Wood Nanocellulose Materials and Effects from Surface Modification of Nanoparticles

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AKADEMISK AVHANDLING

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“A person who never made a mistake never tried anything new.”

– Albert Einstein
ABSTRACT

Nanocellulose is an interesting natural material that is gaining interest in the field of materials science, particularly nanocomposites. Depending on the disintegration route, nanocellulose can be isolated either in the form of long and flexible fibres (nanofibrillated cellulose, NFC), or stiff, rod-like crystals (cellulose nanocrystals, CNC). Nanocellulose can be utilized in nanocomposites either as a reinforcement element or as a network matrix due to its ability to form a strong network. In this thesis, nanocellulose based materials are prepared by evaporation of a liquid medium. The key step in this processing route is a good dispersion of the nanoparticles in the selected matrix. Therefore the importance of surface modification in order to ensure favourable nanocellulose dispersion is clarified in a variety of materials systems.

In Paper I, poly(methyl methacrylate) (PMMA) based fibres prepared by electrospinning were reinforced with nanofibrillated cellulose. Native NFC appeared to show a good compatibility with PMMA matrix in the electrospinning solution and resulting fibres. Furthermore, a new method for mechanical testing of mats with random fibre orientation as well as aligned fibres was developed.

In Paper II, commingled nanopaper structures with carbon nanotubes (CNTs) were prepared. Several surfactants were used to disperse hydrophobic CNTs in water. A nonylphenol phosphate ester (NPPE) was found to work well for both dispersing CNTs in water and providing compatibility with NFC through electrostatic repulsion between the phosphate ester groups of the surfactant and the carboxylate groups of NFC.

In Paper III, a new water based route for functionalization of cellulose nanocrystals was developed. In this approach, inspired by organo-modified layered silicates, quaternary ammonium salts were adsorbed. It was demonstrated that different functionalities (alkyl, phenyl, glycidyl or diallyl) can be introduced onto the cellulose and the dispersibility in organic solvents was studied. Subsequently, in Paper IV, nanocomposites with poly(vinyl acetate) (PVAc) were prepared. The effect of modification on the degree of dispersion of the CNC within the matrix was studied as well as the strong effects on the properties of the resulting nanocomposites.

In Paper V, taking advantage of the entangled NFC network and the possibility to tailor the pore size and surface chemistry, lubricant-infused slippery films and coatings based on NFC were prepared for the first time.

Keywords: Nanocellulose; nanocomposite; dispersion; surface modification; surfactant; poly(methyl methacrylate); poly(vinyl acetate); carbon nanotubes; electrospinning; lubricant-infused surfaces.
SAMMANFATTNING


I artikel I (Paper I) skapas elektrospunna fibrer från polymetylmetakrylat (PMMA) som förstärkts med NFC. Det visade sig att NFC har god kompatibilitet med PMMA matrisen i lösningen för elektrospinning, samt god dispergering i de resulterande fibrerna. Dessutom utvecklades en ny metod för att göra riktade fibermattor och för att mäta deras mekaniska egenskaper.

I artikel II (Paper II), framställdes hybrider av nanopapper från NFC blandat med kolnanorör (CNT). Flera typer av ytaktiva ämnen användes för att dispergera hydrofob CNT i vatten. Nonylphenol fosfatester (NPPE) fungerade bra, både för att dispergera CNT i vattnet samt skapa god kompatibilitet med NFC. Mekanismen är troligen elektrostatisk repulsion mellan fosfatester-gruppen hos det ytaktiva ämnet och karboxylgruppen hos NFC.


I artikel IV (Paper IV) framställdes sedan nanokompositer med polyvinylacetat. CNC med och utan modifiering dispergerades i lösningsmedel och i polymermatris. Nanokompositerna visade dramatiskt förbättrade egenskaper, och mekanismerna analyseras i studien.

LIST OF PAPERS

This thesis is a summary of the following papers:

I. **Micromechanical Tensile Testing of Cellulose-Reinforced Electrospun Fibres Using a Template Transfer Method (TTM)**
   Richard Andersson, Michaela Salajková, Peter Mallon, Lars Berglund, Mikael Hedenqvist, and Richard Olsson

II. **Tough nanopaper structures based on cellulose nanofibres and carbon nanotubes**
    Michaela Salajková, Luca Valentini, Qi Zhou and Lars Berglund
    Composites Science and Technology 2013, **87**, 103-110.

III. **Hydrophobic cellulose nanocrystals modified with quaternary ammonium salts**
     Michaela Salajková, Lars Berglund and Qi Zhou

IV. **Strong surface treatment effects on reinforcement efficiency in biocomposites based on cellulose nanocrystals in poly(vinyl acetate) matrix**
    Michaela Salajková, Farhan Ansari, Qi Zhou and Lars Berglund
    Manuscript.

V. **Super-slippery omniphobic self-standing films and coatings based on nanocellulose**
   Michaela Salajková, Nicholas Cervin, Christina Schütz, Lars Berglund, Lennart Bergström, Lars Wågberg and German Salazar-Alvarez
   Manuscript.

My contributions to the above listed papers are:

I. Part of the experimental work and part of the manuscript preparation.

II. Most of the experimental work and most of the manuscript preparation.

III. All experimental work and part of the manuscript preparation.

IV. Most of the experimental work and most of the manuscript preparation.

V. Part of the experimental work and most of the manuscript preparation.
Other relevant publications not included in the thesis:

VI. Mechanical performance tailoring of tough ultra-high porosity foams prepared from cellulose I nanofibres suspensions
Houssine Sehaqui, Michaela Salajková, Qi Zhou and Lars Berglund
Soft Matter 2010, 6, 1 824-1 832.

VII. Determination of Young’s modulus for nanofibrillated cellulose multilayer thin films using buckling mechanics
Emily Cranston, Mohamed Eita, Erik Johansson, Julia Netrval, Michaela Salajková, Hans Arwin and Lars Wågberg
Biomacromolecules 2011, 12 (4), 961-969.

VIII. A transparent hybrid of nanocrystalline cellulose and amorphous calcium carbonate nanoparticles
Denis Gebauer, Vitaliy Oliynyk, Michaela Salajková, Jordi Sort, Qi Zhou, Lennart Bergström and German Salazar-Alvarez
Nanoscale 2011, 3 (9), 3 563- 3 566.

IX. Cellulose Nanofibre Orientation in Nanopaper and Nanocomposites by Cold Drawing
Houssine Sehaqui, Ngesa Ezekiel Mushi, Seira Morimune, Michaela Salajková, Takashi Nishino and Lars A Berglund
ACS Applied Materials and Interfaces 2012, 4 (2), 1 043-1 049.

X. Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films
Jan Lagerwall, Christina Schütz, Michaela Salajková, JungHyun Noh, Ji Hyun Park, Giusy Scalia, and Lennart Bergström
Accepted in NPG Asia Materials.

XI. Cellulose Nanofibres Decorated with Magnetic Nanoparticles – Synthesis, Structure and Use in Magnetized High Toughness Membranes for a Prototype Loudspeaker
Sylvain Galland, Richard Andersson, Michaela Salajková, Valter Ström, Richard Olsson and Lars Berglund
Submitted manuscript.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>C=C</td>
<td>Diallyldimethylammonium chloride</td>
</tr>
<tr>
<td>C12</td>
<td>Dodecyltrimethylammonium chloride</td>
</tr>
<tr>
<td>C18</td>
<td>Stearyltrimethylammonium chloride</td>
</tr>
<tr>
<td>CA</td>
<td>Contact angle</td>
</tr>
<tr>
<td>CNC</td>
<td>Cellulose nanocrystals</td>
</tr>
<tr>
<td>CNC-C</td>
<td>Cellulose nanocrystals with carboxylic groups</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>COC</td>
<td>Glycidyltrimethylammonium chloride</td>
</tr>
<tr>
<td>CO2</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CPh</td>
<td>Phenyltrimethylammonium chloride</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analysis</td>
</tr>
<tr>
<td>DSP</td>
<td>Digital speckle photography</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>FD</td>
<td>Freeze-drying</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field-emission scanning electron microscopy</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier-transformed infrared spectroscopy</td>
</tr>
<tr>
<td>FTCS</td>
<td>(tridecafluoro-1,1,2,2,-tetrahydrooctyl)trichlorosilane</td>
</tr>
<tr>
<td>G</td>
<td>Shear modulus</td>
</tr>
<tr>
<td>H2SO4</td>
<td>Sulphuric acid</td>
</tr>
<tr>
<td>L/D</td>
<td>Length/diameter</td>
</tr>
<tr>
<td>MTM</td>
<td>Montmorillonite clay</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotubes</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium chloride</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NFC</td>
<td>Nanofibrillated cellulose</td>
</tr>
<tr>
<td>NPPE</td>
<td>Nonylphenol poly(oxyethylene) (10) phosphate ester</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Poly(propylene)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>PVAc</td>
<td>Poly(vinyl acetate)</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SCD</td>
<td>Supercritical carbon dioxide</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TB</td>
<td>Tert-butanol</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TEMPO</td>
<td>(2,2,6,6-tetramethylpiperidin-1-yl)oxyl</td>
</tr>
<tr>
<td>( T_g )</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TO-NFC</td>
<td>TEMPO-oxidized nanofibrillated cellulose</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Strain to failure</td>
</tr>
<tr>
<td>( \eta_0 )</td>
<td>Orientation factor</td>
</tr>
<tr>
<td>( \eta_l )</td>
<td>Fibre length efficiency</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Tensile strength</td>
</tr>
<tr>
<td>( \sigma_{DC} )</td>
<td>Direct current conductivity</td>
</tr>
<tr>
<td>( \theta_f )</td>
<td>Fibre volume fraction</td>
</tr>
</tbody>
</table>
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1. OBJECTIVES

The background to the present thesis is the rapid development of the field of cellulose nanocomposites. It means that the diameter of the cellulose reinforcement in biocomposites is decreased from the 10 µm range for plant fibers to the 3-10 nm range, the surface characteristics of the reinforcement then become much more important. Not only is the nanocellulose behavior in liquid suspension strongly influenced, but the interfacial adhesion in the solid material is also affected. For this reason, the general objective of the present thesis is to create surface modification methods for nanoparticles in order to extend the property range of nanocellulose-based materials. The scientific objective is to improve the understanding of how surface modification of nanocellulose is influencing processing, structure and properties of the materials. As an example, the goal to clarify the effect of interfacial characteristics and degree of nanoparticle dispersion on physical properties of polymer nanocomposites was addressed in the PVAc/CNC nanocomposites study.
2. INTRODUCTION

2.1. Nanocellulose

Natural cellulose based materials (wood, hemp, cotton, linen, etc.) have been used as engineering materials for thousands of years, due to their functionality, flexibility, high mechanical strength, low density and widespread availability. In all these materials, there is a fundamental unit that is used to strengthen all subsequent structures within trees, plants, some marine creatures, and algae i.e. cellulose nanofibrils. In this work, wood, in particular Norway spruce was chosen as a source of cellulose.

Cellulose is a crystalline structural polysaccharide. The basic repeating unit consists of two anhydroglucose rings joined via the β-1,4-glycosidic linkage. In wood, 30-40 cellulose polymer chains aggregate into nanofibrils (also referred to as elementary fibrils or microfibrils) that are 3-5 nm wide. Within each of these nanofibrils, there are regions, where the cellulose chains are arranged in highly ordered crystalline structures, and regions that are disordered (amorphous). As is schematically illustrated in Figure 1, the nanofibrils agglomerate further into larger aggregates and these, together with hemicellulose and lignin, form the plant cell wall (i.e. wood fibre).

The diversity of cellulose nanoparticle geometries results from the plant origin and the disintegration processes, which also influence the types of functional groups introduced to the cellulose, see Table 1.

![Figure 1](image)

**Figure 1.** Hierarchical structure of wood biomass and the characteristics of cellulose nanofibrils consisting of disordered (amorphous) and ordered (crystalline) regions.

2.1.1. Cellulose nanofibrils

A mild enzymatic or chemical pre-treatment followed by mechanical disintegration results in mixture of individual fibrils (3-5 nm wide) and fibril aggregates (10-20 nm wide), that are several micrometres long. Pre-treatments with enzymes does not introduce any charged groups and the fibrils keep their native structure with hydroxyl groups (Figure 2). The absence of any charged groups can make the disintegration
difficult and fibril aggregates may form. In the chemical pre-treatment developed by Saito et al., involving TEMPO-mediated oxidation, the primary hydroxyls are converted to carboxyl groups. Another example is pretreatment with chloroacetic acid, which leads to formation of carboxymethyl groups. A chemical route described by Pei et al. uses surface quaternization, which introduces positively charged trimethylammonium groups on the surface of cellulose nanofibrils. In all cases, the amount of charges is rather high and can be controlled by the reaction conditions. Subsequently, the electrostatic repulsion facilitates the disintegration process.

### 2.1.2. Cellulose nanocrystals

A strong acid hydrolysis leads to removal of all disordered regions in fibrils resulting in highly crystalline, rod-like particles called cellulose nanocrystals (CNC) or whiskers (3-5 nm wide and 100-300 nm long). This was found as early as in the fifties by Battista who subjected cellulose to hydrolysis with hydrochloric acid. Soon after, Rånby et al. prepared CNC by sulphuric acid hydrolysis. Compared to hydrochloric acid hydrolysis, the later method results in colloidal suspension of CNC stabilized by electrostatic repulsion of negatively charged sulphate ester groups. If followed by cationization, the suspension is stabilized by positively charged groups. Recently, phosphoric acid or mildly acidic aqueous ionic liquids have been used to isolated CNC.

![Figure 2](image.png)

**Figure 2.** Illustration of functional groups introduced onto cellulose during disintegration. Adopted from Moon et al.

---

4
Table 1. Overview of the common treatments for isolation of nanocelluloses.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Particle type</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enzymatic</td>
<td>Fibrils</td>
<td>Hydroxyl</td>
</tr>
<tr>
<td>TEMPO-mediated oxidation</td>
<td>Fibrils</td>
<td>Carboxyl</td>
</tr>
<tr>
<td>Carboxymethylation</td>
<td>Fibrils</td>
<td>Carboxymethyl</td>
</tr>
<tr>
<td>Surface quaternization</td>
<td>Fibrils or crystals</td>
<td>Trimethylammonium</td>
</tr>
<tr>
<td>Hydrolysis with hydrochloric acid</td>
<td>Crystals</td>
<td>Hydroxyl</td>
</tr>
<tr>
<td>Hydrolysis with sulfuric acid</td>
<td>Crystals</td>
<td>Sulphate esters</td>
</tr>
</tbody>
</table>

2.2. Surface modification

Surface functionalizations can be performed with the aim of introducing stable electrostatic charge on the surface of nanocellulose to obtain better colloidal dispersions. Another purpose is to tune hydrophilicity/hydrophobicity of the nanocellulose to improve compatibility in various solvents, especially when used together with nonpolar or hydrophobic matrices in nanocomposites.\(^{13}\)

The terms hydrophobic/hydrophilic may be applied to any interaction between water and other materials. These terms are commonly used for classification of liquids and solids in terms of their solubility in water, as well as solid surfaces with regard to their wettability by water.\(^{14}\)

Wettability of a solid surface is usually measured by the contact angle (CA) between water and the solid surface. A surface is defined as “hydrophilic” when its contact angle with water is smaller than 90° and hydrophobic otherwise (Figure 3).\(^{14}\)

![Figure 3. Illustration of contact angle with water for hydrophilic and hydrophobic surfaces.](image)

In general, the surface functionality of cellulose nanoparticles can be categorized into 3 groups: (1) native surface chemistry of the particles as a result of their extraction (as discussed earlier), (2) physical adsorption of surfactants or polyelectrolytes and (3) covalent modification such as esterification, etherification, silylation and polymer grafting (Figure 4).\(^{1}\)
The main challenge for the chemical functionalization of nanocelluloses is to perform the modification in such a way that it only changes the surface of nanocellulose, while preserving the original fibrilar morphology.\textsuperscript{13}

As discussed in following sections, surface functionalization of nanocellulose is important tool in design of new materials.

![Figure 4](image)

**Figure 4.** Illustration of common surface functionalization of nanocelluloses. Adopted from Moon et al.\textsuperscript{1}

### 2.3. Utilization of nanocellulose – material concept

Nanocelluloses have attracted great interest due to their unique properties such as high stiffness and strength, high specific surface area, low density, low coefficient of thermal expansion, optical transparency and self-assembly behaviour. Thanks to their ability to form a strong network, they can be utilized in bio/nanocomposites either as matrix or reinforcement.

#### 2.3.1. Neat nanocellulose materials and their applications

It has been shown that cellulose nanofibrils can form nanopaper structures of high toughness.\textsuperscript{15} In these structures, the nanofibrils form a physically entangled network (also interacting through strong hydrogen bonds). The preparation route is inspired by conventional paper making process (Figure 5) and it involves careful dispersion of nanofibrils in water followed by vacuum filtration, which results in wet gel consisting of mechanically entangled nanofibrils. Remaining water is removed by drying.\textsuperscript{15, 16} Nanopapers have been prepared from cellulose nanofibrils with hydroxyl groups,\textsuperscript{15, 17} carboxylic groups\textsuperscript{18} and trimethyl ammonium groups.\textsuperscript{5} Moreover, their porosity could be controlled depending on the drying technique as discussed in the following section.
Remaining water of the wet gel obtained by filtration can be removed by drying in oven\textsuperscript{13, 16} or by evaporation using solution casting\textsuperscript{20}. These are however very time-consuming methods and often result in samples with wrinkles due to moisture concentration gradient. Sehaqui at al.\textsuperscript{16} used a vacuum drying, which resulted in flat nanopapers with low porosity. Moreover, it was demonstrated that sheets with diameter as large as 20 cm could be prepared using a semiautomatic sheet former\textsuperscript{16}.

 Freeze-drying (lyophilisation) is a drying technique that consists of removing water (or other solvent) by sublimation after freezing (Figure 6). It has been widely used in food industry, pharmaceutical industry, biological applications and recently, it has been explored as a route for production of novel porous materials\textsuperscript{21}. Freeze-drying can be performed from water as well as organic solvents. Although water is the preferred solvent from the environmental point of view, organic solvents offer an advantage in some cases, as they do not produce ice crystals upon freezing\textsuperscript{22}. Tert-butanol is commonly used, because it is easy to mix with water or other organic solvents, it is easy to freeze (due to its high melting point around 25 °C) and easy to evaporate (high vapour pressure of 4.1 kPa at 20 °C)\textsuperscript{23}.

 The supercritical drying process uses fluid mixtures above their critical point without remains of any liquid phase. This drying procedure thus avoids the presence of any vapor-liquid transition and surface tensions in the gel pores, preventing the gel structure from collapsing, resulting in individualized cellulose fibrils network with the structure similar to that in wet sample, Figure 6\textsuperscript{24, 25}. Supercritical drying is suitable for solvents having low critical temperature and pressure. Therefore water is not applicable for this technique and instead, CO$_2$ is commonly used\textsuperscript{25, 26}.
Using the above-mentioned techniques, the porosity of nanopapers can be easily tailored in the range of 20-88 % and the specific surface area can be as high as 482 m²/g.²⁷

Compared to conventional paper, nanopaper has higher density (depending on the drying technique) and better mechanical properties.²⁸ It is flexible in bending and can be optically transparent,¹⁷ has low coefficient of thermal expansion¹⁷ and has excellent oxygen barrier properties.²⁹, ³⁰

Many potential applications for nanocomposites based on NFC have been suggested, such as packaging,³¹ loud-speaker membranes,³² foldable substrates for electronic displays¹⁷, ³³ or battery membranes.⁵¹

Moreover, tailoring of the surface characteristics of nanocellulose opens up possibilities for the design of functional materials. For example, Aulin et al.³⁵ prepared aerogels from nanofibrillated cellulose with tuneable oleophobicity by fluorination of NFC aerogels with 1H,1H,2H,2H-perfluorodecyltrichlorosilane via chemical vapor deposition. Shortly after, similar approach was used by Jin et al.,³⁶ who modified NFC aerogels with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane and demonstrated application of hydrophobic and oleophobic aerogels as cargo carriers on water and oil. Recently, Cervin et al.³⁷ prepared NFC aerogels modified with octyltrichlorosilane that selectively absorb oils and therefore could be used as lightweight porous media for the separation of oil and water mixtures. Mertaniemi et al.³⁸ mimicked the lotus leaves by spray drying of NFC modified with tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane, leading to hydrophobic hierarchically structured surfaces.
2.3.1. Cellulose nanocomposites

2.3.1.1. Functional materials

The remarkable properties of nanocelluloses can be further extended by addition of inorganic entities. Hybrid materials with interesting properties can be prepared by taking advantage of the continuous nanofibrous NFC network or the stiffness and optical properties of rod-like cellulose crystals. Nanocellulose therefore essentially serves as a matrix.

It was demonstrated, that NFC-montmorillonite (MTM) clay nanopaper could be prepared using non-charged enzymatically derived NFC,\textsuperscript{16, 30, 39, 40} negatively charged NFC\textsuperscript{41, 42} or NFC bearing cationic functional groups.\textsuperscript{43} Resulting hybrids exhibit interesting oxygen-barrier properties combined with self-extinguishing behaviour,\textsuperscript{16, 30, 39} remarkable mechanical properties\textsuperscript{42} and tuneable water vapour barrier properties.\textsuperscript{41} Cellulose nanofibrils can also be combined with TiO\textsubscript{2} nanoparticles through electrostatic interaction between the carboxylic group of the cellulose and positively charged groups present on the particles resulting in flexible, transparent and hard films.\textsuperscript{44} Galland et al.\textsuperscript{45} prepared ferrite decorated cellulose fibrils via \textit{in-situ} precipitation of aqueous metal ion complexes onto the surface of enzymatically derived NFC. Using simple paper-making approach, membranes with high toughness and tuneable magnetic properties were prepared and used in the design of an ultrathin prototype loudspeaker.

To further extend the possible applications by incorporating a wider range of nanoparticles, surface functionalization is an important tool. For example, it has been shown that carbon nanotubes (CNTs), which are electrically conductive and extremely high strength nanomaterials can be combined with cellulose by using surfactants. However, in previous work, electrically conductive paper was prepared by addition of carbon nanotubes to wood pulp,\textsuperscript{46-48} bacterial cellulose\textsuperscript{49-52} or regenerated cellulose.\textsuperscript{53, 54} Only recently, cellulose nanofibrils from wood were used as a matrix for incorporation of functionalized CNTs for preparation of films\textsuperscript{55} or aerogels.\textsuperscript{56}

Optically transparent hybrid nanocomposites of cellulose nanocrystals and amorphous calcium carbonate were obtained by pre-complexation of sulphate ester groups of cellulose with calcium ions followed by reaction with sodium carbonate.\textsuperscript{57} This approach prevents crystallization of calcium carbonate, allows control over the hybrid composition and results in composite with properties similar to dentin (natural composite of hydroxyapatite and collagen). Shopowith et al.\textsuperscript{58} used the hydroxyl groups of cellulose nanocrystals as template for synthesis of silica nanoparticles. With subsequent pyrolysis, the cellulose was removed, resulting in ordered mesoporous structure. Recently, cellulose nanocrystals were also used as dispersing medium for single-wall carbon nanotubes.\textsuperscript{59} A suggested mechanism for the stabilization of the
dispersion is the interaction of the hydrophobic faces of cellulose nanocrystals and hydrophobic carbon nanotubes.

2.3.1.2. Mechanical reinforcement

The focus of this section is on nanocomposites where nanocelluloses are used as reinforcement and is divided according to the type of nanocellulose.

Theoretical estimates of Young’s modulus of cellulose single crystal give values in the range of 100-160 GPa, making nanocellulose an ideal candidate for reinforcement. Good dispersion of nanocellulose within a certain matrix is however a key issue to be addressed. Therefore, mutual compatibility between the two components needs to be tailored by selection of nanocellulose with suitable surface characteristics, as discussed below.

Composites with nanofibrillated cellulose can be prepared either by careful mixing of the NFC suspension with a polymer matrix or by impregnation of nanopaper structures. Water soluble polymer matrices such as starch or hydroxyethyl cellulose were reinforced with enzymatically derived NFC, resulting in materials with very high toughness. In both cases high NFC loadings were used, which together with good compatibility with matrix ensured good load transfer in the material. Optically transparent nanocomposites with improved mechanical properties were prepared from TEMPO-oxidized NFC and poly(styrene) matrix by solution casting from DMF.

Alternatively, dried nanopaper structures prepared from enzymatic NFC were impregnated with water-soluble melamine formaldehyde resin followed by hot pressing. A similar approach was adopted for the preparation of nanocomposites with hyperbranched polyesters and epoxy. However, in these cases the nanopapers were not dried. Instead, water remaining after filtration was exchanged to methanol (in case of polyesters) or acetone (in case of epoxy) prior to impregnation and the amount of solvent was used to control the matrix content in the composite. In all examples, composites with improved mechanical properties and moisture sensitivity due to the strong interaction between hydroxyl groups of cellulose and respective matrix were obtained. NFC nanopaper was also impregnated with acrylic resin, resulting in optically transparent nanocomposites. Recently, hydroxyl groups in porous NFC nanopaper were used for grafting of ε-caprolactone. Due to the high surface area of the material, exceptionally high grafting density could be achieved, providing a good control over NFC distribution within the composite.

Pei et al. showed that the introduction of as little as 1% of unmodified cellulose nanocrystals into a polyurethane matrix using in-situ polymerization results in nanostructured composites with ultra high tensile strength and strain to failure, as well
as Young’s modulus. Rueda et al.\textsuperscript{68} studied the effect of unmodified nanocrystals on the morphology of nanocomposites with polyurethane matrix. They found that a low CNC content led to a material of very high toughness without loss in ductility. An increase in CNC content, on the other hand, enhanced the soft and hard segment crystallization, causing an increase in the material stiffness and the thermal stability. Rueda et al.\textsuperscript{69} demonstrated the importance of surface chemistry in nanocomposites with a polyurethane matrix prepared by \textit{in-situ} polymerization of unmodified and isocyanate modified cellulose nanocrystals. Resulting nanocomposites showed significantly different morphologies. Preferential location of modified nanocrystals in the hard domains of the polyurethane matrix was observed, leading to enhancement of the segment crystallization.

Well-dispersed silylated cellulose nanocrystals have been used to increase the crystallinity of poly(lactic acid) (PLA) by more than 20\%, resulting in stiffer nanocomposites. Unmodified nanocrystals formed aggregates in the matrix, which did not significantly change the crystallinity and mechanical properties of the composite.\textsuperscript{70} Attempts were made to improve compatibility between PLA and CNC using surfactants and the nanocomposites were prepared either by solution casting\textsuperscript{71,72} or by extrusion.\textsuperscript{73} In all cases, surfactant significantly improved the dispersion of CNC in the hydrophobic PLA matrix, leading to a homogenous material. Recently, the same approach was used to produce ternary composites with PLA, CNC and silver nanoparticles.\textsuperscript{74} Moreover, Ljungberg et al.\textsuperscript{75} compared the performance of surfactant-modified CNC and maleated polypropylene-grafted whiskers in atactic polypropylene matrix (aPP). Surfactant provided better dispersion of CNC in aPP matrix than grafting, resulting in material with better mechanical properties.

\subsection*{2.3.2. Electrospun fibres}

Electrospinning, a broadly used method for fibre formation, has gained a tremendous interest in the field of research and commercial community over the past decade.\textsuperscript{76} During the electrospinning process, a strong electric field is applied over a polymer solution, which becomes charged and stretched and eventually forms a fibre (Figure 7).\textsuperscript{77} The fibre accelerates rapidly towards the collector and exhibits regular long waveform instabilities during spinning. During the elongation, as the solvent evaporates, the diameter of the fibre decreases and the fibre is collected.\textsuperscript{78} The collector can be either static (flat substrate), resulting in mat with random fibre orientation, or rotating (drum), leading to fibre alignment. There are several parameters that need to be optimized for successful fibre formation during electrospinning, including properties of the solution (such as molecular weight of the polymer, viscosity, dielectric constant and vapour pressure), voltage, flow rate and distance between the capillary and collector.\textsuperscript{77}
Various polymers, including polyolefins, polyamides, polyesters, polyurethanes, polypeptides, and polysaccharides, have successfully been electrospun into micro- and nanofibre mats. Currently, numerous efforts have been focused on the use of nanocelluloses as reinforcement in electrospun fibres. For example, Olsson et al. reinforced electrospun fibres based on poly(methyl methacrylate) with bacterial cellulose fibrils. Furthermore, cellulose nanocrystals were used as reinforcement for poly(vinyl alcohol) or poly(caprolactone). However, it is very challenging to accurately characterize the mechanical performance of electrospun fibres due to the lack of reliable methods for mechanical testing of these delicate fibre mats.
3. EXPERIMENTAL

This part is a summary of experimental techniques used in this thesis. More detailed information can be found in attached papers at the end of the thesis.

3.1. Materials

Sulphite pulp (with a cellulose degree of polymerization of 1200, cellulose content approximately 86 %, the rest mainly hemicelluloses) was provided by Nordic Paper, Seffle AB, Sweden. Softwood pulp (dissolving pulp, cellulose degree of polymerization 780, cellulose content approx. 93 %) was provided by Domsjö Fabriken AB, Sweden. Multi-walled carbon nanotubes (Elicarb®, purity 70-90%) were provided by Thomas Swan and nonylphenol poly(oxyethylene) (10) phosphate ester (STEPFAC 8170) was provided by Stepan Company, Northfield, IL, USA.

The rest of the chemicals used in this work were purchased from commercial suppliers.

3.2. Nanocelluloses preparation

3.2.1. Enzymatic pretreatment (Papers I and V)

The nanofibrillated cellulose was prepared from never dried softwood sulphite pulp using the enzymatic procedure developed by Henriksson et al.4 with a few modifications. The pulp was first subjected to a pre-treatment step involving enzymatic degradation and mechanical beating. During the enzymatic pre-treatment, a buffer solution was used to keep pH at 7. The amount of enzyme (Novozym 476) was 5 µl per 1 g of pulp and the fibres were incubated at 50 °C for 2 h and washed. The enzyme activity was afterwards stopped by incubation at 90 °C for 30 min. Subsequently, pre-treated fibres were disintegrated by a homogenization process using a Microfluidizer M-110EH (Microfluidics Inc., USA). A suspension of approximately 2 wt% of NFC was obtained and stored at 4 °C before use.

3.2.2. TEMPO-mediated oxidation (Papers II and III)

TEMPO-mediated oxidation of wood pulp was performed according to the method described by Saito et al.6 Briefly, the softwood fibres were suspended in water containing catalyst TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, free radical) and sodium bromide. The TEMPO-mediated oxidation was started by adding the desired amount of the sodium hypochlorite solution and was continued at room temperature while stirring. The pH was kept at 10 by adding sodium hydroxide until no further
consumption was observed. The TEMPO-oxidized cellulose was thoroughly washed with water by filtration. Afterwards, the TEMPO-oxidized fibre suspension (approximately 1 wt%) was disintegrated using a Microfluidizer M-110EH. The resulting suspension of microfibrillated cellulose (TO-NFC) was stored at 4 °C before use.

3.2.3. HCl hydrolysis (Paper III)
Cellulose nanocrystals (CNC-C) were isolated from nanofibrils using hydrochloric acid hydrolysis. Typically, 100 g of wet TO-NFC (corresponds to 1 g of dry weight) were diluted to 316 ml of deionized water and dispersed using shear forces (Ultra Turrax T18 basic, IKA Werke GmbH & Co. KG, Germany) for 2 min at 13 500 rpm and stirred with a magnetic stirrer overnight. Hydrochloric acid (37 %) was added drop-wise until a concentration of 2.5 M was obtained. The system was heated to 105 °C and refluxed for 3-7 h. The reaction was stopped by dilution with deionized water. The resulting suspension was centrifuged at 4 754 g for 20 min. The precipitate was collected and diluted to approximately 100 ml of water and dialyzed against water for 5-7 days. After that, the suspensions were sonicated 2 x 5 minutes (Sonics VibraCell, VCX 750, Sonic & Materials, USA) to obtain individual nanocrystals, and stored at 4 °C.

3.2.4. H$_2$SO$_4$ hydrolysis (Paper IV)
Cellulose nanocrystals (CNC) were prepared from wood pulp using sulphuric acid hydrolysis according to method described by Beck-Candanedo with minor modifications. Briefly, 20 g of dry wood pulp was added to 175 ml of 64 wt% sulphuric acid. The reaction was performed at 45 °C for 60 min and afterwards stopped by diluting 10 times. The suspension was washed twice with centrifugation followed by dialysis. The resulting suspension of cellulose nanocrystals was sonicated for 2 x 5 min. The suspension was then purified by centrifugation at 4 754 g for 60 min and kept at 4 °C prior to use.

3.3. Surface modification of nanocelluloses

3.3.1. Adsorption of quaternary ammonium salts (Papers III and IV)
The surface of the cellulose nanocrystals was modified by adsorption of quaternary ammonium salts. A series of quaternary ammonium salts was used to study the versatility of the approach: stearyltrimethylammonium chloride (C18), glycidyl trimethylammonium chloride (COC), diallyldimethylammonium chloride (C=C) and phenyltrimethyl-ammonium chloride (CPh). A more detailed study was then done using
C18 and the effect of cellulose-quinernary amine ratio was studied as follows (Paper III). First, 0.1 % w/v cellulose nanocrystals suspension (CNC-C) was prepared and the pH was adjusted to 10. The desired amount of C18 (or other quaternary amine) was dissolved in water resulting in concentration of 0.1 % w/v (3 mmol/L). Both suspensions were heated up to 60 °C. The CNC-C suspension was added dropwise to the C18 solution to obtain molar ratios of 1:1, 1:2 and 1:4 (carboxyl content of nanocrystals:C18). The temperature was kept at 60 °C for 3 hours. After that, suspensions were stirred at room temperature overnight. The NaCl and unbound C18 was washed away by dialysis. The modified nanocrystals were freeze-dried and the final weight was noted after freeze-drying and this value was used to estimate the amount of C18 on the surface of cellulose. For the rest of the quaternary amines, the ratio 1:2 was used.

The same procedure with minor changes was used in Paper IV. In this study, CNC obtained by sulfuric acid hydrolysis were used and modified with dodecyltrimethylammonium chloride (C12).

### 3.3.2. Partial silylation (Paper IV)

The NFC was partially silylated according to method developed by Gousse et al. with minor modifications. The water of the original NFC suspension (20 g/L) was exchanged to dry toluene. The [(tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (FTCS) was added with a molar ratio of 3:1 for FTCS and anhydroglucose units in cellulose. Triethylamine was added in the amount equimolar to FTSC to trap HCl released during the reaction. The silylation was carried out for 15 h at room temperature (21 °C) under vigorous stirring. The reaction was terminated by addition of a mixture of tetrahydrofuran (THF) and methanol in volume ratio 80/20. The fluorinated fibrils were washed thoroughly with THF three times by centrifugation, followed by dispersion in fresh THF using homogenization at 13 500 rpm. The final suspension of fluorinated nanofibrils (f-NFC) was further dispersed by sonication.
3.4. Nanocomposite preparation

3.4.1. Electrospinning (Paper I)

The solvent for electrospinning was chosen based on the compatibility with both PMMA and NFC. Afterwards the solutions with different solid contents (PMMA/NFC) were screened to establish conditions for preparation of uniform fibres with similar diameter. The PMMA/DMF solution was prepared by dissolving 10 wt% of PMMA ($M_w = 410\ 000$) in DMF under stirring at a temperature of 50 °C for a minimum of 12 h. The water of the original NFC suspension was exchanged to DMF by repeated centrifugation followed by homogenization in fresh solvent. The PMMA/NFC/DMF solution was prepared by mixing 90 wt% of the NFC/DMF suspension with 10 wt% PMMA, resulting in 4.0 wt% of NFC in PMMA.

The fibre solutions were electrospun from a flat tip needle (internal diameter 0.84 mm) at a rate of 40 µL/min. The needle tip was positioned 20 cm vertically above the collector, and the electric field from the needle to the substrate was maintained at 45 kV/m. Two different collectors were used: a flat metallic surface for the collection of non-aligned fibre mats, and a rapidly rotating cylindrical aluminium drum (Figure 8) for the collection of aligned and stretched fibre mats. The rotational speed was set to 2 000 rpm based on an earlier evaluation of speeds from 200 to 6 000 rpm, in order to minimize stretching of the fibres. The fibre mats were collected over a time of ca. 30 min in all cases.

Figure 8. Schematic illustration of cylindrical collector for fibres alignment.

3.4.2. TO-NFC/MWCNT nanopapers (Paper II)

3.4.2.1. MWCNT dispersion

Multi-walled carbon nanotubes (MWCNT) were purified prior to use. The crude material was stirred in 3 M nitric acid and refluxed for 12 hours at 60 °C to dissolve metal particles. After that, MWCNT were suspended and refluxed in 5 M hydrochloric acid solution for 6 hours at 120 °C to dissolve metal oxides.\cite{49,83}
Purified MWCNT were dispersed in water using a nonylphenol poly(oxyethylene) \((10)\) phosphate ester (NPPE). Typically, 2 \% solution of surfactant (20 mg/mL) was used and the concentration of MWCNT was 5 mg/mL. After sonication, a stable suspension without visible agglomerates was obtained.

### 3.4.2.2. TO-NFC/MWCNT dispersion

A suspension of NFC was diluted to approximately 0.1 wt\% and dispersed using shear forces for 5 min at 13 500 rpm. The MWCNT suspension was added dropwise until desired MWCNT content (0.5 – 16.7 wt\%) was obtained. The suspension was sonicated and stirred with magnetic stirrer overnight in order to obtain homogenous distribution of MWCNT. After that, water was removed by filtration on a glass filter funnel (7.2 cm in diameter) using filter membrane (0.22 \(\mu\)m GV, Millipore, USA). The obtained wet cake was dried at 93 °C under vacuum for 10-20 min in a sheet former (Rapid Köthen, RK3A-KWT PTI, Germany). Control samples containing only NFC (0 % control) and NFC/4.8 wt\% surfactant (4.8 % control) were prepared using the same procedure. The resulting nanopaper sheets had 7 cm diameter and a thickness of 25 and 50 \(\mu\)m, respectively.

### 3.4.3. PVAc/CNC nanocomposites preparation (Paper IV)

Nanocomposites containing 1, 3, 5, 10 and 20 wt\% of C12-modified CNC as well as unmodified CNC were prepared by dispersing the desired amount of CNC in 10 ml of toluene by sonication for 30 s. Afterwards, PVAc was added and the total weight of the nanocomposite was fixed at 1 g. The suspensions were stirred overnight to ensure complete dissolution of PVAc and cast in aluminium petri dishes.

### 3.4.4. Preparation of slippery surfaces

#### 3.4.4.1. Porous NFC nanopapers

NFC nanopapers were prepared from NFC hydrogels using three different drying techniques as described by Schauü et al.\(^{27}\) First, the NFC gel (200 mg of dry content) was diluted to 200 ml of deionized water and dispersed using shear homogenization at 13 500 rpm, followed by gentle stirring overnight. The suspension was degassed and filtrated over 0.65 \(\mu\)m filter membrane (DVPP, Milipore, USA) until a strong hydrogel of approx. 15 wt\% was formed. In order to control the porosity and the pore size of the resulting nanopapers, three different drying techniques were used: freeze-drying from water (water FD), freeze-drying from tert-butanol (TB FD) and drying from supercritical carbon dioxide (SCD).
The nanopapers were fluorinated using procedures previously described by Jin et al. A piece of nanopaper (approximately 60 mg) was placed in a sealed jar together with 50 µL of (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (FTCS). The liquid silane was put in an aluminium cup inside the jar to avoid direct contact with the nanopapers before evaporation. The jar was heated to 100 °C in an oil bath for 60 min.

3.4.4.2. Coatings

The coatings on glass substrates were prepared from suspension of fluorinated NFC (f-NFC) in THF (7 g/L) by repeated deposition of 400 µL of f-NFC suspension followed by slow evaporation of the solvent. The fluorinated nanopapers and coatings prepared from f-NFC were infused with the lubricating oils Fluorinert FC-70, Krytox 100 and Krytox 103.

3.5. Characterization

3.5.1. Mechanical properties (Papers I, II and IV)

Mechanical properties of electrospun fibre mats (Paper I) were studied with a Deben Microtensile equipped with a 50 N load cell. All the samples were tested within 24 h after the electrospinning at a strain rate of 10 %/min (22 °C, relative humidity of ca. 20 %). To ensure safe transfer of delicate fibres mats from the collector to the tensile tester, a new method using template-transfer was developed. Masks from aluminum foil were attached to the collector prior to electrospinning, enabling lifting of the mats and transferring to the tensile tester without stretching or breaking (Figure 9).

![Figure 9](image)

**Figure 9.** (a) Mask from aluminium foil attached to the collector and covered by aligned fibres, (b) the fibre mat secured in the template and (c) template cut along edges prior to tensile test.

Mechanical properties of the conductive nanopaper (Paper II) were studied using Universal Material Testing Machine Instron 5566 with 100 N load cell at strain rate 10 %/min (23 °C, 50 relative humidity). The samples were conditioned for 24 h.

Nanocomposites with PVAc (Paper IV) were characterized using Universal Material Testing Machine Instron 5944 equipped with a 50 N load cell at strain rate 50 %/min.
The samples were conditioned at 23 °C and 50 % relative humidity for 6 days prior to testing. Strain in the initial elastic region (up to 0.8 %) was calculated using 2D Digital Speckle Photography (DSP). White (for transparent samples) or black (for opaque samples) paint was sprayed on the samples, resulting in uniform fine pattern. Correlation was done using a LIMESS software.

3.5.2. Electrical conductivity (Paper I)

Electrical conductivity of the nanopaper was measured using a Keithley 6517B Electrometer/High Resistivity Meter together with a Keithley 8089 Resistivity Test Fixture.

3.5.3. Density measurement (Paper II)

The density of nanopapers was determined using the mercury displacement method.\sup{84}

3.5.4. Conductometric titration (Papers III and IV)

The amount of charge on cellulose was determined by conductometric titration. Typically, 50 mg of nanocellulose was suspended in 50 mL of water containing 1 mM NaCl. The titration was performed using a 0.01 M solution of NaOH (solution was standardized against oxalic acid) and the conductivity was monitored with a Mettler Toledo Conductivity meter (USA).

3.5.5. Infrared spectroscopy (Papers III, IV and V)

The presence of specific functional groups was determined using infrared spectroscopy with a Perkin-Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate, single reflection attenuated total reflectance (ATR) system (Specac Ltd., London, UK). The ATR crystal was a MKII heated diamond 45° ATR top plate.

3.5.6. Differential scanning calorimetry (Paper IV)

Differential Scanning Calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 820. Samples of approximately 5-10 mg were sealed in aluminum pans.

3.5.7. Dynamic mechanical thermal analysis (Paper IV)

Dynamic Mechanical Thermal Analysis (DMTA) was done using a TA instrument Q800 in tensile mode on rectangular samples (4 mm by 10 mm). The glass transition temperature was estimated from the onset of the storage modulus drop since the tan δ peak could not be obtained in a satisfactory manner.
3.5.8. Contact angle and roll-off angle (Papers III and V)

Contact angle (Papers III and V) and roll-off angle (Paper V) measurements were done with a CAM 200 (KSV Instruments Ltd, Helsinki, Finland) contact angle goniometer. Measurements were performed at 23 °C and 50 % relative humidity with Milli-Q water (Papers III and V) and hexadecane (Paper V). Tilting angles (Paper V) were measured by placing a water or hexadecane drop on top of the slippery surface. At a certain tilting angle the drop started to steadily move and the roll-off angle was recorded.

3.5.9. Microscopy

3.5.9.1. Scanning electron microscopy (Papers I – V)

The morphology of the samples was observed using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan). To observe flat surfaces (Papers I, II, V), specimens were fixed on a metal stub using carbon tape (nanopapers or fibre mats) or colloidal graphite (porous nanopapers). To study cross sections (Paper IV), samples were fractured under liquid nitrogen and attached to a metal split specimen holder. In all cases, samples were coated with thin layer of gold-palladium (Paper II) or platinum-palladium (Papers I, IV, V) using Cressington 208HR Sputter coater prior to observation.

To capture transmitted electrons (STEM), suspensions of CNC-C (Paper III) were deposited on copper grid (Ultrathin Carbon Type-A, Ted pella).

3.5.9.2. Transmission electron microscopy (Papers I, IV and V)

Diluted suspensions were deposited on copper grid, stained with fresh 2 wt% uranyl acetate solution and visualized using a transmission electron microscope (Hitachi HT-7700, Japan) operated at 80 kV.

3.5.9.3. Atomic force microscopy (Paper I, II and III)

The surfaces of the specimens were imaged with tapping-mode atomic force microscopy (AFM; Multimode IIIa, Veeco Instruments, Santa Barbara, CA). RTESP silica cantilevers (Veeco Instruments, tip radius 8 nm and spring constant 40 N/m) were oscillated close to resonance frequency. The scan size was 1-5 µm².
4. RESULTS AND DISCUSSION

4.1. Preparation of nanocelluloses

4.1.1. Fibrils vs. crystals

In this thesis, different types of nanocelluloses were used and this section summarizes their morphology and functionalization depending on the disintegration route.

Nanofibrillated cellulose (NFC) isolated by enzymatic pre-treatment according to Henriksson\(^4\) consisted of mixture of individual fibrils and somewhat larger fibril aggregates, which were several micrometres long (Figure 10). Apart from cellulose hydroxyls, there are no other functional groups on the surface of the fibrils (Figure 11) and the charge content is very low (Table 2). Possibly, some hemicelluloses may be present at the surface.

Mild chemical pre-treatment by TEMPO-mediated oxidation as described by Saito\(^6\) resulted in suspensions of well-individualized cellulose nanofibrils (TO-NFC, Figure 10). During the reaction, the primary hydroxyl groups are converted into carboxyl groups (Figure 11), resulting in rather high charge content (Table 2).

Stiff, rod-like cellulose nanocrystals (Figure 10) were obtained after sulphuric acid hydrolysis of wood pulp according to Beck-Candanedo.\(^81\) The suspension was stabilized by electrostatic repulsion of sulphate ester groups, but the charge is not as high as for TO-NFC (Table 2).

To broaden the toolbox of available nanocelluloses, in Paper III, TO-NFC was subjected to hydrolysis with hydrochloric acid and a new route for isolation of CNC (CNC-C) was developed (Figure 10). The carboxylic groups introduced during TEMPO-mediated oxidation remain intact after the hydrolysis, leading to highly charged cellulose nanocrystals with a carboxylate content of 1.5 mmol/g (Table 2). When wood pulp is subjected directly to hydrolysis with hydrochloric acid, the resulting nanocrystals do not have any charged groups and therefore the suspensions tend to flocculate. Attempts were made to improve the stability of the aqueous suspensions in water by subsequent post-treatment with TEMPO-mediated oxidation to introduce charged carboxylic groups.\(^85-87\) The maximum amount of charged groups introduced during this reaction was 1.2 mmol/g.\(^85,86\) However, Saito et al.\(^88\) showed that the charge content introduced by TEMPO-mediated oxidation of non-hydrolyzed pulp can be as high as 1.5 mmol/g and therefore provided inspiration to the approach developed in Paper III.
4.2. Electrospun fibres

One of the objectives of this thesis was to develop new materials based on nanocelluloses from wood. When nanocellulose or nano-reinforcements in general are combined with other matrices, mutual compatibility is a key issue. Here, poly(methyl methacrylate) (PMMA, Figure 12) was chosen as a matrix. Several studies\textsuperscript{17, 89-92} have shown favourable compatibility between nanocellulose and acrylic resins and used cellulose’s native surface functional groups. Moreover, PMMA is soluble in a large range of organic solvents and is known to be suitable for electrospinning\textsuperscript{93}. The aim of the study is to prepare mats of composite fibres based on PMMA and NFC and to develop a reliable method for mechanical testing of these mats. The main challenge in successful preparation of composite fibres was to ensure a good dispersion of NFC in the electrospinning solution.
4.2.1. Fibre preparation

In order to prepare composite fibres based on PMMA as matrix and NFC as reinforcement, the solvent choice plays an important role. The dielectric constant and vapor pressure of the solvent are important parameters and it needs to be suitable for the chosen polymer. To ensure good dispersion of NFC in composite fibres, it is crucial that NFC can be well dispersed in the solvent. PMMA is soluble in large range of solvents including methyl methacrylate, toluene, dichloromethane, acetone and DMF.

To choose the best solvent for preparation of composite fibres, the water of original NFC suspension was carefully exchanged to above-mentioned solvents and the quality of the dispersion was visually evaluated. However, it was found that in methyl methacrylate, toluene, acetone and dichloromethane, NFC fibrils formed agglomerates and flocculated. This would result in clogging of the needle during the electrospinning and more importantly, lead to agglomeration in the composite fibres. On the contrary, well-dispersed and stable suspension of NFC in DMF was obtained and DMF was therefore chosen as solvent for electrospinning for both neat PMMA and composite fibres.

The solution of NFC and PMMA in DMF showed no visible agglomeration or flocculation of the fibrils even months after the preparation (Figure 13b). After optimization of electrospinning parameters, mats of randomly oriented as well as aligned fibres were prepared by collecting the fibres on either static or rotating collector, respectively. The morphology of the random and aligned fibre mats is shown in Figure
The individual fibres are uniform in shape and do not contain any visible beads or inhomogeneity. The presence of beads or other defects would decrease the mechanical performance of the fibres. The mats of non-aligned fibres contained randomly oriented fibres and occasionally coils of fibres (Figure 14a). The average diameter of neat PMMA fibres is $2.02 \pm 0.34 \, \mu m$ (Figure 15a) while the diameter of aligned fibres was found to be smaller, $1.74 \pm 0.35 \, \mu m$ (Figure 15b). The difference is most likely due to stretching of the fibres during the collection on the rotating drum (speed 2 000 rpm). Aligned PMMA/NFC has however larger diameter, $2.70 \pm 0.58 \, \mu m$ (Figure 15c), even though the conditions for collection were the same as in case of the neat PMMA fibres. This is believed to be due to the increased viscosity of the electrospinning solution after addition of NFC.

**Figure 14.** FE-SEM micrograph of (a) a non-aligned fibre mat (static collector) and (b) a mat of aligned fibres in the horizontal direction (rotating cylindrical collector), and magnified parts in each case.

**Figure 15.** Size distribution of (a) non-aligned and (b) aligned PMMA fibres and (c) aligned PMMA–NFC fibres.

### 4.2.2. Reinforcement with nanocellulose

Mechanical properties of the fibre mats were tested using uniaxial tensile test. Typical stress-strain curves for randomly oriented and aligned PMMA fibre mats as well as aligned PMMA/NFC fibre mats are shown in Figure 16. Average mechanical properties of the mats of random and aligned fibres are summarized in Table 3. For neat PMMA fibre mats, the tensile strength of the aligned fibres was three times higher.
compared to the randomly oriented fibres. The increase in Young’s modulus is even more significant: from 0.27 GPa for the randomly oriented fibres to 1.49 GPa for the aligned fibres. In both cases, the fibres are made of neat PMMA and therefore the difference in mechanical properties is purely due to the different morphology of the fibre mats. As visible from the SEM images (Figure 14a), the mat of randomly oriented fibres contains loops of fibres. In the initial stages of tensile test, these looped fibres were not loaded. Instead, they went through an un-coiling (alignment) process as the load increased. This poor load bearing of the fibre mats as well as the stress-induced alignment could explain the low strength/stiffness and the high strain to failure observed in the neat PMMA samples. In contrast fibres that had been aligned before testing were instantaneously stretched as the test started, leading to higher initial modulus of aligned mats and therefore giving superior mechanical performance. Furthermore, the results are in agreement with previously published data for poly(caprolactone), poly(ethylene oxide) and PMMA,\textsuperscript{94-96} as well as for composites of impregnated electrospun fibres.\textsuperscript{97}

Table 3. Average mechanical properties for mats of electrospun fibres.

<table>
<thead>
<tr>
<th>Mat type</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Toughness (kJ/m\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA random</td>
<td>5.0 ± 0.7</td>
<td>0.27 ± 0.05</td>
<td>---</td>
</tr>
<tr>
<td>PMMA aligned</td>
<td>16.8 ± 3.7</td>
<td>1.49 ± 0.29</td>
<td>126 ± 38</td>
</tr>
<tr>
<td>PMMA/NFC aligned</td>
<td>21.9 ± 1.7</td>
<td>1.93 ± 0.34</td>
<td>157 ± 18</td>
</tr>
</tbody>
</table>

The addition of just 4 wt\% of NFC further enhanced the mechanical performance of fibre mats. Approximately 30 \% increase in strength and modulus is observed as compared to neat PMMA fibres (Table 3). Moreover, the toughness of the aligned fibres (fracture energy calculated from the area under the stress-strain curve) increased by approximately 25 \% from 126 ± 38 kJ/m\textsuperscript{3} to 157 ± 18 kJ/m\textsuperscript{3}.

Figure 16. Stress-strain data for the aligned PMMA and cellulose- reinforced PMMA fibre mats, and for the non-aligned (random) PMMA fibres.
The modified rule of mixture was used to estimate the theoretical modulus of composite fibres reinforced with NFC:

\[ E_C = \eta_o \eta_l \phi_f E_f + (1 - \phi_f)E_m \]

where \( \eta_o \) is the NFC orientation factor and \( \eta_l \) is the fibre length efficiency. \( E_c, E_f \) and \( E_m \) are the modulus of the composite, NFC and PMMA matrix, respectively. \( \phi_f \) is the volume fraction of NFC (estimated from weight fraction and the densities of NFC and PMMA). \( \eta_l \) can be estimated from the shear lag model obtained by Cox:

\[ \eta_l = 1 - \frac{\tan (\frac{\beta L}{D})}{\beta} \]

where

\[ \beta = 2 \left( \frac{L}{D} \right) \left( \frac{G_m}{E_f \ln}\left( \frac{k}{\phi_f} \right) \right) \]

\( L \) and \( D \) are the length and diameter of the NFC and \( G_m \) is the shear modulus of the PMMA matrix (estimated from: \( G_m = E_m/(2(1 + \nu)) \)) where \( E_m \) is experimentally obtained and equal to 1.49 GPa, and \( \nu \) is the Poisson’s ratio for PMMA\(^{100} \). \( k \) is 0.907 if hexagonal packing of fibres is considered. From the micrographs of the NFC suspension, fibril length \( L \) was estimated to be between 0.5 and 2 \( \mu \)m and diameter \( D \) between 15 and 30 nm, giving a maximum and a minimum \( L/D \) ratio equal to 133 and 17. \( E_f \) was assumed to be 60 % of the 130 GPa modulus of 100 % crystalline cellulose (corresponding to a sample with 60 % crystallinity).

Assuming NFC is perfectly aligned within PMMA matrix, predicted values of the fibre modulus were 2.42 and 3.69 GPa, depending on aspect ratio of NFC, which is higher than measured modulus of 1.93 GPa. The difference between theoretical and experimental values of the modulus could be caused by assumption of perfect alignment of NFC within the fibres, lower modulus of neat NFC than used in the model and deviations in fibre orientation and packing. Furthermore, even for aligned mats, all fibres are not uniformly loaded. Taking into account all these factors, adhesion between NFC and PMMA appeared to be favourable.

### 4.2.3. Morphology

The improvement of mechanical properties suggests good dispersion of NFC within PMMA matrix as well as good adhesion between the two. Agglomerates would act as defects and possibly cause a reduction in the strength of the fibres. To confirm this, the dispersion of the NFC within the PMMA matrix was studied using FE-SEM. From Figure 17b it seems that the PMMA and NFC show favourable interaction. The fracture
surface of the composite fibre shows that the cellulose fibrils were homogenously distributed in the PMMA matrix without any agglomerates. Moreover, only very short NFC pull-out lengths were apparent, indicating good interaction between the components.

**Figure 17.** FE-SEM micrographs of fracture surfaces of (a) neat PMMA and (b) PMMA/NFC composite fibres after tensile testing, with a magnified image illustrating NFC pull-out.

### 4.3. MWCNT/TO-NFC hybrids

The aim of Paper II is to develop a water-based route for the preparation of electrically conductive nanopaper by combining for the first time cellulose nanofibrils from wood and multi-walled carbon nanotubes (MWCNT). Cellulose and CNT appear to be mutually incompatible because of their contrasting surface characteristics. Thus, to prepare high performance materials by combining these two, it is important to either modify cellulose to make it hydrophobic or modify CNT to make it hydrophilic. The former requires the use of organic medium, so the route of CNT modification (keeping water as the medium throughout) was adopted in this study. To avoid alteration of CNT structure by covalent modification a surfactant, nonylphenol polyoxyethylene (10) phosphate ester (abbreviated as NPPE, Figure 18), was used.

![Nonylphenol polyoxyethylene (10) phosphate ester (NPPE).](image)

It seemed impossible to disperse unmodified MWCNT in water without any surfactant (Figure 19a). Even after sonication, hydrophobic MWCNTs formed bundles and agglomerates. Similarly, MWCNTs precipitated when added directly to TO-NFC suspension (Figure 19c). However, after addition of MWCNTs into NPPE solution, hydrophobic parts of surfactant molecules adsorbed onto the surface of MWCNTs, and the hydrophilic phosphate ester groups ensured formation of stable suspension in water (Figure 19b). The desired amount of MWCNTs suspension in the presence of surfactant
was added to TO-NFC and, after thorough mixing, MWCTs were homogenously dispersed in TO-NFC. Strong electrostatic repulsion between the phosphate groups and the carboxylic groups on the surface of TO-NFC kept the suspension stable and no visible agglomerates were formed even when the suspension was left standing for more than 6 months.

Figure 19. Photography of: MWCNT suspension (5 mg/mL) in water (a) without and (b) with 20 mg/mL NPPE surfactant, MWCNT mixed with NFC suspension in water (c) without and (d) with NPPE (concentration is 0.1 mg/mL for NFC and 0.01 mg/mL for MWCNT; this corresponds to a nanocomposite composition of 9.1 wt% MWCNT and 90.9 wt% NFC).

4.3.1. Morphology

Hybrid nanopapers with a MWCNT content between 0.5 and 16.7 wt% were prepared by conventional paper-making approach previously described by Schaqqui et al.16 This process involves thorough mixing of the components prior to filtration and therefore enables control of the structure in the resulting material. This offers a considerable advantage as compared to previous studies where CNTs were added directly to bacterial cellulose pellicles49,101 both in terms of structural control and possible up scaling. FE-SEM micrographs and AFM phase images of nanopaper structures are presented in Figure 20 (FE-SEM) and Figure 21 (AFM). Pure NFC nanopaper possessed a random-in-plane network structure of cellulose nanofibrils (Figure 20a and Figure 21a). The NPPE modified MWCNT were well individualized in water and an entangled network was obtained after drying (Figure 20b and Figure 21b). To confirm the homogenous distribution of CNTs, the top (Figure 20c and Figure 21c) as well as the bottom surface (Figure 20d and Figure 21d) of the composite samples (9.1 wt%) were observed. Comparison of the two surfaces suggested that MWCNTs were homogenously incorporated in the cellulose nanofibrils network. Even though other commonly used surfactants such as sodium dodecyl sulphate (SDS) and Triton x-100 could also provide a stable dispersion of MWCNT in water, they did not ensure sufficient compatibility between surfactant-modified MWCNT and TO-NFC. In preliminary experiments using SDS and Triton x-100, heterogeneous composites were obtained where most CNTs were concentrated on one side of the sample. This indicates that NPPE surfactant not
only disperse MWCNT sufficiently well in water but, more important, acts as a compatibilizer.

Figure 20. FE-SEM micrographs of (a) NFC nanopaper, (b) NPPE modified MWCNT, (c) top surface and (d) bottom surface of NFC/CNT nanopaper containing 9.1 wt% MWCNT.

Figure 21. AFM phase images of (a) NFC nanopaper, (b) NPPE modified MWCNT, (c) top surface and (d) bottom surface of composite containing 9.1wt% MWCNT.

To study the evolution of percolation of MWCNT in TO-NFC matrix, the morphology of samples with increasing MWCNT content was studied with FE-SEM (Figure 22). Micrographs revealed that in the sample with MWCNT content of 2.0 wt%, the CNTs were individually dispersed in the NFC network and there were almost no connections between CNTs. As the MWCNTs content increased (5.7 wt%), the number of contacts between CNTs increased until a continuous network is formed at 9.1 wt% MWCNT. However, further increase of the MWCNTs content to 16.7 wt% caused agglomeration.

Figure 22. Morphology of nanopaper at different concentrations of MWCNT in NFC by weight: (a) 2.0 wt%, (b) 5.7 wt%, (c) 9.1 wt% and (d) 16.7 wt%.
4.3.2. Mechanical properties

Mechanical properties of nanopapers were studied using tensile test and the typical stress-strain curves are presented in Figure 23. Average physical properties and standard deviations are listed in Table 4. From the stress-strain curves (Figure 23) it is obvious that at low strains (<1%) the stress-strain behaviour is linear elastic. As the stress increases, a knee in the curve appears (apparent yield stress $\sigma_{0.2} \sim 90-120$ MPa) and is followed by a linear and fairly strong strain-hardening plastic region.$^{15}$ The Young's modulus was determined from the slope of the linear elastic regions of the curves.

For the neat NFC nanopaper, the Young's modulus was 9.26 GPa. This value is high considering the porosity of the sample (approximately 40%), which has a strong influence on the mechanical properties of the nanopaper. There seems to be a direct correlation between the amount of surface charges on the cellulose nanofibrils and the porosity of resulting nanopaper prepared from surface quaternized nanofibrils.$^5$ Such nanopaper showed increased porosities (37-48%) as the surface charge increased (0.59-2.31 mmol/g)$^5$, whereas nanopaper prepared from nanofibrils obtained using mild enzymatic treatment having very low surface charge gave porosity in the range of 20-28%.$^5$

As the MWCNT content increases, the Young's modulus as well as the tensile strength slightly decreases. However, even at CNT loading of 7.4 wt% CNT and porosity as high as 47%, the Young's modulus is 7.45 GPa, the strength is 210 MPa and strain to failure 7.2%. These remarkably high values are due to the strength of the NFC network itself and are maintained up to CNT's loading of 9.1 wt%, leading to flexible, tough and at the same time lightweight materials.

Figure 23. Typical stress-strain curves of composite nanopapers at different MWCNT content.
### Table 4. Average properties of nanopapers (the standard deviations are in parentheses).

<table>
<thead>
<tr>
<th>MWCNT content (wt%)</th>
<th>Density (kg/m³)</th>
<th>Porosity (%)</th>
<th>MWCNT content (vol%)</th>
<th>Young’s modulus E (GPa)</th>
<th>Tensile strength σ (MPa)</th>
<th>Strain to failure ε (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.889</td>
<td>40.7</td>
<td>0.0</td>
<td>9.26 (0.43)</td>
<td>239 (23.0)</td>
<td>6.2 (0.9)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.906</td>
<td>39.8</td>
<td>0.4</td>
<td>9.15 (0.65)</td>
<td>199 (35.0)</td>
<td>4.8 (1.2)</td>
</tr>
<tr>
<td>2.0</td>
<td>0.960</td>
<td>36.5</td>
<td>0.9</td>
<td>8.78 (0.33)</td>
<td>212 (8.6)</td>
<td>6.1 (0.4)</td>
</tr>
<tr>
<td>4.8</td>
<td>0.848</td>
<td>44.5</td>
<td>1.9</td>
<td>8.54 (0.43)</td>
<td>208 (13.0)</td>
<td>6.5 (1.0)</td>
</tr>
<tr>
<td>5.7</td>
<td>0.859</td>
<td>44.0</td>
<td>2.3</td>
<td>8.25 (0.27)</td>
<td>205 (13.0)</td>
<td>6.6 (0.8)</td>
</tr>
<tr>
<td>7.4</td>
<td>0.823</td>
<td>46.7</td>
<td>2.9</td>
<td>7.54 (0.22)</td>
<td>210 (15.0)</td>
<td>7.2 (0.6)</td>
</tr>
<tr>
<td>9.1</td>
<td>0.820</td>
<td>47.3</td>
<td>3.5</td>
<td>7.72 (0.24)</td>
<td>183 (8.7)</td>
<td>6.0 (0.4)</td>
</tr>
<tr>
<td>16.7</td>
<td>0.731</td>
<td>54.3</td>
<td>5.8</td>
<td>2.60 (0.16)</td>
<td>66 (8.3)</td>
<td>6.9 (1.1)</td>
</tr>
</tbody>
</table>

### 4.3.3. Electrical conductivity

For composite materials, the electrical conductivity depends strongly on the volume fraction of the conductive phase in the insulating matrix. The values of the direct current (DC) conductivity for samples of two different thicknesses (25 and 50 µm) are shown in Figure 24. At low CNT content, the conductivity remains very close to the conductivity of the matrix (neat TO-NFC nanopaper) due to few contacts between the CNTs (as also obvious from Figure 22a). At compositions between 6 and 9 wt%, the conductivity increases significantly (more than 4 orders of magnitude), indicating that CNTs form a continuous percolated network and then conductivity does not further increase with addition of CNTs. Depending on the matrix, the processing technique and the CNT type used, percolation thresholds ranging from 0.001 wt% to more then 10 wt% have been reported. Similar percolation thresholds were observed previously for the conductive paper prepared from SWCNT and bleached hardwood kraft pulp fibre.

![Figure 24. Conductivity σ<sub>DC</sub> versus MWCNT concentration p (wt%).](image)

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4.4. Surface modification of cellulose nanocrystals

The next objective is to develop a versatile method for surface functionalization of cellulose nanocrystals (CNC) using adsorption of quaternary ammonium salts. CNC were used for this study as they provide better control of the surface modification in the suspension. To explore the versatility, cellulose nanocrystals obtained by two different methods were used: highly charged nanocrystals prepared by hydrochloric acid hydrolysis of TO-NFC, having carboxylic groups on the surface (CNC-C) and medium charged nanocrystals having sulphate ester groups (CNC). To demonstrate the applicability of our approach, different quaternary ammonium salts were used: octyltrimethylammonium chloride (C8), dodecyltrimethylammonium chloride (C12), stearlytrimethylmonium chloride (C18), glycidyl trimethylammonium chloride (COC), diallyldimethylammonium chloride (C=C) and phenyltrimethylammonium chloride (CPh), Figure 25.

![Figure 25. Schematic illustration of adsorption of quaternary ammonium salts onto CNC.](image)

**Figure 25.** Schematic illustration of adsorption of (1) stearlytrimethylmonium chloride, (2) diallyldimethylammonium chloride, (3) glycidyl trimethylammonium chloride, (4) phenyltrimethylammonium chloride and (5) dodecyltrimethylammonium chloride onto CNC.

4.4.1. Modification of CNC-C

An attempt to find the optimal ratio between CNC and quaternary amines was made by testing different molar ratios of the charged groups (either carboxylic or sulphate esters) and quaternary amines.

First a more detailed study was performed with CNC-C and C18, and three different molar ratios were tested (CNC:C18 = 1:1, 1:2 and 1:4). The samples were weighed after the freeze-drying to calculate the adsorbed amount of C18 in the modified sample and the results are summarized in Table 5. It was found that a ratio of cellulose to C18 1:1 is not sufficient to provide complete surface coverage of cellulose. On the other hand, there is no difference in the surface coverage for samples 1:2 and 1:4. The coverage is
approximately 90% in both cases, which seems to be the maximum value that can be achieved with the given method. Therefore, for further experiments with all quaternary amines, a molar ratio 1:2 was deemed sufficient to obtain maximum surface coverage.

Table 5. Determination of C18 content after the adsorption.

<table>
<thead>
<tr>
<th>CNC-C:C18 ratio</th>
<th>Adsorbed amount (mg)</th>
<th>C18 content in the sample (mmol)</th>
<th>Real ratio CNC-C:C18</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>7.30</td>
<td>0.021</td>
<td>1:0.28</td>
</tr>
<tr>
<td>1:2</td>
<td>24.1</td>
<td>0.069</td>
<td>1:0.92</td>
</tr>
<tr>
<td>1:4</td>
<td>23.3</td>
<td>0.067</td>
<td>1:0.89</td>
</tr>
</tbody>
</table>

Modified freeze-dried nanocrystals were dispersed in acetone, THF, chloroform and toluene. In acetone and THF, very poor suspensions were obtained; particles were visible by the naked eye and the suspension sedimented rather quickly. A translucent suspension was obtained after re-dispersion in chloroform and finally, a transparent suspension was obtained in toluene for samples CNC-C/C18 1:2 and higher. Sample CNC-C/C18 1:1 gives translucent suspension in toluene. This could be due to a lower surface coverage of cellulose with C18. On the other hand, ratio 1:4 did not further improve the quality of the suspension. These observations further supported the previous hypothesis that a molar ratio 1:2 between CNC-C and C18 is sufficient. The quality of the dispersion of C18 modified CNC-C in toluene was observed using FE-SEM equipped with transmitted electrons detector (Figure 26) and with unmodified CNC-C in water as control sample. In both cases, individualized rod-like particles were homogenously distributed on the grid. Most likely, the problems at higher CNC-C/C18 ratio (1:4) are due to micelle formation at higher relative C18 concentrations, see coming section.

Figure 26. Transmitted electron images of (a) unmodified nanocrystals dried from water and (b) C18 modified nanocrystals dried from toluene.

Fourier Transform Infrared Spectroscopy (FT-IR) confirmed that the surface modification of CNC-C was successful (Figure 27). Before the adsorption (CNC-C
curve), the spectrum of CNC-C shows a peak at 1730 cm⁻¹ (corresponding to C=O stretching of carboxyl groups in their acidic form), while the spectrum of the modified nanocrystals shows that this peak is shifted to approximately 1600 cm⁻¹, which is assigned to the carboxylate group. Moreover, strong bands at 2900 cm⁻¹ and 2850 cm⁻¹ corresponding to asymmetrical and symmetrical CH₂ stretching from the long alkyl chain of stearyltrimethylammonium chloride, were observed in the spectrum of modified CNC-C. Figure 22b shows FT-IR spectra of CNC modified with CPh, COC, CC and C18. In all cases, the peaks corresponding to carboxyl groups were shifted to peaks corresponding to carboxylates.

Quaternary ammonium salts have already been used in modification of nanofibrillated cellulose to reduce the water wettability. In these studies, adsorption isotherms and contact angle were investigated and the presence of surfactant double layers and undesirable micelles was confirmed. However, re-dispersion of the quaternary amine modified nanocellulose in organic solvent is reported for the first time here. Re-dispersion in organic solvent (or washing of model surface with toluene) might lead to reorganization of the micelles. The presence of a monolayer of surfactant is likely to result in a more hydrophobic cellulose surface.

The main advantage of surface modification of cellulose nanocrystals in water using the present clay chemistry is its simplicity, flexibility, high yield and broad scale of possible functional groups.

4.4.1. Effects of washing step and alkyl chain length

The effects of the washing step in toluene and the alkyl chain lengths of the quaternary ammonium salts were studied on smooth model films (approximately 30 nm thick) prepared by spin-coating of the nanocrystal suspension on Si wafers.
The model surface containing unmodified CNC-C had a contact angle with water of 12°. The model surface prepared from C18-modified cellulose nanocrystals washed with water showed a higher contact angle with water of 48°. The model surface of C18-modified CNC-C washed with toluene showed on the other hand much higher contact angle with water of 71°. This demonstrates the importance of the washing step, during which the micelles reorganize themselves and the possible excess of surfactant is removed. The water drops and the AFM images of the corresponding surfaces are shown in Figure 28.

The effect of alkyl chain length was studied on model surfaces of CNC-C modified with C8 and C12 and washed with toluene. It was found that adsorption of C8 resulted in a contact angle of 74° and surprisingly, modification with C12 lead to contact angle of 85° (Figure 28). Similar comparison was done by de Menezes et al.,106 where alkyl chains of different lengths (hexanoyl, lauroyl and stearoyl chlorides) were introduced onto cellulose nanocrystals via esterification reaction with organic acid chlorides. However, in de Menezes et al.,106 the highest contact angle with water was measured for nanocrystals modified with stearoyl chloride (18 carbons). The difference could be caused by different arrangement of covalently grafted or physically adsorbed molecules on the surface of CNC. For further experiments, C12 will be used, because it resulted in the highest contact angle with water compared to other quaternary ammonium salts.

![Figure 28. Contact angle and corresponding AFM image of model surface of (a) unmodified CNC-C and (b) C18 modified CNC-C washed with water, (c) C18 modified CNC-C washed with toluene, (d) C8 modified CNC-C washed with toluene and (e) C12 modified CNC-C washed with toluene. The size of the AFM images in the upper corners corresponds to 5 µm.](image)

4.4.2. Modification of CNC

Due to the gel-like consistency of the CNC-C suspension at a solid content higher than 0.5 wt% (caused by the high surface charge density), the adsorption needs to be performed at very dilute suspensions (less than 0.1 wt%). Large quantities of water thus needed to be removed in the later stage of the modification. This increases the energy needed for the process. CNC prepared by sulphuric acid hydrolysis are only moderately charged and therefore their suspensions flow even at high solid content (few wt%). Adsorption can therefore be performed at higher concentrations and the amount of
water to be removed can be reduced. Moreover, CNC can be prepared in large scale and therefore it is more suitable for further applications.

In this study, the previously developed approach based on adsorption of quaternary ammonium salts is applied on CNC with sulphate esters, and dodecyltrimethylammonium chloride (C12) is used for hydrophobization.

To optimize the reaction conditions, four different molar ratios between CNC sulphate ester groups and C12 were chosen (1:2, 1:4, 1:8 and 1:16). The adsorption was successful in all cases as confirmed by FT-IR (Figure 29). The intensity of the bands at 2900 cm\(^{-1}\) and 2850 cm\(^{-1}\) corresponding to the presence of alkyl chain of C12 molecules increased with increasing content of C12 (CNC:C12 ratios 1:8 and 1:16). This could indicate that C12 formed micelles at such high content.

![Figure 29. FT-IR spectra of unmodified and C12 modified CNC with four different CNC:C12 ratios.](image)

The freeze-dried nanocrystals were thereafter dispersed in toluene (Figure 30). Similarly to our previous study with CNC-C, it was not possible to properly disperse CNC modified with C12 at the lowest ratio (1:2). The suspension contained large agglomerates and sedimented over a period of a few minutes. For C12-modified CNC with CNC:C12 ratios of 1:4, 1:8 and 1:16 stable suspensions in toluene were obtained (Figure 30). The transparency of the suspensions decreased with increasing amount of C12. This is likely to be caused by formation of C12 micelles at higher CNC:C12 ratios.\(^{102,103}\) This also explains higher intensity of peaks corresponding to long alkyl chain of C12 in the FT-IR spectrum (Figure 29). Based on the observations, a CNC:C12 ratio of 1:4 was chosen for further experiments, because it provided stable suspension in toluene with the least amount of C12.
Figure 30. Photography of CNC suspensions - left to right: unmodified CNC in water, unmodified CNC in toluene, C12-modified CNC with different ratios CNC:C12 of 1:2, 1:4, 1:8 and 1:16.

The quality of the dispersion of the modified CNC in toluene was studied using a transmission electron microscope (TEM). Unmodified CNC in water and in toluene were used as reference. Unmodified CNC was well dispersed in water (Figure 31a), but formed large micrometre scale agglomerates in toluene (Figure 31b). In contrast, modified CNC (modCNC) 1:4 in toluene was well dispersed and individualized without forming any agglomerates (Figure 31c).

Figure 31. (a) TEM image of unmodified CNC dried from water, (b) TEM image of unmodified CNC dried from toluene and (c) TEM image of C12 modified CNC (ratio 1:4) dried from toluene.

4.5. Nanocomposites with PVAc

Cellulose nanocrystals are commonly used as reinforcement in nanocomposites. However, it is often very difficult to efficiently disperse CNC in various matrices and often studies with inhomogeneous nanocellulose dispersion are reported. Due to the presence of agglomerates, the material properties were not improved as expected. The focus here is on the importance of good dispersion of CNC in the matrix and the structure-property relationships. Even though freeze-drying makes it possible to use modified CNC powder in melt mixing, we chose processing in solution as a model system to study the dispersion of modified CNC in PVAc.

CNC nanocomposites with PVAc matrix were prepared by direct addition of PVAc into a CNC suspension in toluene followed by thorough mixing and solvent casting (Figure 32). The CNC content was 1-20 wt%. In order to observe the effect of the surface
functionalization on the properties of the nanocomposite, samples with both modified CNC (1:4) and unmodified CNC were prepared. CNC/PVAc nanocomposites were translucent with visible agglomerates, whereas modCNC/PVAc nanocomposites were homogenous and transparent.

**Figure 32.** Schematic illustration of nanocomposite preparation: isolation of CNC from wood pulp by sulfuric acid hydrolysis ([Reprinted with permission from Saito et al.](https://doi.org/10.1021/ja0740195) © 2007 ACS) followed by surface modification with C12 in aqueous suspension, freeze-drying and redispersion of modified CNC in toluene, addition of PVAc and removal of the solvent by casting and resulting nanocomposite.

PVAc is known to undergo physical aging at and around its glass transition temperature ($T_g$). This is generally due to the molecular rearrangements and will influence those properties which undergo drastic changes at $T_g$ such as mechanical properties — the material will become stiffer and more brittle. In this study, aging was not studied per se, but the composite $T_g$ was studied as a function of time using differential scanning calorimetry (DSC) in an attempt to find a stable state for further characterization.

In the case of nanocomposites with unmodified CNC, there is a significant decrease of $T_g$ on day 3 followed by slight increase (Figure 33a). In contrast, the $T_g$ of composites with modCNC gradually increases up to day 5 and remains constant afterwards (Figure 33a). Similar behavior was observed for a pure PVAc film, where the increasing trend levels off after 3 days (Figure 33a). The presence of modCNC in the PVAc matrix seems
to slow down the aging process. This phenomenon can be related to a reduction of the polymer segmental dynamics, likely originating from adsorption of the polymer on the nanofiller surface.\textsuperscript{107} To eliminate effects of aging, further characterizations (DMA, tensile test) were performed 6 days after film casting.

The effect of nanosize confinement on $T_g$ of polymers has been widely studied, commonly on ultrathin films supported with various substrates.\textsuperscript{109} It was found that the $T_g$ is influenced by the polymer-substrate interactions and the free surface factor, which affects the contact area of the two components. In case of poor polymer-substrate interaction, the $T_g$ is reduced and in contrast, moderate or strong polymer-substrate interactions (such as hydrogen bonds) lead to increase in $T_g$. Therefore in nanocomposites $T_g$ decreases (as compared to neat polymer) in case of a poor interaction between polymer and filler and increases when good wetting and polymer-filler interactions occur.\textsuperscript{109}

DMTA was used to study the effect of temperature on the mechanical properties of the nanocomposites. Figure 33b shows the storage modulus as a function of temperature for composites with unmodified and modified cellulose. Addition of 10 wt\% of unmodified CNC caused the $T_g$ to drop down more than 15 °C, whereas addition of only 3 wt\% of modCNC led to almost 20 °C increase in $T_g$ and further increase with increasing modCNC content. This indicates a good interaction between modCNC and PVAc matrix.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure33.png}
\caption{(a) A dependence of $T_g$ on time after casting as determined by DSC analysis and (b) development of $T_g$ with cellulose content measured by DMTA six days after casting.}
\end{figure}

\section*{4.5.1. Mechanical properties}

Effect of the CNC dispersion on the mechanical properties was studied using uniaxial tensile test. Typical stress strain curves for PVAc/CNC and PVAc/modCNC composites are shown in Figure 34 (a) and (b), respectively. Although the unmodified CNC led to improvement in tensile strength and stiffness, the increase was not as
significant as in the case of the modified CNC (Figure 35). With addition of only 5 wt% of modCNC, the Young’s modulus as well as the tensile strength increased ca. 30 times. This composition also showed the maximum reinforcement, and with further addition of modCNC the strength and modulus reached a plateau or even decreased.

It is apparent that the increased modulus and strength correlates with the increase in \( T_c \). However, the preserved high values for strain to failure in composites with modCNC content below 5 wt% indicates very favourable dispersion of modCNC.

4.5.2. Morphology

One of the aims of this study was to evaluate the effect of the dispersion of the nanoparticles on the properties of the nanocomposites. The degree of dispersion was therefore studied using FE-SEM and the fracture surfaces of the samples are shown in Figure 36. Nanocomposites with 20 wt% of unmodified CNC (Figure 36b) contained large micrometre size agglomerates of undispersed CNC. On the other hand the fracture surfaces of nanocomposite with 20 wt% modified CNC (Figure 36c) was very
uniform with well individualized CNC homogenously dispersed in the PVAc matrix. FE-SEM images provide further evidence that modification of CNC with C12 significantly improves mutual compatibility between otherwise hydrophilic CNC and PVAc.

![FE-SEM images of fracture surfaces of (a) pure PVAc, (b) nanocomposite containing 20 wt% unmodified CNC (arrows pointing to agglomerates) and (c) nanocomposite with 20 wt% modified CNC. Inlets show magnified sections of corresponding samples.](image)

**Figure 36.** FE-SEM images of fracture surfaces of (a) pure PVAc, (b) nanocomposite containing 20 wt% unmodified CNC (arrows pointing to agglomerates) and (c) nanocomposite with 20 wt% modified CNC. Inlets show magnified sections of corresponding samples.

### 4.6. Super-slippery films and coatings

Apart from utilizing the ability of nanofibrillated cellulose to form entangled network and act as reinforcement, the presence of reactive hydroxyl groups on its surface offers further possibilities for covalent functionalization. Taking advantage of the large specific surface area and the possibility to tailor the porosity as demonstrated by Schaqqui et al., functional membranes that can be infused with lubricant and result in surfaces that repel water and oil were manufactured. This work was inspired by Wong et al., replacing commercial Teflon membranes with renewable cellulose based materials.

Slippery surfaces were designed based on criteria defined by Wong et al., (I) the lubricant must wet and adhere within the substrate, (II) the solid substrate must be preferentially wetted by the lubricant rather than the liquid that is supposed to be repelled and (III) the lubricant and repelled liquid must be immiscible. In order to fulfill the first criteria, porous nanocellulose-based membranes were prepared by three different drying techniques. To ensure good wetting and chemical affinity between cellulose and lubricant, porous nanopapers were fluorinated with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (FTCS, Figure 38) prior to impregnation. In the case of the coatings, NFC was fluorinated in suspension before deposition on glass substrate. To fulfill the third criteria, low-surface tension perfluorinated liquids (3M Fluorinert FC-70, DuPont Krytox 100 and 103) were chosen. They are non-volatile and immiscible with water and hydrocarbon based liquids. Water (72.4 mN/m) and hexadecane (27.1 mN/m) were chosen as the liquids to be repelled.
Figure 37. Schematic illustration of (a) preparation of slippery films by fluorination of porous nanopaper and subsequent infusion with lubricant and (b) preparation of the slippery coatings by deposition of fluorinated NFC of glass substrate and followed by infusion with lubricant. The inlets in the gray frames show the droplet behavior on respective surface.

Figure 38. Tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane molecule (FTCS).

The success of fluorination was confirmed by FT-IR, where new bands characteristic of polyfluorinated compounds due to strong coupling of the C–F and C–C stretching vibration appear in the region between 1360 and 1090 cm\(^{-1}\) (Figure 39). A second evidence of the attachment of the fluorochlorosilanes to NFC surface is the presence of deformation vibration of the CF\(_2\) between 780 and 680 cm\(^{-1}\).\(^{111}\) A third indirect evidence is the significant increase in contact angle from 43 ± 3 \(^{\circ}\) for unmodified NFC to 168 ± 2 \(^{\circ}\) for f-NFC coating, making the surface superhydrophobic (Figure 39).
4.6.1. Roll-off angle

When a droplet of test liquid (water) was placed on the unmodified porous nanopaper, it got immediately absorbed in the structure (Figure 37a inlet 1). Despite the fact that fluorination with FTCS made the nanopaper hydrophobic, the drop of water pinned to the surface and did not slide away, even if sample was turned upside down (Figure 37a inlet 2). On the other hand when a droplet of water was placed on the surface of f-NFC coating, the droplet bounced off the surface instantaneously (Figure 37b inlet 4).

The surface roughness has a significant influence on the contact angle between the substrate and test liquid. Two most common cases may occur: the test liquid can either be in full contact with the rough surface (filling the voids of the roughness) and this situation is described by Wenzel model. The second case occurs when liquid does not fill the roughness and air pockets are created and this phenomena is described by the Cassie model. Surfaces described by Cassie model exhibit interesting behaviour, such as movement of test liquid droplets, as it was in the case of f-NFC. The friction between the surface and liquid might be reduced due to vapour that lies underneath.

After infusion with lubricant liquid, very smooth surfaces were obtained. Impregnation of unmodified porous nanopaper did not however result in slippery surface either. In this case, the substrate was preferably wetted by water instead of the lubricant due to the lower interfacial energy of water-cellulose configuration compared to lubricant-cellulose system. This resulted in displacement of the lubricant film and exposing of neat NFC substrate. This is an example of a situation, where criteria (II) was not fulfilled, a slippery surface was not obtained and the drop of water was pinned. Impregnation of fluorinated porous nanopaper with lubricant fulfilled all criteria defined by Wong et al. The surface of f-NFC nanopaper was preferably wetted by lubricant instead of water, which floated on the top of the lubricant film due to lower interfacial energy for the lubricant-f-
NFC than water-f-NFC system. Nanocellulose-based slippery surface was thus obtained for the first time.

To demonstrate that cellulose-based lubricant infused material is slippery for liquids with wide range of surface tension, the roll-off angle (angle to which the sample needs to be tilted for drop of liquid to slide) was studied for both water and hexadecane and the effect of the porous nanopaper structure was evaluated. The results are shown in Table 6. The roll-off angle for hexadecane was very low in case of all samples (in the range of 0.9° to 4.0°), but the roll-off angle for water varied depending on the substrate (from 1.3° to 19.7°). The lowest roll-off angle was observed for film based on f-NFC nanopaper (SCD) – 1.3° for water and 0.9° for hexadecane. Similar low angles were observed in case of f-NFC coating (3.5° and 0.8° respectively). The highest roll-off angle was measured for film based on f-NFC nanopaper prepared by freeze-drying from tert-butanol (19.7° for water) whereas f-NFC nanopaper prepared by freeze-drying from water gives tilting angle of 8.8° for water. The data obtained for lubricant infused f-NFC nanopaper (SCD) and f-NFC coating are in good agreement with work done by Wong et al.,110 where slippery films were prepared by impregnation of Teflon porous membranes or epoxy based nanostructured films infused with lubricant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Roll-off angle (°)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Hexadecane</td>
</tr>
<tr>
<td>f-NFC SCD</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>f-NFC TB FD</td>
<td>19.7</td>
<td>1.9</td>
</tr>
<tr>
<td>f-NFC water FD</td>
<td>8.8</td>
<td>4.0</td>
</tr>
<tr>
<td>f-NFC coating</td>
<td>3.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>

4.6.2. Morphology

Porous nanopapers prepared by different drying techniques and subsequently fluorinated with FTCS resulted in slippery films with different roll-off angles for water. This suggests that the chemistry is not the only parameter determining whether the surface is slippery or not and that morphology of the nanopaper plays an important role as well. FE-SEM was used to observe the structure both at low and high magnifications (Figure 40 and 41), and the pore size was estimated using image analysis.

There is a significant difference in the roughness of the samples on the micrometre scale. F-NFC nanopaper prepared by SCD has a homogenous and smooth structure (Figure 40a). There are only occasionally fibrils aggregates sticking out. Nanopaper prepared by freeze-drying from tert-butanol on the other hand contains cracks and inhomogeneity,
but is fairly flat otherwise (Figure 40b), as opposed to nanopaper prepared by freeze-drying from water, which is very rough and uneven (Figure 40c). The unevenness of the surface will create obstacles and cause the drop to pin and therefore lead to higher roll-off angles as compared to smooth nanopaper prepared by SCD. Interesting architecture was observed in case of f-NFC coating (Figure 40d), showing pores in micrometre as well as nanometre range.

At higher magnifications, open pore structure was observed in all cases. However, the pore size was very dependent on the drying technique (Figure 41), as previously reported by Sehaqui et al. Nanopapers prepared by drying with supercritical CO$_2$ (Figure 41a) had fairly uniform pores with an average size of 59 ± 28 nm and the structure represented individualized fibrils and fibril aggregates. By freeze-drying from tert-butanol, nanopapers with much smaller pores were obtained (35 ± 23 nm, Figure 41b) and fibrils were more aggregated than in the previous case. The more dense structure of the TB FD nanopaper could lead to poorer impregnation with lubricant and together with the cracks and inhomogeneity on the micrometre scale causing higher roll-off angle for water droplet. The most aggregated structures were obtained by freeze-drying from water (Figure 41c), and contained both small and large pores (average size of 75 ± 43 nm). Sheet-like structure of aggregated fibrils was observed. The coatings morphology (Figure 41d) was similar to those of nanopaper prepared by SCD – consisting of fibrils and fibril aggregates and fairly uniform pores (46 ± 25 nm), also representing well the structure of fibrils in suspension.

Figure 40. Low magnification FE-SEM images of f-NFC nanopapers prepared by (a) SCD, (b) TB FD, (c) water FD and (d) f-NFC coating.

Figure 41. FE-SEM images of f-NFC nanopapers prepared by (a) SCD, (b) TB FD, (c) water FD and (d) f-NFC coating.
5. CONCLUSIONS

The overall objective of this thesis was to develop new surface modification routes for nanoparticles in order to extend the property range of nanocellulose materials. Scientifically, the focus is on the effect of surface treatments on processing, structure and properties of nanomaterials. In many cases, the materials can simply not be made without surface modification of nanoparticles.

In Paper I, a method for mechanical testing of electrospun fibres was developed and the effect of nanofibrillated cellulose on the mechanical properties of the fibres mats was studied. It was found that by selection of suitable matrix and careful solvent exchange, good dispersion of NFC in the PMMA matrix could be achieved with the advantage of cellulose’s native functional groups.

In Paper II, a simple method for preparation of tough, lightweight and electrically conductive nanopaper was developed. By proper selection of surfactant, stable MWCNT suspension in water was obtained and by using a papermaking process commingled nanopaper structures were prepared. It was found that the requirement for MWCNT treatment is not only to disperse the MWCNT in water, but also, more importantly, provide compatibility with nanocellulose.

In Paper III, a new route for isolation of cellulose nanocrystals was developed and the desired charge characteristics could be controlled. Moreover, a green and simple procedure was then established for water based adsorption of quaternary ammonium salts, so that different functionalities could be introduced to nanocellulose. The new type of hydrophobic CNC could be dried without agglomeration and dispersed in non-polar solvents, enabling to combine new CNC with various types of polymer matrices.

In Paper IV, modification with quaternary ammonium salts is used to facilitate dispersion of CNC in PVAc matrix. The performance of both modified and unmodified CNC was compared and it was found that the quality of dispersion played key role in utilization of the reinforcing potential of nanocellulose. Unmodified CNC caused a decrease T_g of PVAc, whereas the highly compatible modCNC resulted in strongly increased T_g, as estimated by DMTA.

In Paper V, surface functionalization together with structure control was used for design of functional films and coatings. By combining synergistic effect of the morphology and surface properties, good compatibility with a lubricant could be achieved, resulting in a material that repels both water and hexadecane, extending the application of nanocellulose-based materials. A super-slippery surface was obtained, where the nanocellulose network provides mechanical support and a nanoporous network for the lubricant.
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