceived and developed the study, designed the experiment, optimized the methodology, and performed characterizations (excluding mechanical tests and AFM) and wrote the manuscript.

II. **Reduced Radial Thermal Conductivity in Anisotropic Cellulose Nanofiber Foams by Hierarchical Incorporation of Reduced Graphene Oxide**

*Seyed Ehsan Hadi*, Elias Möller†, Sina Nolte, Agnes Åhl, Olivier Donzel-Gargand, Lennart Bergström, Alexander Holm (Manuscript)

**My contribution:** I contributed to the experimental design, conducted foam characterizations using SEM and BET, and analyzed TOCNF dispersions and contributed in manuscript writing. Upon receiving feedback from reviewers, I revised the manuscript accordingly and prepared the final version for submission.

III. **Rheo-SAXS Study of Shear-Induced Orientation and Relaxation of Cellulose Nanocrystal and Montmorillonite Nanoplatelet Dispersions**


**My contribution:** Pierre Munier designed the experiments, collected the Rheo-SAXS data and prepared a preliminary manuscript. I

\[1 \] † indicating the equal contribution
prepared responses to address the comments provided by the reviewers. I recalculated the results, conducted the rheology analysis, and revised and rewrote the manuscript and prepared the final version of it.

IV. Unravelling the Hydration Barrier of Lignin Oleate Nanoparticles for Acid- and Base-Catalyzed Functionalization in Dispersion State


**My contribution:** I conducted nanoparticle characterization using TEM and contributed in manuscript writing.

V. Comparing the production energy, structure and properties of TEMPO-Oxidized Lignocellulose and Cellulose Nanofibers Foams

Seyed Ehsan Hadi, Saeed Davoodi, Erfan Oliaei, Mohammad Morsali, Agnes Åhl, Elisabetta Nocerino, Fengyang Wang, Matilda Andersson, Malwine Lühder, André L. C Conceição, Mika Sipponen, Lars A. Berglund, Lennart Bergström, Fredrik Lundell. (Manuscript)

**My contribution:** I conceived the study, lead the project, prepared foams, and performed extensive characterizations on dispersions and foams and wrote the draft of the manuscript.
The following publications are not included in the thesis:

VI. **Hybrid Foams based on Multi-Walled Carbon Nanotubes and Cellulose Nanocrystals for Anisotropic Electromagnetic Shielding and Heat Transport**


VII. **Thermally Insulating and Moisture-Resilient Foams Based on Upcycled Aramid Nanofibers and Nanocellulose**

Andi Di, Carina Schiele, Seyed Ehsan Hadi, and Lennart Bergström. *Advanced Materials*, (2023), 2305195

VIII. **A Stiff, Tough, and Thermally Insulating Air- and Ice-Templated Plant-Based Foam**


IX. **Assembly of Cellulose Nanocrystals and Clay Nanoplatelets Studied by Time-Resolved X-Ray Scattering**

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List of abbreviations

3ITT Three interval thixotropy test
AFM Atomic Force Microscopy
BET Brunauer-Emmett-Teller
BJH Barrett-Joyner-Halenda
BTCA Butane Tetracarboxylic Acid
CED Cumulative Energy Demand
CI Crystallinity Index
CNC Cellulose Nanocrystals
CNF Cellulose Nanofibers
Cryo-SEM Cryogenic Scanning Electron Microscopy
D Actual Diameter
DE Degree of Esterification
D_eq Equivalent Diameter
DLS Dynamic Light Scattering
DMSO Dimethyl Sulfoxide
D_r Rotational Diffusion Coefficient
DSC Differential Scanning Calorimetry
EMIS Electromagnetic Interference Shielding
ENZHO Enzymatic Pre-treatment + Homogenization
FIB-SEM Focused Ion Beam Scanning Electron Microscopy
FTIR Fourier Transform Infrared Spectroscopy
GO Negatively Charged Graphene Oxide
GO+ Positively Charged Graphene Oxide
IPDT Integral Procedural Decomposition Temperature
LbL Layer-by-Layer
LCNF Lignocellulose Nanofibers
LNPs Lignin Nanoparticles
MFC Microfibrillated Cellulose
MFLC Microfibrillated Lignocellulose
MFUIT Magnet Field-Enhanced Unidirectional Ice Templating
MNT Montmorillonite Nanoplatelets
MWCNT Multi-Walled Carbon Nanotubes
N_2 Nitrogen
NMR Nuclear Magnetic Resonance
NP Nanoparticles
<table>
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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>OLNPs</td>
<td>Lignin Oleate Nanoparticles</td>
</tr>
<tr>
<td>$\mathbf{P}_2$</td>
<td>Herman’s Orientation Parameter</td>
</tr>
<tr>
<td>$\mathbf{P}_{2,0}$</td>
<td>Herman’s Orientation Parameter at Last Second of Shear</td>
</tr>
<tr>
<td>$\mathbf{P}_{2,ss}$</td>
<td>Steady-State Herman’s Orientation Parameter</td>
</tr>
<tr>
<td>rfc</td>
<td>Relative Centrifugal Force</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced Graphene Oxide</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>Rheo-SAXS</td>
<td>Rheology-Small-Angle X-Ray Scattering</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>Bulk Density</td>
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<tr>
<td>$\rho_r$</td>
<td>Relative Density</td>
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<tr>
<td>$\rho_s$</td>
<td>Skeleton Density</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small-Angle X-Ray Scattering</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SLK</td>
<td>Softwood Kraft Lignin</td>
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<tr>
<td>TA</td>
<td>Tannic Acid</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TOCNF</td>
<td>TEMPO-Oxidized Cellulose Nanofibers</td>
</tr>
<tr>
<td>TOHO</td>
<td>TEMPO-Oxidization + Homogenization</td>
</tr>
<tr>
<td>TOLCNF</td>
<td>TEMPO-Oxidized Lignocellulose Nanofibers</td>
</tr>
<tr>
<td>TOSO</td>
<td>TEMPO-Oxidization + Ultrasonication</td>
</tr>
<tr>
<td>TPS</td>
<td>Transient Plane Source</td>
</tr>
<tr>
<td>UIT</td>
<td>Unidirectional Ice Templating</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>WBNM</td>
<td>Wood-Based Nanomaterials</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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1. Introduction

The optimal selection of materials with properties that make them suitable for specific applications is a challenge. It has also become increasingly important to consider the carbon footprint and environmental impacts, along with their performance under different conditions [1], [2]. Wood-based nanomaterials, e.g., cellulose and lignocellulose nanofibers, cellulose nanocrystals, and lignin nanoparticles, have the potential to be alternatives to petroleum-based materials in material selection [3], [4], [5]. To facilitate and enable wood-based nanomaterials as an alternative to petroleum-based materials, it is necessary to evaluate their renewability, abundance, and performance, and optimize their production efficiency [6], [7], [8]. This is only possible if a holistic approach to material selection, production, process, and usage is applied [9]. Deciphering the process-structure-property relationships in wood-based nanomaterials is essential for controlled manipulation of properties and desired performance [10]. Multiscale characterization of wood-based nanomaterials is critical for determining their physical and chemical properties for processing optimization and enhancing performance under various conditions [11], [12]. As the understanding of the suitability, versatility, and adaptability of wood-based nanomaterials advances, the applications and industrial production of these materials are expected to grow [13], [14], [15].

1.1 Wood-based Nanomaterials: Properties, Applications and Challenges

Wood-based nanomaterials (WBNM), including cellulose nanocrystals (CNC), cellulose and lignocellulose nanofibers (CNF) and (LCNF), and lignin nanoparticles (LNPs), are a class of nanoscale materials derived from wood, offering unique properties (Figure 1) [16], [17].

CNC are rod-like crystalline nanoparticles derived from cellulose fibers through acid hydrolysis with a width of 4–100 nm and a length of 100 nm to almost 1000 nm, depending on the source [18], [19]. As the name indicates, cellulose nanocrystals exhibit high crystallinity, which contributes to their high strength and large surface area. The true density of CNC ranges from 1.5
to 1.6 g cm$^{-3}$, which primarily depends on the degree of crystallinity [20], [21]. CNC are characterized by high surface area, high strength, and the ability for surface modification [22], and have been used in optical and electronic devices, sensors, and biomedical applications [23], [24]. Moreover, due to their low true density and high aspect ratio, they can be used as reinforcing agents in nanocomposites to enhance mechanical properties [25]. However, challenges such as aggregation in non-polar solvents, incompatibility with hydrophobic polymer matrices, and high production costs hamper the use of CNC in many applications [20], [26], [27].

CNF are nanosized cellulose fibers with widths ranging from 2 nm to less than 100 nm and lengths ranging from several hundred nanometers to several micrometers, depending on the production method and source [28], [29], [30]. The true density of CNF ranges from 1.3 to 1.8 g cm$^{-3}$, primarily dependent on their surface functionality [31]. CNF possess very a high aspect ratio and exhibit high flexibility and strength [32], [33]. Furthermore, CNF have been utilized in various domains, including packaging [34], papermaking [35], electronics [36], and biomedical fields [37], [38]. However, challenges associated with CNF include energy-intensive and high-cost production processes [39], [40], hornification during drying [41] and, incompatibility with hydrophobic matrices [42], [43].

Lignin nanoparticles are nanosized particles derived from lignin, with diameters ranging from 5 to 500 nm depending on the preparation method and the type of lignin used [44], [45], [46], [47]. Lignin nanoparticles possess properties such as radical scavenging [48], UV-absorbing [49], and biocompatibility [50], which enable them to be utilized in a range of applications. LNPs have, for example, been used as reinforcing fillers in nanocomposites to enhance mechanical properties [51]. Furthermore, lignin nanoparticles have potential applications in drug delivery and various biomedical applications [52], [53]. However, there are challenges to controlling the size distribution and morphology of lignin nanoparticles during production, as well as their colloidal stability in various solvents and conditions [54], [55], [56], [57].
1.2 Production of Cellulose and Lignocellulose Nanofibers and Lignin Nanoparticles: Methods, Challenges and Energy Demand

1.2.1 Production of CNF

The production of CNF begins with removing lignin and hemicellulose, which are naturally integrated with cellulose fibers in a complex matrix. This delignification process is key as it prepares cellulose for further processing [59], [60], [61], [62]. CNF can be produced mechanically by using high-shear forces to break down fiber bundles into nanoscale fibers, as in high-shear homogenization [29]. However, this technique, without any pretreatments, suffers from high energy input, and low yields. To address these issues, chemical or enzymatic pretreatments can be applied beforehand [63], [64]. In the TEMPO oxidation process, for example, the C6 primary hydroxyl groups on cellulose are selectively converted into carboxylate groups, introducing a negative charge on the surface of the fibers, and facilitating nanofibrillation during the mechanical processing, and increasing the yield [40], [65].
However, chemical methods suffer from hazards such as toxic reagents and waste [66], [67].

Another possible pretreatment is to use enzymes, such as cellulase, to selectively hydrolyze amorphous cellulose regions while preserving crystalline nanofibers and their properties [68]. Enzymatic pretreatment offers an eco-friendly approach to CNF extraction but, currently, suffers from high costs, low yields, and slow kinetics, which limit its industrial-scale production [69]. Combining pretreatments (chemical and enzymatic) with mechanical techniques (homogenizer, ultrasonication) can significantly improve CNF production yield, and lower both the cost and input energy. For instance, the TOHO and TOSO methods oxidize cellulose using TEMPO before mechanical homogenization and ultrasonication, respectively. Similarly, the ENZHO method utilizes enzymatic pretreatment before homogenization [70]. A comparison of different techniques reveals trade-offs between efficacy, scalability, sustainability, product quality, cost and, input energy [70].

1.2.2 Lignocellulose Nanofibers as an Alternative to CNF

Lignocellulose nanofibers (LCNF) is another type of wood-based nanomaterials [71], [72], but unlike CNF, LCNF retain lignin and hemicellulose components in addition to cellulose nanofibers [73] by skipping certain standard steps like delignification and bleaching that are typically used to produce CNF. Skipping these steps lowers the cost, increases the yield, and reduces the environmental impact of LCNF production compared to CNF production [74], [75], [76]. Because of the presence of lignin and hemicellulose in LCNF, these fibers perform differently than CNF. Lower cost of production, lower environmental impact, improved UV-blocking, thermal stability, and antioxidant properties make them a competitive alternative to CNF [74], [75], [76], [77]. However, challenges remain for LCNF related to alteration in the optical properties of LCNF-based materials compared to CNF-based materials [77]. Finally, the choice between LCNF or CNF depends on the desired properties and performance needs for a specific application, the availability of source material and production technology, as well as environmental impact considerations [78].

1.2.3 Lignin Nanoparticles

Lignin nanoparticles can be synthesized using established methods such as solvent-shifting, pH-shifting, as well as enzymatic processes [79]. In the solvent-shifting method, lignin is dissolved in a solvent like tetrahydrofuran (THF) or acetone, and then mixed with water or dimethyl sulfoxide (DMSO), which results in precipitation and formation of nanoparticles [80]. The selection of a solvent system is based on factors like the lignin type, concentration, temperature, and pH of the solution, and desired nanoparticle
properties, e.g., their morphology [80], [81]. Furthermore, the LNPs can also be formed by the pH-shifting method, wherein adjusting the pH, leads to the precipitation of lignin nanoparticles [82]. Moreover, the enzymatic processes involve the use of enzymes such as laccases to form lignin nanoparticles [83], [84]. Each of these production methods has its own advantages and limitations. The choice of synthesis method depends on the desired properties, e.g., morphology and surface charge, and the intended applications of the lignin nanoparticles [85], [86].

1.3 Colloidal Processing and Process-structure-property Relationships in Wood-Based Nanomaterials

Fabricating functional wood-based materials requires a systematic approach to characterization and processing [6], [7]. This involves careful selection of the wood nanomaterial source, detailed analysis to optimize processing conditions, and comprehensive characterization of dispersions using microscopy, scattering, and rheology [87]. Selecting suitable fabrication techniques is crucial, as this dictates the final properties, performance, and functionality [88]. With optimal conditions established, novel wood nanomaterials can be fabricated. Blending with polymers creates nanocomposites that combine the properties of each component [89], [90]. Advanced coating techniques allow the precision deposition of functional layers with tunable properties [56], [91]. 3D printing enables the fabrication of complex, customized structures [92]. Moreover, the ice templating technique provides a well-established approach for fabricating porous materials with controlled structures that possess unique properties such as high surface area, anisotropy, and low relative density [93]. By carefully integrating results from each step using different processing techniques with multiscale characterization approaches, the process-structure-property relationships in WBNM can be deciphered. This knowledge can then be used to design and fabricate novel functional wood-based nanomaterials [87].
1.3.1 Colloidal Stability of Wood-Based Nanomaterials

Colloidal stability in WBNM is critical for their processing, functionality, and performance in applications. Colloidally unstable WBNM aggregate, making processing extremely difficult [7], [95]. WBNM colloidal stability is primarily based on two types of mechanisms: electrostatic and steric interactions. Electrostatic stabilization induces a counterbalance between the attractive van der Waals forces between nanoparticles and repulsive electrostatic (Coulombic) interactions by introducing a surface charge on the nanoparticles. On the other hand, steric stabilization uses steric repulsion from polymers/surfactants to prevent aggregation by providing a solvation barrier. These interactions can be modulated by adjusting the medium's pH, ionic strength, temperature, solvent polarity, and surface chemistry [96], [97], [98].

Surface functionalization of WBNM is the most common strategy for improving their colloidal stability in various mediums [99], [100]. Surface functionalization entails the covalent or non-covalent attachment of functional groups or molecules to the WBNM surface [101]. For example, in the TEMPO oxidation process of CNF, in addition to facilitating mechanical treatment of the fibers, it also increases the colloidal stability of the nanofibers by introducing negatively charged carboxylate groups on them. The electrostatic repulsion between the negatively charged nanofibers makes them hydrophilic and leads to better dispersion [102].
Multiscale characterization involves the use of multiple analytical techniques at different length (and time) scales from nanometer to centimeter. Multiscale characterization provides valuable information that can be interpreted to understand the relationships between the material's process, structure, and properties ultimately facilitating the prediction and rationalization of material's bulk behavior which makes it possible to optimize their performance for targeted applications [103], [104], [105]. Microscopy (atomic force microscopy, scanning electron microscopy, scanning transmission electron microscopy), spectroscopy (Fourier transformed infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance spectroscopy), scattering (X-ray diffraction, small-angle X-ray scattering, dynamic light scattering), and mechanical testing are commonly used in the multiscale characterization of WBNM. Microscopy allows for the nanoscale visualization mapping of WBNM such as nanofibers, as well as their morphology, aspect ratio, and size distribution. Additionally, microscopy enables macroscale visualization of the orientation and the formation of networks within films or porous scaffolds linking aspects such as aspect ratio and morphology to network formation capabilities [106], [107]. Moreover, spectroscopy offers information on intermolecular interactions and helps identify the chemical composition [108], [109], [110]. Scattering techniques can be used to determine the size distribution, aggregation behavior, degree of alignment, and crystallinity of WBNM [111]. Furthermore, Mechanical testing determines the bulk properties as strength, toughness, and stiffness [58]. The connections between nanostructure and macroscale performance in nanomaterials, e.g., WBNM can be deciphered by interconnectedly analyzing and correlating the data obtained from these characterization techniques. This fundamental understanding enables systematically optimizing these materials to achieve the desired properties for specific applications [112], [113]. The complex behavior of wood-based materials at the nanoscale as a result of their complex interactions and dynamics among their components, as well as the influence of processing conditions on the resulting structure and properties of these materials, necessitates multiscale characterization to optimize their performance and functionality [58], [114]. For example, the combination of scanning electron microscopy, and small and wide-angle X-ray scattering could reveal the relationship between nanofiber alignment and microstructure. Furthermore, this method has identified rearrangements in the polymeric chains on a molecular level. Using this information, the improved mechanical properties could be correlated with specific processing conditions [115]. Furthermore, in another study, Fourier transform infrared spectroscopy was used to detect changes in hydrogen bonding caused by crosslinking, which stiffened the structure and was later confirmed through mechanical testing [116].
1.3.3 Directional ice-templating of Anisotropic Lignocellulose and Nanocellulose-Based Aerogels/Foams

Lignocellulose and nanocellulose-based anisotropic aerogels/foams are porous materials possessing anisotropic properties, including thermal conductivity [117], mechanical strength [118], and electromagnetic shielding [119]. These anisotropic aerogels/foams can be produced from lignocellulose and nanocellulose-based nanomaterials, e.g., CNF, LCNF, and CNC [93], [120]. Unidirectional ice templating (UIT) is one of the well-established methods for fabricating anisotropic lignocellulose and nanocellulose-based aerogels/foams (Figure 2A, B) [91]. In UIT, a nanomaterial-containing dispersion is frozen in a controlled, unidirectional manner, typically from the bottom. Subsequently, a freeze-dryer sublimates the frozen foam/aerogel, resulting in the formation of an anisotropic porous structure [121]. Furthermore, UIT enables significant control over the structure of anisotropic lignocellulose and nanocellulose-based aerogels/foams, such as alignment and porosity. This control allows for optimizing the functionality and performance of the foams/aerogels by adjusting various parameters such as freezing rate, freezing direction, nanomaterial concentration, and additive inclusion for specific applications [121], [122], [123].

**Freezing rate:** The freezing rate refers to the rate at which the dispersion is frozen. This parameter influences the size, shape, and distribution of ice crystals, which affect the pore size, shape, and distribution within the resulting aerogels/foams [124], [125].

**Freezing direction:** The freezing direction denotes the orientation in which the dispersion is frozen. This parameter impacts the alignment and orientation of the nanomaterials, consequently influencing the anisotropy and properties of the aerogels/foams. Unidirectional freezing leads to highly aligned nanomaterials and pores, whereas non-unidirectional freezing results in randomly oriented nanomaterials and pores, yielding isotropic foam structures [122], [126].

**Dispersion characteristics:** The properties and concentration of dispersed nanomaterials significantly impact the density, porosity, and mechanical characteristics of the resulting aerogels/foams [93]. Various factors, such as aspect ratio of the nanomaterials, surface functional groups, surface charge, counter ions, and the pH and ionic strength of the dispersion medium, affect the interparticle interactions and lead to significantly different colloidal and viscoelastic behavior [127], [128], [129], [130], [131]. For instance, higher CNF dispersion concentrations enhance fiber-fiber interactions resulting in higher viscosity and the promotion of gel formation [132]. This phenomenon restricts ice crystal growth and alters the ice crystal patterns, ultimately leading to more isotropic structures within the resulting aerogels/foams [133], [134].
Additives: Additionally, the incorporation of additives into lignocellulose and nanocellulose dispersions exerts a notable influence on its viscoelastic properties [135]. These additives not only affect the colloidal and viscoelastic behavior of these dispersions but also play a crucial role in determining the ultimate microstructure and porosity of the lignocellulose and nanocellulose-based aerogels/foams by altering the ice-growing patterns [136]. Additives can form new bonds and change the surface properties of lignocellulose and nanocellulose particles, affecting their interactions with one another and the dispersant, resulting in changes in the overall mechanical and structural properties of the aerogels/foams [137], [138], [139]. As a result, the properties of these aerogels/foams are highly programmable [93]. The optimization of ice templating parameters for lignocellulose and nanocellulose-based aerogels/foams is case-dependent and depends on the desired properties and functionality required for specific applications. For instance, applications necessitating high thermal insulation, such as building materials, may prioritize the fabrication of lignocellulose and nanocellulose-based aerogels/foams with low thermal conductivity [140]. This can be achieved by utilizing the ice-templating technique to fabricate an optimally porous structure, and by incorporating thermally insulating nanofillers into the lignocellulose and nanocellulose scaffold [117]. Moreover, applications demanding high mechanical strength, may focus on fabricating lignocellulose or nanocellulose aerogels/foams with enhanced mechanical properties. This can be accomplished through the use of UIT for their fabrication with an optimized freezing rate and concentration of lignocellulose or nanocellulose and appropriate additives and/or crosslinkers [118]. It is important to note, however, that such enhancements in mechanical properties may come at the cost of higher density in the resultant foams/aerogel indicating the non-existing universal protocol for optimized fabrication of the lignocellulose and nanocellulose-based aerogels/foams.
1.4 Hybrid Nanocellulose-based Nanocomposites with Multifunctional Properties

Hybrid nanocellulose-based nanocomposites are engineered materials that combine nanocellulose as a structural scaffold with various nanoscale fillers such as carbon nanotubes, metal and metal oxide nanoparticles, clays, and organic substances such as tannic acid to achieve multifunctional capabilities [133], [141], [142], [143], [144]. A strategic combination of nanocellulose and specific nanoscale fillers with blending, Layer-by-Layer assembly, coating, and electrospinning results in the formation of nanocomposites with improved electrical, thermal, magnetic, catalytic, and optical properties that vary depending on the nature of the fillers used [133], [141], [145], [146]. For instance, the incorporation of reduced graphene oxide (rGO) and multiwalled carbon nanotubes (MWCNT) can significantly enhance the electrical conductivity and thermal stability of nanocellulose-based nanocomposites, facilitating their use in different applications [147]. Nanoparticles of metal oxides, such as iron oxide, add magnetic characteristics, making the hybrid nanocellulose-based nanocomposites suitable for electromagnetic interference shielding (EMIS) materials and environmental remediation applications (Figure 3) [148], [149], [150], [151], [152]. Incorporating clays into CNF scaffolds can enhance the mechanical properties and flame retardancy of the resulting hybrid nanomaterials [144]. In some cases, fillers may not disperse well within the nanocellulose scaffold due to incompatibilities, which can cause weak filler-matrix bonding [153]. Modification of the surface of the filler, the matrix, or both may be necessary to enhance compatibility [153]. Therefore, using a binding agent is crucial for ensuring satisfactory adhesion between the filler and the matrix. Tannic acid is an example of a binder that has

Figure 3. Illustration of unidirectional ice-templating of a hybrid nanocellulose-based nanocomposite. Adapted from Paper (I) [133] under CC BY license.
been demonstrated to effectively bind metal oxides to the nanocellulose matrix, a task that would otherwise be challenging [133], [154]. The multifunctional properties of these nanocellulose-based foams/aerogels can also be anisotropic and directional, both due to the intrinsic properties of the nanocellulose and through structural control with the UIT fabrication process [133]. For example, cellulose nanofibers have higher thermal conductivity along their crystalline sections than across them [155], [156]. Aligning these nanofibers with UIT produces foams with anisotropic thermal insulating capabilities [157]. Furthermore, the addition of highly anisotropic thermally conductive nanomaterials like rGO to CNF scaffolds as a modification, either pre- or post-foam/aerogel fabrication, can further enhance the thermal anisotropy. These hybrid nanocellulose-based nanocomposites will offer new possibilities for designing advanced thermal management materials [117], [158]. Reduced graphene oxide (rGO) is a sheet-like nanomaterial produced by removing oxygen functional groups from graphene oxide (GO) sheets using chemical, thermal, or electrochemical reduction methods. This causes the rGO to regain most of its reduced electrical conductivity and other graphene-like properties in GO by restoring the sp² carbon network, improving the rGO’s electrical conductivity, strength, and thermal stability compared to GO [159], [160], [161], [162], [163], [164], [165].

1.5 Tannic Acid: A Versatile Compound for Binding and Property Enhancement

Tannic acid (TA), a type of hydrolyzable tannin, is a naturally occurring polyphenolic biomolecule composed of a central glucose molecule with multiple galloyl moieties attached to it (Figure 4a) [166]. This amphiphilic biomolecule with a density of 2.12 g cm⁻³ [133] is water-soluble and slightly acidic due to the presence of numerous phenolic hydroxyls in its structure. The pKₐ of TA is approximately 2.5 to 8.5, depending on the source of the TA and the pH of the dispersion [166]. It can interact with a wide range of materials, including polymers, metal oxides, and nanocellulose networks, via hydrogen bonding, coordinative bonding, and hydrophobic interactions (Figures 4b and 4c). TA readily forms hydrogen bonds with cellulose hydroxyl groups, forming strong nanocellulose networks useful for material development [133], [166], [167], [168], [169]. TA has been successfully utilized to fabricate hybrid nanocellulose-based nanocomposites with multifunctional properties. A study found that incorporating TA into gelatin-crafted nanocellulose films improved their wet strength. Furthermore, the UV-blocking and antioxidant properties of the TA-containing gelatin-crafted nanocellulose films were enhanced [143]. Furthermore, in another study, tannic acid was used to crosslink CNF-bPGEI foams inspired by insect cuticle sclerotization, making those foams moisture-resistant and strong [170].
Figure 4. Tannic acid and its interactions. (a) Structure of tannic acid; TA can be found in many plant sources such as oak trees, grape seeds and gallnuts [169], [171]. (b) Illustration of the interaction between tannic acid and TEMPO-oxidized cellulose nanofibrils (TOCNF) through electrostatic interactions and hydrogen bonding. The carboxyl and hydroxyl groups on the TOCNF surface interact with the hydroxyl groups on tannic acid (R~TA). (c) Interaction of tannic acid with metal ions (e.g., iron ions) through coordination bonds, where the phenolic hydroxyl groups of tannic acid bind to and complex the metal ions (R~TA).
1.6 Scope of the Thesis

This thesis explores the process-structure-property relationships in various wood-based nanomaterials with the aim of improving their properties and incorporating additional functionalities.

To accomplish these goals, a range of techniques, including colloidal processing, surface modification, Layer-by-Layer self-assembly, and unidirectional ice-templating, were employed. These techniques were used to fabricate wood-based nanomaterials with diverse structures and properties. Furthermore, characterization techniques such as rheology-small angle X-ray scattering (Rheo-SAXS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) were utilized to investigate the morphology, alignment, and interactions of the wood-based nanomaterials. Additionally, various tests and measurements have been conducted to evaluate the mechanical, thermal, magnetic, and functional properties of wood-based nanomaterials.

This thesis includes a variety of wood-based nanomaterials, including TEMPO-oxidized cellulose nanofibers (TOCNF), TEMPO-oxidized lignocellulose nanofibers (TOLCNF), cellulose nanocrystals (CNC), and lignin oleate nanoparticles (OLNPs), as well as inorganic and organic nanomaterials such as montmorillonite nanoplatelets (MNT), iron oxide nanoparticles (IONP), tannic acid (TA), and reduced graphene oxide nanosheets (rGO).

Furthermore, this thesis provides examples of wood-based nanomaterials suitable for applications that require properties such as low density, magnetic responsiveness, thermal insulation, thermal and colloidal stability, and mechanical compression resistance.

Lastly, this thesis can serve as a valuable reference for future studies in the field of sustainable materials and nanotechnology, particularly in the development of wood-based nanomaterials.
2. Preparation and Characterization of Materials

2.1 Preparation of Dispersions

2.1.1 Preparation of TEMPO-oxidized CNF (TOCNF) (Papers (I) and (II))

The preparation of TOCNF (for Papers (I) and (II)) was conducted using a well-established method [172]. TEMPO-oxidized cellulose nanofibers (TOCNF) were prepared from sulfite softwood dissolving pulp obtained from Domsjö Fabriken in Sweden. The pulp was washed by vacuum filtration until the filtrate conductivity was <5 μS cm^{-1}. 40 g dry pulp was suspended in 1.87 L water, with 0.64 g TEMPO and 4 g NaBr added. The pH was adjusted to 10 with NaOH then oxidation was initiated by adding 60 mmol sodium hypochlorite solution gradually, maintaining pH 10. After oxidation, the pulp was washed by filtration until filtrate conductivity was <5 μS cm^{-1}. TOCNF was obtained by passing the oxidized pulp through a microfluidizer at 1600 bar, with successive cycles through 200 μm and 100 μm chambers.

2.1.2 Preparation of TEMPO-oxidized CNF and LCNF (TOCNF and TOLCNF) (Paper (V))

Dispersions of TOCNF and TOLCNF were prepared from never-dried bleached and unbleached softwood thermomechanical pulps (provided by RISE Research Institute of Sweden) using a well-established method [173], [174], [175]. The pulps were subjected to 2000 PFI mill revolutions to improve fiber modification. To disperse, pulps were stirred at 500 rpm for 30 min and rinsed repeatedly with 0.01 M HCl by vacuum filtration, then washed with DI water until filtrate conductivity was <5 μS cm^{-1}. Bleached and unbleached pulps were then oxidized via TEMPO-mediated reactions to make CNFs and LCNFs. For each, a mixture of 30 g dry-weight washed pulp, 0.48 g TEMPO, 3 g NaBr and, DI water at pH 10 was prepared. Oxidation was triggered by adding 120 mmol NaOCl dropwise under stirring and pH 10. After 60 min for CNF and 75 min for LCNF, pulps were washed thoroughly...
with DI water by filtration. Aqueous dispersions at 1 g L\(^{-1}\) were passed through a Microfluidics M-110EH Microfluidizer twice at 400/200 μm and twice at 200/100 μm to obtain TOCNF and TOLCNF. Conductometric titration gave surface charge densities around 928 and 983 mequiv g\(^{-1}\) respectively.

2.1.3 Preparation of IONP/TA Dispersion (Paper (I))
In Paper (I), the preparation of a homogeneous dispersion of iron oxide nanoparticles (IONP) and tannic acid (TA) was carried out following a standard procedure. In a 6 mL water solution, 82.5 mg of TA, along with the specified amount of IONP, and 1 mL of 0.1 M NaOH were added. The resulting mixture was sonicated using a Sonics VCX-130 sonicator from the USA, equipped with a 6 mm probe. The sonication process was performed at an intensity of 75% for a duration of 30 minutes, ensuring the formation of a uniform IONP/TA dispersion. For the (1:0.5:1) dispersion, 165 mg of IONP was used. In the case of the (10:0.5:1) dispersion, a higher amount of IONP, specifically 1650 mg, was employed. These different amounts of IONP were utilized to achieve the desired ratios and properties of the respective dispersions in Paper (I).

2.1.4 Preparation of Mixed TOCNF and IONP or IONP/TA Dispersions (Paper (I))
In Paper (I), for the IONP/TOCNF dispersion, a specified amount of IONP (165 mg) or TA/IONP (ratios mentioned in 2.1.3) was mixed with 16.5 g of TOCNF stock dispersion (1 wt%) at a pH of 7. Similarly, for the IONP/TA/TOCNF dispersion, the specified amount of TA/IONP was mixed with 16.5 g of TOCNF stock dispersion (1 wt%) at a pH of 7. After the mixing step, water was added to the resulting dispersions to dilute them to a TOCNF concentration of 0.5 wt%. Subsequently, the dispersions were vigorously vortexted for 30 minutes to ensure thorough mixing and homogeneity.

2.1.5 Preparation of GO+ (Paper (II))
In Paper (II), the synthesis of GO+ was performed by modifying a previously established protocol for amine functionalization [176]. Purification of GO was done by repeated centrifugation (Fiberlite F15-8x50cy rotor in a Sorvall Lynx 6000 centrifuge, Thermo Fisher Scientific) to remove small and unexfoliated sheets. The GO suspension was centrifuged at 22,800 rcf for 20 min, the supernatant was removed, and sediment was redispersed in water. This was repeated 3 times. The suspension was then centrifuged at 1,050 rcf for 10 min,
retaining the supernatant as the GO stock. To produce GO+, water and b-PEI were mixed in a flask. The pH was adjusted to 11.5 with NaOH solution. GO stock was added and stirred for 40 min. HCl solution was introduced to lower the pH to 1, precipitating GO+. The GO+ was purified by centrifuging at 22,800 relative centrifugal force (rcf) for 5 min and redispersion in water. This was repeated 3 times. Finally, GO+ was redispersed in water at 0.5 mg mL$^{-1}$. The final GO+ stock dispersion had a pH of 7. It exhibited a zeta potential of $+35 \pm 5$ mV, indicating successful attachment of b-PEI to GO and colloidal stability of the resulting GO+.

2.1.6 Preparation of CNC-only, MNT-only and CNC:MNT Dispersions (Paper (III))

For Paper (III), to prepare the dispersions, the CNC and MNT powders were individually dispersed in deionized water under mechanical stirring. The resulting dispersions had concentrations of approximately 4 wt% for CNC and 1.6 wt% for MNT. The MNT dispersion underwent high-shear mixing using an Ultra Turrax™ apparatus and was subsequently dialyzed against ultrapure (Milli-Q) water for a duration of 7 days. Cellulosic tubular membranes from Sigma-Aldrich, with a molecular weight cut-off of 14,000 Da, were utilized for the dialysis process. After dialysis, the sediment was discarded. If necessary, the concentrations of the aqueous dispersions were adjusted by removing water through evaporation. To obtain CNC:MNT composite dispersions (MNT-only 2.5 wt%, CNC 3.6 wt% : MNT 2.5 wt% and CNC-only 3.6 wt%), the desired amounts of the CNC and MNT dispersions were mixed using magnetic stirring, supplemented with vortex mixing and/or Ultra Turrax™ mixing as needed.

2.1.7 Preparation of Lignin Nanoparticles (LNPs and OLNPs) and Lignin-oleic Acid Esters (Lig-Ol) (Paper (IV))

All lignin nanoparticles used in Paper (IV) were synthesized by a solvent exchange method adapted from a well-established method [177]. Lignin-oleic acid esters were dissolved in THF/water or acetone/water mixtures, and then slowly mixed with water to induce nanoparticle precipitation. The dispersions were purified by filtration, rotary evaporation, and dialysis. This yielded aqueous dispersions of oleic acid lignin nanoparticles (OLNPs), THF lignin nanoparticles (LNPs$_{THF}$), and acetone lignin nanoparticles (LNPs$_{Acetone}$) at concentrations of 1-4 g/L, with lignin mass yields of 83-87%. Lignin-oleic acid esters like Lig-OI$_{80}$ were synthesized by reacting lignin with oleoyl chloride in THF/DMF using pyridine as a catalyst (N$_2$ atmosphere, 40°C, 15h). The product was washed, concentrated and vacuum dried to yield 78% Lig-
The degree of esterification (DE) was quantified by $^{31}$P NMR by comparing hydroxyl groups before and after the reaction.

2.1.8 Preparation of TOLCNF and TOCNF Dispersion (Paper (V))

In paper (V), the dispersions of TOCNF and TOLCNF were prepared by diluting predetermined quantities of TOCNF and TOLCNF from their original stock solutions (see 2.1.2) to achieve approximate concentrations of 0.5 wt% and 0.75 wt%, respectively. The pH of the mixtures was adjusted to 7 by the addition of NaOH. Following pH adjustment, the dispersions were vigorously vortexed for a duration of 30 minutes.

2.1.9 Preparation of TOLCNF/TA Dispersion (Paper (V))

In paper (V), the preparation of the TOLCNF/TA dispersion involved mixing precise amounts of TOLCNF and TA to attain a final weight percentage of approximately 0.75 wt% for TOLCNF and 0.25 wt% for TA. The pH of the mixture was adjusted to 7 by the addition of NaOH. Subsequently, the dispersion was vigorously vortexed for a duration of 30 minutes.

2.2 Preparation of Foams

2.2.1 Preparation of Foams (Papers (I), (II), and (V))

In Papers (I) and (V), several types of foams, including TOCNF, TOCNF/TA, TOLCNF, TOLCNF/TA, IONP/TA/TOCNF, and IONP/TOCNF, were prepared through the process of unidirectional ice-templating (UIT) of their respective aqueous dispersions. The preparation process involved the following steps: First, 5 g of freshly vortexed dispersions were poured into a cylindrical Teflon mold. This mold measured 2 cm in diameter and 2 cm in height and was sealed with a removable copper bottom plate. For the TOCNF, TOCNF/TA, TOLCNF, and TOLCNF/TA foams, the mold containing the samples was positioned atop a chilled plate set at a constant temperature of $-120^\circ$C to ensure uniform and controlled directional freezing of the dispersions.

For the preparation of the IONP/TA/TOCNF and IONP/TOCNF foams, two methods were utilized. The first method involved conventional UIT, similar to the process used for the other foams. The second method, however, involved...
magnetic field-enhanced UIT (MFUIT). In this method, a directional and homogeneous magnetic field (with a strength of 35 mT at the center of the mold) was applied to the sample-holding mold using two identical magnets. This magnetic field was maintained while a directional thermal gradient was applied by placing the mold on dry ice at a temperature of -78.5 °C. For all the foams, after the complete freezing of the dispersions, they were carefully removed from the mold. Finally, the frozen dispersions underwent freeze-drying for a minimum of 48 hours using an Alpha 1-2 LDplus freeze dryer (CHRIST, Germany) to obtain the dry foams.

In Paper (II), the anisotropic TOCNF foams were produced by adapting previous protocols [122], [178], [179]. A 5 mg mL\(^{-1}\) CNF suspension was mixed at 10,000 rpm for 2 min. BTCA (9 wt%) and SHP (4 wt%) were added as crosslinkers and mixed for 8 min at pH 7. The suspension was degassed and cooled to 0°C. For directional freeze-casting, the suspension was poured into a Teflon mold on a −135°C copper plate and frozen for 60 min. To open axial macropores, 16 mm, and 2 mm were filed from the bottom and top of the frozen foams, respectively. The frozen foams were freeze-dried for 5 days at 0.045 mbar. Finally, foams were crosslinked at 170°C for 10 min.

2.2.2 GO+ and GO Self-assembly in Anisotropic TOCNF Foams (Paper (II))

In Paper (II), GO+ and GO dispersions (0.08 mg mL\(^{-1}\)) were prepared in 5:1 methanol:water by diluting aqueous stocks with methanol and sonicating for 3 hours. For impregnation, CNF foams were affixed to a Styrofoam plate and soaked dropwise, first with pure methanol, then with methanol:water mixtures of increasing water content. After soaking in 5:1 methanol:water, GO+ then GO dispersions were added. Methanol:water mixtures of decreasing water content were then added until pure methanol. Finally, foams were dried at 55°C for 20 hours. Control CNF foams were impregnated similarly but without GO+ or GO addition. One batch of native CNF foams was used for both rGO-CNF and CNF control foams.

2.2.3 Reduction of GO+/GO – TOCNF foams to rGO – TOCNF foams (Paper (II))

In Paper (II), a protocol from Moon et al. was adapted for the vapor reduction of GO+ / GO thin films within anisotropic TOCNF foams [180]. For that, acetic acid and hydroiodic acid were mixed in a desiccator. The foams were
quickly added onto a desiccator stage, avoiding contact with the acid mixture. The desiccator was sealed and placed at 40°C for 23 hours. The foams were then transferred to an oven at 55°C for 23 hours to remove residual vapor. After treatment, the GO+/GO-CNF foams turned black, forming rGO-CNF foams. CNF control foams underwent the same treatment as the rGO-CNF foams.

2.3 Characterization Methods

2.3.1 Scanning Electron Microscopy (SEM)
Scanning Electron Microscopy (SEM) was employed in Papers (I), (II), and (V) to investigate various structures and distributions. Papers (I), (II), and (V) all utilized a tabletop TM 3000 (Hitachi High Tech, Japan) device, equipped with a backscattered electron detector and operating at a 15-kV accelerating voltage, to study the overall structure of the foams. Further investigation in Paper (I) involved analyzing the distribution of IONP on the foam walls. This process was conducted using a JSM-7400F (JEOL Ltd, Japan) SEM, equipped with a secondary electron detector and operating at a 15-kV accelerating voltage. In Papers (I) and (V), the foams were sectioned both horizontally and vertically while still frozen.

Statistics:
In Paper (II) and (V) ImageJ software was used to quantify pore sizes of the foams. The areas of 100 individual pores from each foam sample were measured using ImageJ. To convert the irregular pore area measurements into an equivalent and representative numerical value, the measured pore areas were converted to equivalent circle diameters.

2.3.2 Cryo-Scanning Electron Microscopy (Cryo-SEM)
Cryo-SEM was performed using a JEOL IT800 with Leica EM VCT500 for sample preparation and transfer. Small sections (~5 mm cubes) of the foam were fractured under vacuum to expose an internal surface and etched by sublimation at −95°C for 3 min to remove contamination. Uncoated samples were imaged at −150°C with a 5-kV beam to view the internal microstructure. Multiple areas were imaged to characterize overall foam morphology and pore structure before freeze-drying.
2.3.3 Transmission Electron Microscopy (TEM)

In all papers except Paper (II), Transmission Electron Microscopy (TEM) was used to obtain images of the dispersions and assemblies. The process for sample preparation was consistent across all these papers. A small quantity of each dispersion, at a concentration of 0.005% (for Paper (IV), colloidal dispersions of LNPs and OLNPs diluted by a factor of 1:40), was deposited onto a carbon-coated copper TEM grid (01840, Ted Pella Inc.). The grid was then treated with PELCO easiGlow™ for 60 seconds to render the carbon film hydrophilic and remove any residues. Any excess liquid was blotted off with filter paper, and the grid was allowed to air-dry for 10 minutes.

The difference between the studies lies in the specific TEM devices used and their operating conditions. For Paper (V), images were captured using a Themis Z (Thermo Fisher Scientific, USA) operating at an acceleration voltage of 300 kV. The captured images were then processed using GATAN DigitalMicrograph® software with a BM-one view camera. On the other hand, for Papers (I), (III), and (IV), a JEM-2100F (JEOL Ltd, Japan) was used, operating at a lower acceleration voltage of 200 kV.

Statistics:

In Paper (I), TEM images of 20 particles were analyzed to ascertain the average size of the IONP. In Paper (III), MNT platelets were characterized in terms of their average diameter. This was determined based on counts from 50 irregularly shaped, disk-like particles. In Paper (V), TOCNF and TOLCNF diameters were statistically analyzed using ImageJ. The assessment was based on examining 50 individual nanofibers.

2.3.4 Atomic Force Microscopy (AFM)

AFM was employed in Papers (I), (II), (III), and (V) to image TOCNF, TOLCNF, CNC, and GO/GO+. In Papers (I), (II), (III), TOCNF and CNC were imaged using a Bruker Multimode-8 AFM in peak-force tapping mode with ScanAsyst. A 0.005% dispersion droplet was deposited on mica and air-dried. In Paper (II), GO/GO+ was imaged by depositing a droplet of dilute GO/GO+ in 5:1 methanol:water on SiO₂. In Paper (V), a 0.005% dispersion droplet was spin-coated on mica and air-dried.

Statistics:

In Paper (I), the average length of TOCNF was determined from AFM micrographs of 50 particles based on the height of nanofibers. In Paper (II), image statistics were generated for 10 GO and 10 GO+ sheets (for height and
roughness) as well as 100 TOCNF fibers (for average length and height). Paper (III) involved evaluating the average diameter and length of CNC particles based on measurements from 50-100 particles.

In Paper (V), to account for AFM artifacts like fiber flattening during drying and tip convolution, an equivalent diameter \( D_{eq} \) was calculated assuming half-elliptical flattened fibers using Equation 1:

\[
D_{eq} = \sqrt{hw'}
\]

where \( h \) is height and \( w' \) is the AFM-measured width (including tip convolution) (Figure 5). This analysis for Paper (V) was done for 50 fibers to provide a better approximation of the true diameter compared to using just the height or width values from AFM.

\[ h < D \leq D_{eq} = \sqrt{hw'} < w' \]

**Figure 5. Illustration of the method used to calculate the equivalent diameter \( D_{eq} \) of nanofibers in Paper (V).** The AFM-measured height \( h \) and width \( w' \) of a flattened nanofiber are used to estimate \( D_{eq} \) assuming a half-elliptical shape, accounting for the flattening of nanofibers during drying. \( D_{eq} \) is equal to or larger than the actual diameter \( D \) based on the degree of tip convolution. Adapted from Paper (V).

### 2.3.5 Surface Charge Assessment of Dispersions

The charged surface groups of CNC, TOCNF, and TOLCNF in Papers (I), (II), (III), and (V) were quantified using conductometric titration. In Paper (III), manual titrations were done using a Mettler Toledo setup with conductivity and pH electrodes. The CNC required pre-treatment with an ion exchange resin to remove impurities and convert sulfate half-esters to the acid form. For titration, CNC was introduced into a 1 mM NaCl solution and titrated with 1.23 mM NaOH. The OH- neutralized protons on charged groups, decreasing conductivity. The equivalent volume allowed calculation of sulfate half-ester content in mmol g\(^{-1}\) (Equation 2) and %S (Equation 3) [181], [182].
\[
X = \frac{C_{OH} \times V_{eq}}{m} \\
\%
S = \frac{C_{OH} \times V_{eq} \times M_W \left( S \right)}{m \times C}
\]

(2)  
(3)

In Papers (I), (II), and (V), to determine the carboxylic content in TOCNF (and TOLCNF) the pH was first lowered using hydrochloric acid, taking advantage of the weak acidity of carboxylic acids (pKa 3-4). Then sodium hydroxide was added until the pH exceeded 11. From the equivalent volume, the carboxyl content in millimoles per gram of cellulose was calculated [183].

2.3.6 Zeta Potential Measurement of Dispersions

In Papers (I), (II), (III), (IV), and (V), the zeta potential of the dispersions was measured using a Zetasizer Nano ZS90 instrument equipped with a dip cell probe and/or disposable cuvettes. Three measurements were taken for each sample and averaged. The final results are reported as the mean value ± standard deviation (reported by the Zetasizer software). In Paper (IV), additional zeta potential measurements were done in a 9 mM phosphate buffer to study the effect of the electrolyte in the dispersion.

2.3.7 Rheological Properties of Dispersions

The rheological properties of dispersions were studied in Papers (I), (III), and (V) using a Physica MCR 301 rheometer (Anton Paar GmbH, Austria). All tests were conducted at 25°C.

In Paper (I), a concentric cylinder geometry (CC27, 27 mm diameter) was used. Samples were pre-sheared at 1000 s\(^{-1}\) for 2 minutes before measurements. Amplitude sweep tests were done at 10 rad s\(^{-1}\) while the frequency sweep tests were conducted at 0.1% strain. Three-interval thixotropy tests (3ITT) were performed at shear rates of 10 s\(^{-1}\) (120 s), 1000 s\(^{-1}\) (30 s) and 10 s\(^{-1}\) (600 s). Recovered viscosity was measured 30 s after a high shear interval. Additionally, ramp-up and flow curves of dispersions were measured from 0.01 s\(^{-1}\) to 1000 s\(^{-1}\).

In Paper (III), a concentric cylinder geometry (CC27/T200/SS, 27 mm diameter, 1.13 mm gap) was used. Moreover, ramp-up and flow curves of dispersions were measured from 0.01 s\(^{-1}\) to 1000 s\(^{-1}\). Amplitude sweep tests were done at 1 rad s\(^{-1}\) while the frequency sweep tests were conducted at 3 % strain.
In Paper (V), a cone-plate system (CP25-2) was used. Amplitude sweep tests were done at 10 rad s$^{-1}$ while the frequency sweep tests were conducted at 0.5 \% strain. 3ITT were performed similarly to Paper (I). The linear viscoelastic region limit was set at 1\% drop in $G'$. Additionally, ramp-up and ramp-down flow curves were measured from 0.01 s$^{-1}$ to 1000 s$^{-1}$ and vice versa.

### 2.3.8 LCNF Composition Assessment

In Paper (V), the unbleached pulp sample was analyzed using standardized methods. It was extracted with acetone (SCAN-CM 49:03) and the extract was evaporated, weighed, and hydrolyzed (SCAN-CM 71:09). Monosaccharides were quantified by ion chromatography with pulsed amperometric detection. The acid-insoluble residue was determined gravimetrically (TAPPI T222 om-11) and the acid-soluble residue by UV spectroscopy at 205nm (TAPPI UM 250), using water as a blank. The lignin content was calculated as the sum of the acid-soluble and insoluble residues. Standardized procedures were followed throughout the pulp characterization to ensure consistent and reliable results.

### 2.3.9 Fourier-Transform Infrared Spectroscopy (FT-IR)

Fourier-transform infrared spectroscopy (FT-IR) was utilized in Papers (I), (IV), and (V) to analyze samples using a Varian 610-IR FTIR spectrometer. Measurements were performed with a resolution of 2 cm$^{-1}$ across a wavelength range of 450–4000 cm$^{-1}$. Samples were tested in their dry powder and foam physical form for Papers (I), (IV), and (V), respectively.

### 2.3.10 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted on foams in Papers (I) and (V) using a Discovery TG instrument from TA Instruments (USA).

In Paper (I), the foams were prepared for TGA by cutting into ~2 mg pieces and placing in platinum pans. The analysis was carried out under nitrogen atmosphere (20 mL min$^{-1}$) with a temperature ramp from room temperature to 600°C at 10°C min$^{-1}$. The thermal data was recorded using TA Universal Analysis software and processed with Origin Pro to determine foam thermal stability through calculation of integral process decomposition temperature (IPDT) values using provided Equations 4 to 6 [184], [185]:

\[
IPDT (°C) = A^* K^* (T_f - T_i) + T_i \tag{4}
\]
In Paper (V), high-resolution TGA was conducted on the foams under argon atmosphere (20 mL min\(^{-1}\)). Prior to heating, samples were purged isothermally (at room temperature) to remove residual oxygen. The TGA instrument resolution was set to 4, and each sample was analyzed in triplicate to ensure accuracy and reliability. The data was processed and analyzed using the same software as in Paper (I).

\[ A^* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (5) \]

\[ K^* = \frac{S_1 + S_2}{S_1} \quad (6) \]

2.3.11 Differential Scanning Calorimetry (DSC)

In Paper (II) the specific heat capacity (\(C_P\)) of foams at different relative humidity levels (RH) was estimated by differential scanning calorimetry (DSC), using a Mettler Toledo 820 calorimeter under nitrogen atmosphere. 10 mg samples were loaded in an aluminum crucible with a pierced lid and dried at 105 °C for 24 hours, then heated from −20 °C to 50 °C at 10 K min\(^{-1}\). \(C_P\) at each RH was then estimated using the measured moisture uptake (\(w_{H_2O}\)) and the rule of mixtures (Equation 7).

\[ C_{P, wet} = (1 - w_{H_2O}) C_{P, dry} + C_{P, H_2O} w_{H_2O} \quad (7) \]

where, \(w_{H_2O}\) is the weight fraction of absorbed water, \(C_{P, dry}\) is the \(C_P\) of dry foam, and \(C_{P, H_2O}\) is the \(C_P\) of water.

2.3.12 Water Uptake Assessment of Foams

In Papers (II), (V), the foams were placed on a precision balance (BP 210 S, Sartorius) inside a humidity chamber (CLIMACELL 111 - EVO line) to measure the weight as a function of relative humidity (RH) at different levels (20%, 35%, 50%, 65%, 80%). This allowed the determination of the RH-dependent weight fraction of water (\(w_{H_2O}\)) absorbed by the foams. The foams were allowed to equilibrate at each RH level for 6 hours to ensure steady-state water sorption was reached before recording the weight.

In Paper (II), the dry weight of the foams was found by weighing them after drying at 105°C to remove all moisture. While, in Paper (V), the dry mass was
determined by weighing the foams inside a glovebox that maintained a water vapor concentration of 14 ppm. Prior to weighing, the foams were subjected to a vacuum for a duration of 3 hours inside the glovebox to remove the remaining moisture.

2.3.13 Small Angle X-ray Scattering and Rheo-SAXS Analysis

In Paper (III), for Rheo-Small Angle X-ray Scattering (Rheo-SAXS) experiments, aqueous dispersions (1.2 mL) were loaded into an Anton Paar MCR 501 rheometer with a polycarbonate concentric cylinder setup (bob/cup diameter 10 mm, gap 0.5 mm). The dispersions underwent rotational shearing while being exposed to 12 keV X-rays (beam size 388 x 8.1 μm²) at the SWING beamline, Synchrotron Soleil. SAXS data (q=0.00154 to 0.31702 Å⁻¹) were collected using an EigerX4M detector (pixel size 75 x 75 μm²) under vacuum at 3.5 m distance, at 1 frame s⁻¹. This allowed simultaneous rheological measurements and time-resolved SAXS characterization of the sheared dispersions.

In Paper (V), SAXS measurements were performed on TOCNF, TOLCNF, and TOLCNF/TA foams at PETRA III (DESY) using 0.124 nm X-rays with a scattering angle from 0.01° to 2.5°. The detector distance was 3.5 m. Samples in an aluminum chamber were exposed for 1.1 s per humidity point (11 x 100 ms frames). Humidity was controlled with an MHG32 generator. Fibers were oriented perpendicular to the beam. Measurements were taken at 10% RH (30 min equilibration) and 80% RH (30 min equilibration after increasing from 10% RH).

In Paper (III), Herman’s orientation parameters, denoted as $P_2$, were computed by fitting curves using Equations 8 to 10. This process was performed after the normalization of the intensity function $I(\phi)$ using Equations 8:

$$\int_0^{\pi/2} I(\phi) \sin(\phi) d(\phi) = 1$$  \hspace{1cm} (8)

$$I(\phi) \approx \sum_{n=0}^5 a_n P_{2n}(\cos\phi)$$  \hspace{1cm} (9)

$$P_2 = \frac{a_1}{5}$$  \hspace{1cm} (10)
where, $\phi$ represents the azimuthal angle (the integration variable), and $I(\phi)$ is the corresponding intensity. This intensity is fitted to a series expansion of even Legendre polynomials, denoted as $P_{2n}$, with $a_n$ symbolizing their respective coefficients (the fitting parameters). Upon normalizing the intensities such that $a_0$ equals 1, the orientation parameter, $\overline{P}_2$, is derived from the $a_1$ coefficient. In Paper (III), the degree of particle orientation was calculated by shifting the $\phi$ value by $-90$ degrees. This adjustment results in a $\overline{P}_2$ range between 0 and 1. In this range, a value of 0 corresponds to random orientation, while a value of 1 signifies perfect orientation of all the particles in the direction of flow.

In Paper (V), the averaged orientation index of samples was determined in the method section using intensity distribution profiles and azimuthal integration [186]. Equation 11 was used to calculate the orientation index:

$$f_c = \frac{180 - \text{FWHM}}{180}$$  \hspace{1cm} (11)

The FWHM (Full Width at Half Maximum) of the azimuthal integration was used as the input parameter in Equation 11. The resulting $f_c$ value ranged between 0 and 1, where a value of 0 represented an isotropic structure, while a value of 1 indicated a fully anisotropic structure.

2.3.14 Determination of The Rotational Diffusion Coefficient ($D_r$)

The rate at which Herman's orientation parameter diminished was calculated and then used to determine the rotational diffusion coefficient ($D_r$) of the rod-like particles, as outlined in Equation 12.

$$\overline{P}_2(t) = (\overline{P}_{2,0} - \overline{P}_{2,ss}) \exp \left( -6 D_r \cdot t \right) + \overline{P}_{2,ss}$$  \hspace{1cm} (12)

Where $\overline{P}_{2,0}$ is Herman’s orientation parameter at the last second of shear and $\overline{P}_{2,ss}$ is the steady-state Herman’s orientation parameter.

2.3.15 Thermal Conductivity Measurements of Foams

In Paper (III), the thermal conductivities ($\lambda_a$ and $\lambda_c$) of rGO-CNf foams and CNF control foams were measured using a TPS 2500 S Hot Disk Thermal Constant Analyzer. The measurements were performed in anisotropic mode with a Kapton transient plane sensor sandwiched between two cylindrical
foam samples. Measurements were taken at five different RH levels, with each level tested five times at 15-minute intervals. The chamber temperature was maintained at 295 K throughout the measurements. A heating power of 10 mW and a measurement time of 10 seconds were used for each measurement. The wet specific heat capacity and density of the foams at each RH condition were determined separately. Three pairs of foam samples per material were tested, and the Hot Disk software was used to calculate the thermal conductivities, accounting for the wet specific heat capacity and density of the foams at each RH condition.

Statistics:
In Paper (III), t-tests were performed to compare the thermal conductivity of rGO-CNF foams and CNF control foams. Specifically, two types of t-tests were used: a two-sided, paired t-test was used to judge the significance of the difference in radial thermal conductivity between rGO-CNF foams and CNF control foams. Additionally, a paired t-test was used to judge the significance of the difference in axial thermal conductivity between the two types of foams. The tests were conducted at different relative humidity (RH) levels to assess the impact of moisture on thermal conductivity. The null hypothesis for both tests was that there is no significant difference in thermal conductivity between rGO-CNF foams and CNF control foams. The alternative hypothesis was that there was a significant difference in thermal conductivity between the two types of foams. The level of significance was set at 0.05 for all tests.

2.3.16 Mechanical Compression Test of Foams
In Papers (I) and (V), the mechanical performance of the foams was evaluated through compression tests conducted using an Instron 5966 universal testing machine from Instron, USA, which was equipped with a 100 N load cell. Prior to conducting the tests, all foams underwent a conditioning period of at least 24 hours at a temperature of 23 °C and a relative humidity of 40%. The dimensions of the foams were measured using a digital caliper, and their moist weight was determined using an analytical balance. The bulk density of both the moist foams was calculated prior to the testing (see 2.3.17). To ensure proper contact between the sample and the platens, a preload of 0.1 N was applied. During the compression tests, a strain rate of 10% per minute was uniformly applied to all the samples. The slope of the initial linear segment of the stress-strain curve was calculated to determine Young's modulus. Additionally, the toughness of the foams was determined by calculating the
area under the stress-strain curve up to 70% displacement. The collected data were processed and analyzed using Bluehill® Universal software.

Statistics:
For each sample, four measurements were taken, and the average results, along with one standard deviation, were reported.

2.3.17 Density and Porosity of Foams
In Paper (I), the bulk density ($\rho_b$) of the moist foams was calculated using their wet mass divided by their volume (Equation 13).

In Paper (II), the $\rho_b$ of the dry foam was determined by measuring the dry weight of the foams by their volume (Equation 13).

In Paper (V), to determine the skeleton density ($\rho_s$) of each foam, the true densities of their constituent materials were averaged based on their respective proportions, as outlined in Equation 14. The true density of TOCNF was estimated using the findings of Diacho et al. [31]. The true densities of lignin, hemicellulose, and tannic acid were obtained from Wypych et al. [187], Kellogg et al. [188], and Hadi et al. [133], respectively. The bulk density ($\rho_b$) of the foams was calculated by dividing their dry mass by their volume, as indicated in Equation 13. Moreover, the relative density ($\rho_r$) was determined by dividing the bulk density by the skeleton density, following Equation 15. Additionally, the porosity of the foams was calculated using Equation 16.

\[
\rho_b = \frac{m}{v} \quad (13)
\]
\[
\rho_s = \sum_{i=1}^{n} \rho_i \times w_i \quad (14)
\]
\[
\rho_r = \frac{\rho_b}{\rho_s} \quad (15)
\]
\[
Porosity(\%) = (1 - \rho_r) \times 100 \quad (16)
\]

2.3.18 X-Ray Diffraction (XRD) Analysis
In Papers (I), (III), and (V), X-ray diffraction (XRD) analysis was performed using a Panalytical X'PERT PRO X-ray diffractometer. The diffractograms of
MNT and IONP obtained from both studies were compared with an existing database in order to determine the chemical formulas of the respective materials.

In Paper V, the Crystallinity Index (CI) of these samples was estimated using the Segal method, as expressed in Equation 17. This method bases the calculation on the peaks corresponding to the crystalline (2θ=22–23) and amorphous phases (2θ=18–19) of cellulose.

\[
CI(\%) = \frac{I_{200} \times I_{Amp}}{I_{200}} \times 100
\]

(17)

2.3.19 Specific Surface Area Assessment

In Paper (I), the specific surface area of IONP and in Paper (II), the specific surface area of the rGO – CNF foams and CNF control foams was determined using the Brunauer-Emmett-Teller (BET) analysis of nitrogen adsorption/desorption isotherms. Moreover, the pore size distributions of the samples were assessed by Barrett-Joyner-Halenda (BJH) analysis of the nitrogen adsorption/desorption isotherms. The measurements were carried out at a temperature of −196 °C using a Micrometrics ASAP 2020 instrument (Micromeritics Instrument Corporation). Prior to analysis, the samples were degassed under vacuum at 105°C for 12 hours.
3. Results and Discussion

This chapter contains a summary of the main results from the appended five papers on wood-based nanomaterials. The results and discussion are divided into three main focus areas, each investigating different aspects of wood-based nanomaterials.

**Focus 1: Dispersion Properties of Wood-Based Nanomaterials**
The dispersion characteristics of wood nanomaterials are examined, including colloidal stability, particle size distribution, surface chemistry, and rheological behavior. The importance of surface functionalization is highlighted. The analysis aims to provide not only insights into dispersion properties but also to enable understanding of particle interactions in multicomponent wood-based nanomaterials.

**Focus 2: Process-structure-property Relationships and Multi-Scale Characterization in Wood-Based Nanomaterials**
The relationships between fabrication processes, nano- and microstructures formed, and resultant wood-based nanomaterial properties are analyzed for several different wood-based nanomaterials.

**Focus 3: Performance Evaluation of Wood-Based Nanomaterials**
The performance of wood-based nanomaterials, mainly mechanical strength, thermal conductivity, and saturation magnetization, and additional properties such as thermal stability have been examined. The evaluation also includes an examination of the materials’ durability under various conditions, e.g., different humidity levels, which provides valuable insight into their real-world performance.
3.1 (Paper I), Highly Magnetic Hybrid Foams Based on Aligned Tannic Acid-Coated Iron Oxide Nanoparticles And TEMPO-Oxidized Cellulose Nanofibers

During the production of CNF-based magnetic foams, one of the key challenges encountered is the prevention of aggregation of uncoated iron oxide nanoparticles (IONP). This issue becomes particularly pronounced when the foams incorporate high concentrations of IONP. If not adequately addressed, this aggregation can lead to a deterioration in both the mechanical strength and magnetic characteristics of the resultant foams [189], [190].

In Paper (I), the significance of surface chemistry is highlighted, with a focus on using TA to coat IONP for improved dispersion and processability. This facilitates the incorporation of a large amount of IONP into the TOCNF scaffold, resulting in the fabrication of lightweight, highly magnetic anisotropic TOCNF-based foams.

3.1.1 Preparation and Characterization of Dispersions

The TOCNF had an average length of 460 ± 208 nm, surface charge of 1.1 mmol g⁻¹ and zeta potential of −50 ± 5 mV at pH 7 and 25 °C indicating their colloidal stability. To incorporate IONP into the TOCNF scaffold, colloidally stable IONP is essential. The IONP used had an average size of 195 nm ± 11 nm and exhibited insufficient colloidal stability with a zeta potential of approximately −20 mV ± 2 mV. To improve stability, tannic acid was added to the IONP dispersion, coating them and reducing the zeta potential to approximately −38 mV at pH 7. Tannic acid provided two key advantages: hydrogen bonding with TOCNF as a binder, and interacting with IONP by binding surface defects [154], [168], [169], [191], [192]. Through these mechanisms, tannic acid enhanced IONP colloidal stability while enabling binding to TOCNF, making it an ideal intermediary compound. The successful interaction between IONP and tannic acid was confirmed through various analyses, including TEM images of TA@IONP, FTIR of TA@IONP, and a decrease in the zeta potential. The efficacy of coating IONP with tannic acid was assessed using nitrogen adsorption/desorption isotherms and TEM. The bare IONP exhibited a BET (Brunauer-Emmett-Teller) surface area approximately 26% higher than the theoretical surface area, indicating inherent porosity and the potential of tannic acid to fill pores and form a layer.

The coating of IONP with TA (TA@IONP) was confirmed via TEM, FTIR, and zeta potential analysis. A decrease in zeta potential from −20 mV to −38 mV, a visible TA layer on IONP in TEM images, and the appearance of new FTIR peaks at 1176 cm⁻¹ and 1452 cm⁻¹, all validated the TA@IONP
formation, as shown in Figure 6a-b. Coating efficiency was evaluated using nitrogen adsorption/desorption and TEM, revealing that BET surface area of the bare IONP was 26% above theoretical, suggesting ability of tannic acid to fill pores and create a coating layer. TEM analysis determined the tannic acid coating to be approximately 5 nm thick. The tannic acid needed to coat different IONP concentrations was greater than initially added, indicating potential coating of cellulose nanofibers in the dispersion. This insight helped correlate the data with the viscoelastic properties of dispersions.

In Paper (I), the study examined the viscoelastic properties of three dispersions: TOCNF-only (D(0:0:1)), TOCNF combined with tannic acid and 40 wt% IONP (D(1:0:5:1)), and TOCNF with tannic acid and a higher IONP concentration of 87% (D(10:0:5:1)). It is crucial to mention that prior to conducting measurements, each dispersion was subjected to intense vortexing for 5 minutes to mimic processing conditions. This information provides valuable insights into the dispersion state during processing, which can later be linked to possible relationships between dispersion properties, post-processing structure, and final properties of products.

Figure 7a displays the ramp-up flow curves for the three samples, indicating shear thinning behavior. At high shear rates (100 s$^{-1}$ and higher), the viscosity of IONP-containing samples is reduced compared to the TOCNF-only dispersion, suggesting that IONP disturbs the gel network at such rates, facilitating flow. On the other hand, at lower shear rates, the dispersion with the greatest IONP content, D(10:0:5:1), shows increased viscosity, implying that IONP enhances gelation at low shear rate. This observation was further explored using amplitude sweep test, which verified that IONP promotes gelation (Figure 7c); the crossover strain for D(10:0:5:1) was greater than for D(1:0:5:1), whereas the TOCNF dispersion remained predominantly liquid.

![Figure 6](image-url)  
*Figure 6. (a) TEM image of TA@IONP showing the TA coating. FTIR spectra of TA, IONP, and TA@IONP. Adapted from Paper (I) [133] under CC BY license.*
throughout the test. Frequency sweep test revealed that both D(10:0.5:1) and D(1:0.5:1) have a weak gel-like behavior at low angular frequencies and undergo crossover at high angular frequencies. Notably, the crossover frequency for D(10:0.5:1) was higher, signifying a more robust gel network, as shown in Figure 7b. Insights into the recovery rate of the dispersions were obtained through the 3ITT (Figure 7d). The results revealed that TOCNF recovers much faster than the other dispersions, with a complete recovery time of 153 seconds compared to 387 seconds for D(10:0.5:1). This suggests that TOCNF fibers have less restriction and higher repulsion, enabling them to reorient more rapidly. These valuable insights will inform discussions on the ice-templating process of the dispersion.

Figure 7. Viscoelastic property of dispersions. a) ramp-up flow curves. b) the frequency sweep test c) the amplitude sweep test and d) 3ITT of dispersions. Adapted from Paper (I) [133] under CC BY license.

Following the insights gained in the previous section, a preliminary processing condition can be formulated. These findings will be used to create a protocol for incorporating IONP into the TOCNF scaffold. Furthermore, multi-scale characterization enables process optimization by improving our understanding of the process-structure-property relationships.
3.1.2 Characterization and Performance Evaluation of Highly Magnetic Anisotropic Foams

The anisotropic foams were fabricated using both UIT and MFUIT. SEM images (Figure 8) revealed aligned pore channels, indicating the successful formation of foams with anisotropic columnar structure for both of techniques. This observation suggests that the macroscopic anisotropic structures are predominantly dictated by the directional growth of ice crystals [193].

Comparing the foams created with bare IONP to those with TA-coated IONP, notable differences in the distribution of nanoparticles within the foam structure were observed. Bare IONP foams exhibited large aggregates on the pore walls, indicating a lack of dispersion and agglomeration of the nanoparticles. In contrast, the TA-coated IONP were more uniformly distributed in a layer along the walls, suggesting that the TA coating played a crucial role in enhancing the colloidal stability of the IONP and preventing aggregation during the process (Figures 9a and 9c).
To improve the distribution of IONP, magnetic field-enhanced ice-templating (MFUIT) was used. Applying a 35 mT field during freezing aligned the TA-coated IONP into chains spanning the pore walls, seen in SEM images (Figures 9b, 9d).

The density of the fabricated foams varied from 12.4 to 56.1 mg cm\(^{-3}\), directly correlating with the IONP content, which ranged from 40 to 87 wt%. The increased loading of IONP had a positive impact on the mechanical and thermal properties of the foams. The Young's modulus of the foams increased by 80%, from 500 to 900 kPa, indicating enhanced structural reinforcement with higher IONP content. The toughness of the foams also improved further highlighting the structural benefits (Figure 10). The foams containing the highest IONP concentration of 87 wt% (FUIT and FMFUIT 10:0.5:1) exhibited a surprising resilience, recovering from 14% axial compression without permanent deformation. This suggests that even minimal quantities of TOCNF are sufficient to impart a degree of flexibility and structural integrity to the hybrid foams, allowing for recovery after compressive stress.
The foams exhibited narrow hysteresis with minimal coercivity and remanence as shown in Figure 11a. As the IONP concentration rose, the saturation magnetization also increased, aligning with earlier research findings. Compared to UIT foams, MFUIT foams showed greater saturation magnetization values and a small increase in both remanence and coercivity, probably because of the magnetic field-induced spin alignment during the MFUIT process [194]. The F_{MFUIT} foam with 87 wt% IONP exhibited a saturation magnetization of 83.2 emu g$^{-1}$, reaching 95% of that of bulk magnetite (Figure 11b) [195].

Figure 10. Compressive behavior of foams. a) all four regions of elastic, uniform and non-uniform deformation and densification are color-coded for clarity. b) the compressive stress-strain curves of foams. Adapted from Paper (I) [133] under CC BY license.

Figure 11. Magnetic characteristics of the foams. a) Magnetic hysteresis loops of foams b) Saturation magnetization of similar foams with density below 200 mg cm$^{-3}$. Adapted from Paper (I) [133] under CC BY license.
3.2 (Paper II) Hierarchical Incorporation of Reduced Graphene Oxide into Anisotropic Cellulose Nanofiber Foams reduces their Radial Thermal Conductivity

Anisotropic CNF foams show promise for thermal insulation due to their uniaxially aligned macropores and mesoporous pore walls, which result in low radial thermal conductivity [179], [196]. Further reductions in axial and radial conductivity may be possible with an innovative approach, resulting in the fabrication of the next generation of anisotropic hybrid CNF-based foams. Paper (II) focuses on improving the thermal insulation properties of anisotropic TOCNF foams by incorporating reduced graphene oxide (rGO) within the foam walls using a liquid-phase Layer-by-Layer (LbL) self-assembly technique. The exceptional thermal properties of rGO, specifically its anisotropic thermal conduction characteristics, are utilized with the aim of enhancing thermal insulation while also showcasing a versatile post-production modification strategy for TOCNF foams. Surface chemistry plays a crucial role in this process with an emphasizes the importance of colloidal stability, where graphene oxide layers are deposited within the TOCNF foam walls and later reduced to r-GO in a separate step.

3.2.1 Preparation and Characterization of Dispersions

The TOCNF used in Paper (II) had a charge of 0.56 mmol g\(^{-1}\), with diameters ranging from 1 to 3 nm and lengths ranging from hundreds of nanometers to several micrometers. Previous studies have shown that negatively charged graphene oxide (GO) monolayer films can be assembled onto positively charged surfaces using LbL deposition [197]. As a result, GO can be assembled on the walls of negatively charged TOCNF foam if GO’s surface is modified to have positive charges. Therefore, positively charged GO (GO+) was prepared by attaching branched polyethyleneimine (b-PEI) to GO. bPEI modifies GO covalently nucleophilic addition to epoxides (Figure 12b) [198]. Zeta potential measurements showed GO in water at pH 7 had a charge of \(-35 \text{ mV} \pm 9 \text{ mV}\), while after attaching b-PEI to GO (GO+), the positively charged GO had a charge of \(+35 \text{ mV} \pm 5 \text{ mV}\), indicating successful attachment of b-PEI to GO. Furthermore, the AFM images of the GO compared to the GO+ show a change in average height (from 0.9 ± 0.1 nm to 2.1 ± 0.2 nm). This increase in height provides visual evidence that the bPEI was attached to the surface of the GO.
3.2.2 Liquid-phase LbL Self-assembly of GO+/GO Within the TOCNF Foam Walls

TOCNF foams were fabricated using UIT technique (Figure 12b). For the post-modification of the foams, using a LbL self-assembly technique, it was crucial for the foams be water resilient. To achieve this, butane tetracarboxylic acid (BTCA) was utilized as a crosslinking agent for the foams (Figure 12b) [170], [178]. After fabricating the anisotropic native CNF foams preparing the dispersions of GO+, using the first method, the GO+/GO aqueous dispersion was then directly added dropwise to the top of the foams before they were dried at 95°C while affixed to a Styrofoam plate using needles along the perimeter of the foams to minimize the shrinkage and collapse of the foam structure during drying. However, this method caused destruction of the foam structure due to drying stresses from water evaporation.

To overcome this issue, a 5:1 methanol:water solvent system was used to reduce the surface tension. The dispersibility and colloidal stability of the TOCNF, GO and GO+ were investigated in the new 5:1 methanol:water solvent system using zeta potential measurements. The zeta potential values obtained were +24 mV ± 8 mV for TOCNF, −25 mV ± 8 mV for GO, and −23 mV ± 2.2 mV for GO+. The zeta potential values obtained indicated colloidal
stability and dispersion of the nanomaterials in the methanol-rich solvent, making layer-by-layer assembly feasible. The second method to deposit the GO+ within the TOCNF foams wall involved first adding pure methanol and then gradually increasing the water volume fraction to 5:1 methanol:water. GO+ dispersed in 5:1 methanol:water was then added to the foam, after which the water volume fraction was gradually decreased back to pure methanol with the same steps. Similarly, the foams were affixed to a Styrofoam plate using needles along the perimeter (Figure 12c) and then, however dried at lower temperature of 55°C. It was expected that utilizing methanol, with its lower surface tension of 20 mN m\(^{-1}\) at 55°C [199] compared to water’s 60 mN m\(^{-1}\) at 95°C [200], would help preserve the foam structure during drying. This emphasizes the importance of processing conditions such as preparation and drying on the final structure of the resulting foams. After the assembly of the GO+ (of which is black) within the foam walls the color of the foams visibly darkened indicating the presence of the GO+ on the walls (Figure 12c). To isolate the effects of the LbL assembly of GO+ on structure and properties, a control foam (TOCNF-control foam) was prepared which underwent all fabrication steps except impregnation with GO+. Finally, the GO+ and GO film was reduced to rGO using hydroiodic acid/acetic acid vapor, yielding rGO-TOCNF foams [180].

3.2.3 Characterization of TOCNF-control and rGO-TOCNF Foams

The structure of the foams was further analyzed using focused ion beam scanning electron microscopy (FIB-SEM) and SEM. As shown in Figure 13, the images clearly demonstrate that the second method successfully assembled rGO within the foam walls while preserving the anisotropic structure in both the rGO-TOCNF and TOCNF-control foams. These results clearly demonstrate the effect of the processing conditions on the structure and properties of the TOCNF-based foams. Observation of the FIB-SEM images of the rGO-TOCNF foam walls reveals the presence of a mostly percolated, discontinuous film of rGO. However, this rGO film is absent in the walls of the TOCNF-control foams, as expected. Additionally, the TOCNF-control foams suffer from charge-up, which are not observed in the rGO-TOCNF foam wall. This observation suggests that the film observed in the rGO-TOCNF foam is a conductive film of rGO [201]. The density, specific heat capacity, macropore size, BET surface area, and mesoporosity of the rGO-TOCNF foams and TOCNF-control foams were found to be very similar. For instance, the bulk density of the dry foams was 11.0 and 11.1 g cm\(^{-3}\) for rGO-TOCNF and TOCNF control foams, respectively.
3.2.4 Thermal Insulation Performance of the Foams

The thermal conductivity of the foams was evaluated under different humidity levels (20%, 35%, 50%, and 80% RH) in both the radial and axial directions utilizing the transient plane source (TPS) method [202], [203] with a custom-designed humidity control chamber. The thermal conductivities were found to exhibit anisotropy, with the ratio of axial thermal conductivity ($\lambda_a$) to radial thermal conductivity ($\lambda_r$) ranging from 1.6 to 2.8. Both the rGO-TOCNF and TOCNF-control foams displayed a monotonic increase in $\lambda_a$ as relative humidity increased as previously been observed [118], [170], [193]. However, the difference between the values of $\lambda_a$ for both the rGO-TOCNF and TOCNF-control foams was not significant and fell within the experimental error range.
On the other hand, the values of $\lambda_r$ were consistently lower for the rGO-TOCNF foams compared to the TOCNF-control foams at all relative humidity levels (Figure 14B). This indicates that the rGO-TOCNF foams have a lower radial thermal conductivity than the TOCNF-control foams. Given the similarities in other properties between the foams, the presence of uniaxially aligned rGO is most likely the primary factor contributing to the observed thermal conductivity difference [179], [204], [205].

Three mechanisms have been proposed to explain the reduction in radial thermal conductivity observed in the rGO-TOCNF foams compared to TOCNF-control foams (Figure 14C):

(i), due to the highly anisotropic nature of the r-GO the phonon transport is more efficient in-plane (along the film) than cross-plane (across the film) therefore, rGO may convert radial energy components to axially aligned phonons [204], [205], [206], [207], [208], [209].
radiative heat transfer can contribute significantly in insulating foams. Moreover, CNF likely allows unsuppressed radial radiative conduction. rGO is known to strongly absorb infrared radiation, converting photons to phonons. This could suppress radial radiative heat transfer while transporting heat axially, reducing overall radial conductivity [204], [210], [211], [212], [213], [214].

Phonon scattering at interfaces is known to limit thermal conductivity in nanomaterials. The rGO-TOCNF interfaces likely have higher thermal boundary resistance than CNF-CNF interfaces. Therefore, more interfacial scattering could reduce radial conductivity [193], [215], [216], [217], [218].

While mechanisms (i) and (ii) would be expected to increase $\lambda_a$, as mentioned earlier, the experimental $\lambda_a$ shows no clear increase within the error bars (Figure 14A). A small increase in $\lambda_a$ is within the larger experimental deviations in measuring $\lambda_a$, making it impossible to draw conclusions about changes in $\lambda_a$. It is also worth noting that the changes in $\lambda_r$ when comparing CNF-native foams ($\lambda_r \approx 14–28 \text{ mW m}^{-1}\text{ K}^{-1}$) [179], [193] and TOCNF-control foams ($29–45 \text{ mW m}^{-1}\text{ K}^{-1}$) indicate presumed partial CNF rearrangement and densification during processing, which may enable more efficient radial conduction and increase intrinsic $\lambda_r$. That said, it can be concluded that to better utilize rGO, process methods are needed that can incorporate it without disturbing the native foam microstructure. This highlights the importance of the relationship between processing, structure, and properties.
3.3 (Paper III) Rheo-SAXS Study of Shear-Induced Orientation and Relaxation of Cellulose Nanocrystal and Montmorillonite Nanoplatelet Dispersions

Understanding the rheological behavior and the impact of shear on the structure is crucial for refining shear-dependent processing methods. The orientation and relaxation induced by shear can be examined by combining rheological tests with light, neutron, or small-angle X-ray scattering techniques, such as Rheo-SAXS. While the shear-induced alignment of pure CNC and MNT dispersions has been previously explored, the behavior of CNC mixed with other nanoparticles under shear has yet to be documented [219], [220], [221], [222], [223], [224].

In Paper (III), the study analyzed how shear forces and particle interactions affect alignment and orientation of wood-based nanomaterials, using Rheo-SAXS to simultaneously apply shear and monitor nanoscale assembly and orientation. This provided insights into how external factors and surface chemistry influence colloidal stability and dispersion properties during processing. This information is essential for comprehending and optimizing processing conditions.

3.3.1 Preparation and Characterization of the CNC-only and CNC:MNT Dispersions

In Paper (III), negatively charged sulfate half-ester CNCs were identified with dimensions of $173 \pm 41$ nm in length and $4.3 \pm 0.8$ nm in thickness, leading to an aspect ratio of ~40. They had a charge density of $314 \, \mu$mol g$^{-1}$ and a zeta potential between $-40$ and $-60$ mV. Chiral nematic domains, which form at about 3.5 wt%, [182] prompted the use of a slightly higher 3.6 wt% concentration in the CNC dispersion to explore the effect of domain formation on particle alignment under shear stress. Additionally, the study utilized MNTs with a uniform thickness of approximately 1 nm [225] and a $122 \pm 65$ nm average diameter, exhibiting a $-35 \pm 1$ mV zeta potential at a pH of 9.
3.3.2 Rheo-SAXS Analysis: In-situ Monitoring of Shear-induced Alignment

The experimental protocol as depicted in Figure 15c for the dispersions in the beamline is detailed as follows:

(i) pre-shear at 0.1 s\(^{-1}\) for 1 min to ensure consistent starting conditions.
(ii) incremental shearing from 1 s\(^{-1}\) to 1000 s\(^{-1}\), with 1 min shear and 5 min 0.1 s\(^{-1}\) relaxation between each step, to study alignment and dispersion under increasing shear.
(iii) final relaxation after 1000 s\(^{-1}\) shear to study relaxation time after high shear stress.

This methodology aims to elucidate dispersion responses to varied shear environments, informing on rheology and particle orientation and relaxation.
dynamics. SAXS data analysis involved radial and azimuthal integration. Radial integration (Figure 16a) revealed a significant structural peak for CNC-containing dispersions between 0.01 and 0.03 Å\(^{-1}\) scattering vectors, with minor shear rate influence on CNC peaks and a shift in CNC:MNT peaks to higher q values under shear. These peaks returned to initial states during relaxation, suggesting temporary shear-dependent structures. Orientation was quantified using azimuthal integration, with Herman's parameter ranging from 0 (no orientation) to 1 (full alignment). The CNC particles demonstrated alignment during shear, as depicted in Figure 16b.

Figure 16. SAXS patterns and particle orientation with shear. (a) Radial integration of SAXS patterns for CNC-only, CNC:MNT composite, and MNT-only dispersions under 1000 s\(^{-1}\) shear. Inset: 2D SAXS pattern for CNC-only at q = 0.0132 Å\(^{-1}\). (b) Azimuthal integration of SAXS patterns for 3.6 wt% CNC-only at varied shear rates. Insets: Calculated Herman's orientation parameter values. Adapted from Paper (III) ref. [226] under CC BY license.

Figure 16b illustrates a direct relationship between the shear rate and Herman's orientation parameter, indicating that orientation intensifies with increasing shear [220]. Figure 17a shows the azimuthal integration of SAXS data for a 3.6 wt% CNC dispersion after cessation of 1000 s\(^{-1}\) shear, revealing a decrease in peak intensity over time, which signals a decline in particle alignment. This aligns with the falling Herman's orientation parameter values during the relaxation phase, allowing the monitoring of the CNC orientation's return to equilibrium. Figure 17b charts the Herman's orientation parameter values for three dispersions immediately after the shear halts at 1000 s\(^{-1}\). The parameter's decline explained the relaxation behavior in terms of speed and extent. Notably, during relaxation, a minor continuous shear was applied, suggesting an eventual stabilization of Herman's orientation parameter value. For the CNC-only dispersion, a constant Herman's orientation parameter of 0.24 was reached in 20 seconds. Conversely, the MNT-only dispersion quickly achieved a Herman's orientation parameter of zero in 3 seconds, indicating a
swift reorientation of both CNC and MNT particles post-shear. The CNC:MNT blend displayed a slower return to equilibrium, failing to reach a constant Herman's orientation parameter within 300 seconds, suggesting a prolonged orientation in the mixed system after shearing. By fitting the obtained results, the $D_r$ values for both the CNC-only and CNC:MNT mixture were calculated. The $D_r$ value for 3.6 wt% CNC-only was $0.048 \pm 0.004 \text{ rad}^2 \text{s}^{-1}$. However, the relaxation of CNC orientation in CNC:MNT composites was strongly retarded and partially quenched in a way that estimated $D_{r,\text{slow}}$ for the CNC 3.6 wt% + MNT 2.5 wt% composite was $(8.0 \pm 0.6) \times 10^{-5} \text{ rad}^2 \text{s}^{-1}$. This shows presence of MNT particles hindered CNC relaxation.

Figure 17. Relaxation dynamics of shear-aligned particles. (a) Azimuthal integration of SAXS patterns for 3.6 wt% CNC-only at $q = 0.0131-0.0133 \text{ Å}^{-1}$ during relaxation after 1000 s$^{-1}$ shear. (b) Herman's orientation parameter values over time for CNC-only, MNT-only, and CNC:MNT composites during relaxation. Dashed lines show exponential decay model fits. Relaxation onset at $t = 1 \text{s}$, immediately after cessation of shear. Adapted from Paper (III) ref. [226] under CC BY license.

Figure 18. Rheological characteristics of CNC-only and CNC:MNT composite dispersions. (a) ramp-up flow curve of both CNC-only and CNC:MNT composite dispersions b) frequency sweep test of CNC-only and CNC:MNT composite dispersions. Adapted from Paper (III) ref. [226] under CC BY license.
Rheological analysis corroborated the SAXS findings, verifying that MNT inclusion promotes gelation in the dispersions. During shear rate escalation (ramp-up), all dispersions exhibited shear-thinning properties indicated by a declining viscosity trend in Figure 18a, attributed to anisotropic particles orienting with the flow [227]. The CNC:MNT composite displayed a consistently higher viscosity than the CNC-only dispersion across all examined shear rates. Notably, the low-shear viscosity of the 3.6 wt% CNC and 2.5 wt% MNT mixture was significantly elevated relative to the single-component CNC or MNT dispersions. Frequency sweep test (Figure 18b) revealed that the composite exhibited more solid-like characteristics, in contrast to the CNC-only dispersion, which behaved more like a liquid with a clear crossover frequency. The data suggest that MNT contributes to gel structure formation, likely due to the electrostatic attractions between MNT's positively charged edges and the negatively charged surfaces of CNC particles [228].
3.4 (Paper IV) Unravelling the Hydration Barrier of Lignin Oleate Nanoparticles for Acid-and Base-Catalyzed Functionalization in Dispersion State

The instability of LNPs within environments of low (pH < 2.5) and high (pH > 10) pH detrimentally affects their processing, functionalization, and utility in practical scenarios as evidenced by references [229], [230], [231], [232], [233]. Although strategies like covalent internal cross-linking of LNPs have been explored [84], [234], [235], there remains a substantial demand for robust methodologies that ensure the stabilization of LNPs, thereby facilitating their functionalization across a range of pH conditions.

Paper (IV) presents oleic lignin nanoparticles (OLNPs) with unprecedented stability in acidic and alkaline conditions. The esterification degree (DE) of lignin with oleic acid controlled OLNPs stability, enabling acid- and base-catalyzed surface reactions directly in dispersion. The enhanced adaptability of OLNPs creates new possibilities as functional wood-based nanomaterials, such as for anticorrosive coatings.

3.4.1 Preparation and Characterization of the Dispersions

As depicted in Figure 19_1, lignin-oleic acid esters were synthesized through the base-mediated esterification of softwood Kraft lignin (SLK) with oleoyl chloride. By using different molar ratio of oleoyl chloride, the degree of esterification (DE) was controlled, yielding values between 18% and 81% (Lig-Oh_{20}, Lig-Oh_{50}, and Lig-Oh_{80}). The successful esterification process was verified through FTIR and $^{31}$P NMR analysis. FTIR results showed a decrease in the intensity of the hydroxyl stretching O-H band at 3400 cm$^{-1}$ and an increase in the intensity of the alkyl chain band in the range of 2920–2840 cm$^{-1}$ indicating a successful esterification process. The DE was capped at around 80%, beyond which the large spatial demands of the oleoyl chloride molecules acted as a steric blockade, preventing complete (100%) esterification of the available hydroxyl sites.
OLNPs were synthesized using solvent exchange precipitation of lignin-oleic acid esters (Lig-OI_{20-80}) adapted from an established method (Figure 19_2) [236]. DLS analysis of the dispersions revealed negligible variation in particle size across the three OLNPs samples. However, when comparing LNPs with OLNPs, because hydrophobic oleic fatty acid chains are located within the inner part of the particle during the precipitation or self-assembly process, a substantial difference in particle size was observed, as presented in Figure 20b. Despite the varying DE, which corresponds to a higher quantity of hydrophobic fatty acid chains, the particle size remained constant. This indicates that the particle formation is largely dictated by the intrinsic properties of the lignin molecules, e.g., their molecular size and solubility. Consequently, the stable nanoparticles tend to form with hydrophobic cores that include lignin molecules of a higher molecular weight, while the surfaces are more hydrophilic, made up of smaller lignin molecules [237]. The lower molecular weight fraction of lignin forms the charged shell of OLNPs, containing abundant carboxylic acid and phenolic hydroxyl groups [237], [238], [239]. During nanoparticle formation, amphiphilic lignin oleate molecules likely arrange with carboxylic groups facing outward towards water. Meanwhile, hydrophobic oleate chains collapse inwards, reducing exposure to water. This creates charged OLNPs surfaces, with oleate chains as a hydration barrier restricting water penetration into the core. As the surface of the nanoparticles are modified it was expected that their interaction with light
would also change. The brown color intensity in digital images (Figure 20c) decreases as DE increases, most likely because of a decrease in π-π interactions between the aromatic rings of lignin as a result of conformational changes during esterification. This is further supported by the nonlinear decrease in UV absorbance [240]. This makes it possible to modify these wood-based nanomaterials to match consumer preferences in color for products like paints and sunscreens [241], [242], [243].

### 3.4.2 Evaluation of Colloidal Stability of OLNPs Under Extreme Conditions

To validate the presence of a core-shell structure, electron microscopy was employed to examine the morphology of the nanoparticles. Figure 20f shows the SEM images of the spherical, uniform OLNPs. Moreover, Figure 20d-e shows TEM images of LNPs and OLNPs. Based on the TEM micrographs, it can be inferred that OLNPs indeed possess a core-shell structure. The observed adhesive nature of the shells and their tendency to aggregate upon drying indicate that the oleate chains reside on the particle surfaces, where electrostatic repulsion becomes less effective.

**Figure 20. Characterization of lignin-oleic acid esters and OLNPs:** a) FTIR spectra of dispersions. b) Size distribution and charge of LNPs and OLNPs. c) Images of LNPs and OLNPs dispersions. d-f) TEM and SEM images of nanoparticles. Error bars indicate ± SD (n=3) and scale bars are 100 nm. Adapted from Paper (IV) ref. [56] under CC BY license.

TEM images confirmed the presence of a hydration barrier that enhances OLNPs stability. This enabled efficient functionalization to develop improved
functional wood-based nanomaterials. Hydrophobic oleate chains act as an outer membrane, restricting access and preventing protonation/ionization of carboxylic acids and phenolics, especially under acidic/basic conditions. Zeta potential measurements supported the dependency of stability on DE (Figure 21a). OLNPs with the highest DE showed the greatest stability, attributable to the higher hydrophobic chain concentration compared to other OLNPs. The hydrophobic barrier enhanced stability, allowing functionalization and development of advanced wood-based nanomaterials.

Figure 21. Stability of LNPs and OLNPs at varied pH levels: a) Zeta potential evolution at pH 2.0. b) Particle size changes at pH 12.0, with colored dashes indicating time-based aggregation/dissolution. c) and d) show LNPs and OLNPs dispersion states after 4 hours at pH 2.0 and 12.0, respectively. Adapted from Paper (IV) ref. [56] under CC BY license.
3.5 (Paper V) Comparing the production energy, structure and properties of TEMPO-Oxidized Lignocellulose and Cellulose Nanofibers Foams

Selecting abundant, renewable nanocellulosic materials like LCNF over scarce petroleum-based ones is crucial for sustainability. LCNF is promising due to its properties, versatility, and renewability. Its production skips energy-intensive processing compared to CNF, resulting in higher yield, lower cost, and reduced environmental impact. Furthermore, the lignin and hemicellulose in LCNF provide improved properties compared to CNF, such as enhanced thermal stability. Thus, usage of LCNF is more sustainable than CNF for many applications [1], [74], [75], [76], [244], [245], [246], [247], [248], [249].

Paper (V) shows that TEMPO-oxidized lignocellulose nanofiber (TOLCNF) foams made from unbleached softwood pulp offer mechanical, thermal, and sustainability advantages over TEMPO-oxidized cellulose nanofiber (TOCNF) foams from bleached pulp. TOLCNF foams showed improved properties while having lower cumulative energy demands than TOCNF foams.

3.5.1 Characterization of the Nanofibers

The morphology, average surface charge, zeta potential and crystallinity of the nanofibers has been investigated and the summery can be found in Table 1. AFM imaging revealed remarkably high aspect ratio, smooth-surfaced TOCNF (Figures 22a). TOLCNF exhibited slightly rougher surfaces due to lignin and hemicellulose content, visualized via AFM (Figures 22b). The AFM diameter statistics indicate that TOLCNF (5.6 ± 1.5 nm) are thicker than TOCNF (4.8 ± 1 nm) on average. All dispersions exhibited good stability without aggregation, with zeta potentials of approximately −50 mV. TOLCNF/TA had smooth surfaces with reduced observable lignin and hemicellulose content around the nanofibers (Figures 22c).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Average diameter by TEM (nm)</th>
<th>Equivalent diameter by AFM (nm)</th>
<th>Average surface charge (mequiv g⁻¹)</th>
<th>Average zeta potential (mV)</th>
<th>Crystallinity index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOCNF</td>
<td>6.7 ± 0.5</td>
<td>4.8 ± 0.9</td>
<td>928</td>
<td>−54.3 ± 0.9</td>
<td>51</td>
</tr>
<tr>
<td>TOLCNF</td>
<td>7.5 ± 0.8</td>
<td>5.6 ± 1.5</td>
<td>983</td>
<td>−55.7 ± 4.9</td>
<td>54</td>
</tr>
<tr>
<td>TOLCNF/TA</td>
<td>6.6 ± 0.4</td>
<td>5.0 ± 1.1</td>
<td>−</td>
<td>−48.8 ± 0.6</td>
<td>61</td>
</tr>
</tbody>
</table>
3.5.2 Viscoelastic Properties of the Dispersions

Rheometry was used to assess the viscoelastic properties of dispersions, which is crucial as they influence the final material characteristics. Factors such as solid content (concentration of nanofibers and additives), surface charge, and aspect ratio of nanofibers affect viscosity, gelation, and solvent crystal growth during freezing, determining pore size, shape, and distribution. Thus, analyzing dispersion rheology is vital for desired results in ice templating. [133] [250]

Amplitude sweep test (Figure 23a) revealed TOLCNF/TA dispersion exhibited the highest yield stress of 9.0 Pa, followed by 7.5 Pa for TOLCNF dispersion and 2.9 Pa for TOCNF dispersion. The lignin, hemicellulose and tannic acid in TOLCNF/TA dispersion create a strong network able to withstand prolonged shear. Their interactions promote denser structures requiring greater stress to rupture compared to TOCNF dispersion which lacks these reinforcing components, resulting in lower yield stresses. Frequency sweep tes (Figure 23b) showed all dispersions exhibited solid-like behavior (G' > G'') across the entire frequency range tested, indicating resistance to deformation. Consistent with amplitude sweep test results, TOLCNF/TA dispersion had the highest G', followed by TOLCNF dispersion, and TOCNF dispersion had the lowest G'. Ramp-down flow curves (Figure 23c) revealed shear-thinning behavior for all dispersions as expected. In 3ITT (Figure 23d) all dispersions exhibited over-recovery of viscosity after high shear, indicating enhanced network regeneration. At low shear in interval (i), tannic acid enhanced viscosity and gel strength of TOLCNF/TA dispersion. Under high shear in interval (ii), these networks broke down as fibers aligned, decreasing viscosity. In interval (iii), network regeneration was more robust for TOLCNF dispersion likely due to more effective short-range interactions attributed to the presence of lignin and hemicellulose. Tannic acid disrupted this enhanced regeneration in TOLCNF/TA dispersion due to alteration in the interactions.
Consequently, TOLCNF/TA dispersion had lower over-recovery compared to TOLCNF and TOCNF dispersions.

**Figure 23. Rheological characteristics of the dispersions.** a) amplitude sweep test b) frequency sweep test c) ramp-down flow curve, and d) 3ITT of the dispersions. Adapted from Paper (V).

### 3.5.3 Characterization of the Foams

Based on the insights obtained from the properties of the dispersions, an optimized processing condition was established. The concentration of TOCNF was consistently maintained in all foams at 0.5 wt% to achieve a balance between processability and properties. Subsequently, samples were fabricated using the unidirectionally ice-templated (UIT) technique.

FTIR spectra showed TOCNF and TOLCNF foams had similar composition and functional groups characteristic of cellulose. A peak at 1508 cm$^{-1}$ in the TOLCNF foam was attributed to lignin content and was absent in TOCNF [251]. TOLCNF/TA exhibited new peaks at 1714 cm$^{-1}$ corresponding to C=O stretching of tannic acid, confirming its coating on TOLCNF fibers [252]. The spectra demonstrated differences in composition related to the presence of lignin and tannic acid in the foams. Moreover, the structure and morphology of the foams were analyzed using the SEM. The electron microscopy techniques provided comprehensive insights into pore characteristics, wall shapes, and anisotropy resulting from the ice-templating process. Cryo-SEM enabled visualization of frozen foams, revealing details of sublimation, and structure development during freeze-drying. Conventional SEM (Figure 24) showed an
oriented cell structures aligned along the freezing direction in all foams, indicating anisotropy. TOCNF foam exhibited the smallest average pore size of 41.7±11.5 μm. TOLCNF and TOLCNF/TA foams had comparable averages of ~47 μm, but TOLCNF/TA foam had a lower median pore size of 44.6 μm vs 46.5 μm for TOLCNF foam, suggesting its overall pore size was smaller. This may be from different ice growth patterns due to altered gel properties and solid content in TOLCNF/TA foam. Lignin and hemicellulose content in TOLCNF foam slightly disturbed the wall structure compared to TOCNF foam but maintained overall anisotropy. Addition of tannic acid in TOLCNF foam did not significantly impact the cellular structure.

Figure 24. SEM images of freeze-dried foams. SEM images of the horizontal cross-sections for a) F_{TOLCNF/TA}, b) F_{TOLCNF}, c) F_{TOCNF}. SEM representations of the vertical cross-sections for d) F_{TOLCNF/TA}, e) F_{TOLCNF}, f) F_{TOCNF}. The scale bars for micrographs a, b, and c denote 500 μm, and those for micrographs d, e, and f indicate 200 μm. Adapted from Paper (V).

SAXS analysis has shown the nanofibers within the foams’ wall are oriented in direction of freezing direction during the UIT process (Figure 25). Orientation index calculations indicated that hemicellulose and lignin in TOLCNF foam result in a lower orientation index (Figure 25b). Moreover, the presence of hemicellulose and lignin broadens the azimuthal intensity peak, while TA addition narrows it, suggesting improved alignment (Figure 25c, d). In all foams, only slight variations in fiber orientation within the foam walls at relative humidity levels of 10% and 80% RH was observed. This suggests that within these specific values, humidity alterations do not significantly influence the orientation of fibers within the foam walls (Figure 25b).
3.5.4 Mechanical and Thermal Properties of the Foams

The performance of the foams was evaluated in various tests, such as axially compression test, and thermal stability assessments. Foam samples were axially compressed to assess mechanical properties like Young’s modulus and toughness, showing typical behavior with an initial elastic response, followed by uniform plastic deformation, and ending in densification with non-uniform deformation (Figure 26). Despite variations in solid content, TOCNF concentration was held constant at 0.5 wt% across all foams to maintain uniform properties and facilitate the study of how presence of lignin, hemicellulose and tannic acid and their interactions affect mechanical performance, with any microstructural efficiency changes likely stemming from these interactions. The TOLCNF/TA foam had the highest Young’s
modulus (290 kPa) and toughness (21 kPa). The TOLCNF foam had the next highest values, while the TOCNF foam foams had the lowest. The lignin and hemicellulose in TOLCNF foam enhanced binding of the nanofibers, creating a more robust network. Moreover, tannic acid further rigidifies the foam. All foams were ultra-low density (<10 mg cm\(^{-3}\)). Moreover, TOLCNF foam had the highest specific Young's modulus (37.4 J g\(^{-1}\)) and 228% higher than TOCNF foam (16.4 J g\(^{-1}\)), despite 50% higher density. This shows higher microstructural efficiency of TOLCNF foams. Similarly, TOLCNF foam had the highest specific toughness (2.3 J g\(^{-1}\)). Added TA did not significantly affect energy absorption, suggesting maintained energy-to-weight ratio, though further optimization on amount of TA is needed.

![Figure 26. Mechanical properties of foams. Stress-strain curves from compressive strength testing of the foams. Inset visuals shows TOCNF foam at incremental strain stages. The densities of the foams are 9.2 mg cm\(^{-3}\) for TOLCNF/TA, 7.0 mg cm\(^{-3}\) for TOLCNF, and 4.7 mg cm\(^{-3}\) for TOCNF. Adapted from Paper (V).](image)

The thermal stability of the foams was investigated through thermogravimetric (TGA) and derivative thermogravimetric (DTG) analyses conducted under an argon atmosphere. The results show that TOLCNF/TA foam had a higher onset and peak degradation temperatures, less mass loss, and more residual mass. TA improved the thermal stability of TOLCNF foam by enhancing interfacial bonding and protecting lignocellulose. In the first degradation stage (110°C –210°C), TOLCNF/TA foam showed slightly better...
stability with less mass loss compared to TOCNF foam. In the final stage above 300°C, TOLCNF/TA foam maintained a higher residual weight at 600°C, suggesting more char content.

3.5.5 Cumulative Energy Demand Assessment for Production Of Nanofibers and Foams

An industrial-scale analysis of the energy requirements for producing nanocellulose materials has been conducted, focusing on the cumulative energy demand (CED) for generating 1 kg of material. Bleached kraft pulp nanofibers (TOCNF) have a CED of 14 MJ kg\(^{-1}\), while unbleached nanofibers (TOLCNF) require approximately 9 MJ kg\(^{-1}\), which is about 30% less energy [248], [253]. Further investigations into the energy demands of foam derivatives of TOCNF and TOLCNF reveal that TOLCNF and TOCNF foams possess CED of 26 MJ kg\(^{-1}\) and 32 MJ kg\(^{-1}\), respectively. This indicates that TOLCNF foams are a more energy-efficient option compared to TOCNF foams [248], [254], [255], [256].
In conclusion, this thesis highlights the importance of surface modification, nano- and microstructure, and multiscale characterization techniques in tailoring the properties of wood-based colloidal dispersions and hybrid functional foams. Colloidal processing strategies and controlled component alignment are particularly important in achieving improved mechanical performance, thermal insulation, and unique functionalities such as magnetism.

Using tannic acid as a stabilizer enabled the production of magnetic foams with a very high iron oxide nanoparticle (IONP) content while preserving porosity and lightness. Tannic acid-covered IONPs promoted a defined foam structure and uniform distribution. Increasing IONP concentration enhanced the Young's modulus, and aligning IONPs with a magnetic field further improved the Young's modulus and compressive strength. The foams' density ranged from 12.4 to 56.1 mg cm\(^{-3}\), with IONP content ranging from 40 to 87 wt\%. Notably, the foam containing 87 wt\% IONP demonstrated a saturation magnetization level equivalent to 95\% of bulk magnetite.

Moreover, the liquid-phase Layer-by-Layer self-assembly method was utilized to deposit rGO onto the macropore walls of anisotropic TOCNF foams, creating a hierarchical structure with improved thermal insulation properties. This enhancement broadens the potential applications for anisotropic TOCNF foams in energy, sensing, and catalysis. This method allows for the post-modification self-assembly of any species that can be dissolved or dispersed in mixtures of methanol and water. Hierarchically incorporating rGO onto the anisotropic CNF foam walls resulted in a reduction of radial thermal conductivity by up to 21\% compared to unmodified anisotropic TOCNF foams. Despite the rGO film not being fully percolated, its presence significantly decreases the radial thermal conductivity. Additional reductions may be achieved by optimizing rGO film percolation protocols, as long as they prevent realigning or densifying the CNF within the foam walls.

Furthermore, Rheo-SAXS measurements showed that shear induced significant particle orientation in both the CNC-only dispersion and the CNC:MNT composite dispersion. Both dispersions demonstrated shear-
thinning behavior, suggesting alignment of the anisotropic particles along the shear direction. In the CNC-only dispersion, shear-induced orientation relaxation took place rapidly and efficiently through an exponential time-dependent condensation process. On the other hand, the CNC:MNT composite dispersion exhibited a delayed and hindered response, with an estimated rotational diffusion coefficient approximately 500 times smaller than that of the CNC-only dispersion. This suggests electrostatic interactions between CNC particles and MNT platelet edges, leading to aggregation and gel formation.

Additionally, TEM imaging showed that the oleate chains on the surfaces of lignin particles formed a hydrophobic barrier, which enhances stability and prevents protonation/ionization of carboxylic acids and phenolics, particularly in acidic/basic conditions, without relying on covalent cross-linking. This improved stability facilitated efficient functionalization for the development of advanced wood-based nanomaterials for anticorrosion coatings.

Lastly, the production of TOLCNF foam is more energy-efficient than that of TOCNF foam, with cumulative energy demands of 26 MJ kg$^{-1}$ and 32 MJ kg$^{-1}$, respectively. TOLCNF foams exhibit enhanced mechanical properties compared to TOCNF foams, such as a two-fold increase in specific Young's modulus and specific toughness, due to a more effective microstructure. Furthermore, thermogravimetric analysis confirmed that tannic acid improves the thermal stability of TOLCNF foam. However, tannic acid does not significantly enhance specific mechanical properties, indicating that further optimization of the amount of TA is needed.
5. Future outlook

The development of sustainable wood-based nanomaterials shows promise, but there are challenges in stability, functionalization, consistency, scalability, and durability. To address these challenges, suggested topics for future research include:

- **New Preparation/Fabrication Techniques:** Developing new preparation/fabrication techniques to enhance the properties and consistency of wood-based nanomaterials and incorporating multiple functionalities.

- **Chemical Functionalization:** Adding functional groups or using surface modification techniques to enhance the properties of the wood-based nanomaterials and incorporating multiple functionalities.

- **Process-structure-property Relationships:** Further deciphering process-structure-property relationships in wood-based nanomaterials using advanced tools and characterization techniques.

- **Improving Durability:** Improving durability and longevity of the wood-based nanomaterials in harsh conditions.

- **Extracting Nanocellulose from Textiles and Other Cellulosic Materials:** Investigating extracting nanocellulose from textile waste and other cellulosic materials to create more affordable and environmentally friendly functional materials with improved properties.

- **Industrial Scalability, Environmental Impact, and Commercial Viability:** Large-scale production of the wood-based nanomaterials while minimizing their environmental impact and evaluating their commercial viability.

By integrating different fillers, such as hexagonal boron nitride, together with a magnetic compound into a nanocellulose scaffold, remarkable thermal conductivity, electrical insulation, and magnetic properties can be imparted. Further research can focus on different material combinations for developing foams with multiple functionalities. The liquid-phase Layer-by-Layer self-assembly method for depositing nanomaterials onto nanocellulose-based foam
walls introduces a programmable post-modification technique. This approach enables the fabrication of hierarchical structures with improved and customized properties in wood-based nanomaterial foams. This technique holds potential for further exploration through the extensive freedom it provides in material selection and optimization, ultimately unlocking its complete capabilities.

Furthermore, the Rheo-SAXS technique has the potential to investigate particle-particle interactions in complex wood-based dispersions, providing insights into the impact of incorporating different nanomaterials and compositions, modulation of pH, and ionic strength on the interactions among wood-based nanomaterials. This can be further studied to optimize processing variables or conditions in applications such as 3D printing. Moreover, advanced TEM imaging techniques applied to wood-based nanomaterials, such as in-situ TEM, could yield new insights. Real-time monitoring of particle interactions during drying, as well as the influence of concentration modulation, pH, and ionic strength, is feasible. Systematic investigations into the stability of dispersions can provide valuable information on the behavior of wood-based nanomaterials in complex systems and setups.

One area of research that has not received enough focused and systematic attention is the benchmarking of wood-based nanomaterials under extreme conditions. This includes exposure to high levels of ultraviolet light, extreme humidity, and temperatures, as well as mechanical stress and varying pH levels required in specific applications. Wood-based coating materials are particularly interesting and warrant further study. These coatings could potentially offer protective benefits, but more research is needed to understand their effectiveness, longevity and applications. Moreover, investigating the potential for extracting nanocellulose from textile waste and other cellulosic materials is a promising strategy that supports waste reduction, resource conservation, and aligns with circular economy principles. However, the extraction methodologies involved require further optimization and development for efficient and consistent large-scale production.

Last but not least, further research is necessary to evaluate the environmental impact, energy demand, industrial scalability, life cycle assessment, and commercial viability of wood-based nanomaterials. A comprehensive study of industrial-scale production methods for these nanomaterials is essential, covering all available techniques. This study should assess the energy demand and environmental impact of each production method. It is crucial to regularly update the evaluation of production methods to reflect new developments or optimizations, as well as changes in the cost of chemicals.
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