Surface Modification of Cellulose by Covalent Grafting and Physical Adsorption for Biocomposite Applications

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Doctoral thesis

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To my family
Abstract

There is a growing interest to replace fossil-based materials with renewable options. Cellulose fibers/cellulose nanofibrils (CNF) are biobased and biodegradable sustainable alternatives. In addition, they combine low weight with high strength; making them suitable to, for example, reinforce composites. However, to be able to use them as such, a modification is often necessary. This study therefore aimed at modifying cellulose fibers, model surfaces of cellulose and CNF. Cellulose fibers and CNF were thereafter incorporated into composite materials and evaluated.

Surface-initiated ring-opening polymerization (SI-ROP) was performed to graft ε-caprolactone (ε-CL) from cellulose fibers. From these fibers, paper-sheet biocomposites were produced that could form laminate structures without the need for any addition of matrix polymer.

By combining ROP and atom transfer radical polymerization (ATRP), diblock copolymers of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and PCL were prepared. Quaternized (cationic) PDMAEMA, allowed physical adsorption of block copolymers onto anionic surfaces, and, thereby, alteration of surface energy and adhesion to a potential matrix. Furthermore, the architecture of block copolymers of PCL and PDMAEMA was varied to investigate effects on morphology/crystallinity and adsorption behavior. In addition, poly(butadiene) was also evaluated as the hydrophobic block in the form of cationic and anionic triblock copolymers.

Polystyrene (PS) was covalently grafted from CNF and used as reinforcement in PS-based composites. In an attempt to determine stress transfer from matrix to CNF, a method based on Raman spectroscopy was utilized.

Covalent grafting and physical adsorption of PCL from/onto CNF were compared by incorporating modified CNF in PCL matrices. Both approaches resulted in improved mechanical properties compared to unmodified CNF, but even at low amounts of modified CNF, covalent grafting gave tougher materials and indicated higher interfacial adhesion.
Sammanfattning

Det finns ett ökande intresse för att ersätta material från fossila källor med mer ”gröna” alternativ. Cellulosafibrer och cellulosananofibrilller (CNF) är miljömässigt hållbara sådana alternativ, då de är både biobaserade och bionedbrytbara. Utöver detta så kombinerar de hög styrka med låg vikt, vilket gör dem till ypperliga alternativ att använda som exempelvis förstärkning i kompositer. Dock krävs ofta att de modifieras för att kunna användas dem i just kompositer. Den här studien syftade till att modifiera cellulosafibrer, cellulosamodellytor och CNF och att utvärdera dessa i kompositer.

Ytinitierad ringöppningspolymerisation (SI ROP) användes för att ympa ε-kaprolakton (ε-CL) från cellulosafibrer. Dessa fibrer användes sedan i pappersbaserade biokompositer, som kunde lamineras ihop utan att behöva tillföras ytterligare polymer.

Genom att kombinera atomöverföringsradikalpolymerisation (ATRP) med ROP, kunde diblocksampolymerer av poly(2-dimetlaminoetyl metakrylat) (PDMAEMA) och PCL syntetiseras. Kvartenäriserad (katjonisk) PDMAEMA möjliggjorde adsorption av blocksampolymererna till anjoniska ytor, vilket ledde till en förändring i ytenergi samt ökad adhesion till en möjlig matris. Vidare varierades arkitekturen av blocksampolymerer av PCL och PDMAEMA för att undersöka effekten det hade på morfologi/kristallinitet samt adsorptionsbeteende. Utöver PCL så användes också polybutadien som hydrofobt block i katjoniska och anjoniska triblocksampolymerer.

Polystyren (PS) ympades från CNF och användes som förstärkning i PS-baserade kompositer. I ett försök att bestämma spänningsöverföringen från CNF till matris så användes en metod baserad på Ramanspektroskopi.

Kovalent ympning och fysikalisk adsorption av PCL från/till CNF jämfördes genom att förstärka PCL matriser i kompositer och utvärdera dessa med avseende på materialegenskaper. Både fysiosorption och ympning var bättre än omodifierad CNF, men redan vid låga halten av modifierad CNF gav kovalent ympning ett segare material och troligtvis en ökad adhesion vid gränsskiktet.
List of appended papers

**Paper 1**

**Paper 2**

**Paper 3**

**Paper 4**
“Bionanocomposites reinforced with cellulose nanofibrils compatibilized through covalent grafting or physisorption of PCL – a comparative study”, C. Bruce, L. Fogelström, M. Johansson, A. Carlmark, and E. Malmström. Submitted
My contribution to the appended papers:

**Paper 1.** The majority of the experimental work, analyses, and most of the preparation of the manuscript.

**Paper 2.** Half of the experimental work and analyses, and part of the preparation of the manuscript.

**Paper 3.** The majority of the experimental work, analyses, and most of the preparation of the manuscript.

**Paper 4.** All experimental work and analyses, and most of the preparation of the manuscript.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AKD</td>
<td>Alkyl ketene dimer</td>
</tr>
<tr>
<td>AGU</td>
<td>Anhydroglucose</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>Al2O3</td>
<td>Aluminum oxide</td>
</tr>
<tr>
<td>ASA</td>
<td>Alkenyl succinic anhydride</td>
</tr>
<tr>
<td>ARGET ATRP</td>
<td>Atom regenerator electron transfer atom radical polymerization</td>
</tr>
<tr>
<td>ATRA</td>
<td>Atom transfer radical addition</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerization</td>
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<tr>
<td>BiB</td>
<td>α-Bromoisobutyryl bromide</td>
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<tr>
<td>BTCA</td>
<td>1,2,3,4-Butanetetracarboxylic acid</td>
</tr>
<tr>
<td>CaH2</td>
<td>Calcium hydride</td>
</tr>
<tr>
<td>ε-CL</td>
<td>ε-Caprolactone</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>CNC</td>
<td>Cellulose nanocrystals</td>
</tr>
<tr>
<td>CNF</td>
<td>Cellulose nanofibrils</td>
</tr>
<tr>
<td>Cu(I)Cl</td>
<td>Copper chloride</td>
</tr>
<tr>
<td>Cu(I)Br</td>
<td>Copper bromide</td>
</tr>
<tr>
<td>Cu(II)Br2</td>
<td>Copper(II) bromide</td>
</tr>
<tr>
<td>D3</td>
<td>Molar-mass dispersity</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-Diazabicyclo[5.4.0]-undec-7-ene</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DMAEMA</td>
<td>2-(Dimethylamino)ethyl methacrylate</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-(Dimethylamino)pyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>DR13</td>
<td>Disperse red 13</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>EBiB</td>
<td>Ethyl α-bromoisobutyrate</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>H2SO4</td>
<td>Sulphuric acid</td>
</tr>
<tr>
<td>HEBI</td>
<td>2-Hydroxyethyl bromoisobutyrate</td>
</tr>
<tr>
<td>HMTETA</td>
<td>1,1,4,7,10,10-Hexamethyltriethylenetriamine</td>
</tr>
<tr>
<td>HTPB</td>
<td>Hydroxy-terminated polybutadiene</td>
</tr>
<tr>
<td>F</td>
<td>Kraft pulp fiber</td>
</tr>
<tr>
<td>FDA</td>
<td>Food and drug administration</td>
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<tr>
<td>FE-SEM</td>
<td>Field-emission scanning electron microscopy</td>
</tr>
<tr>
<td>FRP</td>
<td>Free radical polymerization</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>MeI</td>
<td>Methyl iodide</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>Mn</td>
<td>Number average molecular weight</td>
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<tr>
<td>Mw</td>
<td>Molecular weight</td>
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<tr>
<td>NaAsc</td>
<td>Sodium ascorbate</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NaN3</td>
<td>Sodium azide</td>
</tr>
<tr>
<td>NMP</td>
<td>Nitroxide-mediated radical polymerization</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>P</td>
<td>Primary layer of the plant cell wall</td>
</tr>
<tr>
<td>PDMAMEAq</td>
<td>Quaternized poly(2-(dimethylamino)ethyl methacrylate)</td>
</tr>
<tr>
<td>PEI</td>
<td>Poly(ethyleneimine)</td>
</tr>
<tr>
<td>PET</td>
<td>Polyelectrolyte titration</td>
</tr>
<tr>
<td>PMAA</td>
<td>Poly(methacrylic acid)</td>
</tr>
<tr>
<td>PMDETA</td>
<td>N,N,N’,N”-pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>PP</td>
<td>Poly(propylene)</td>
</tr>
<tr>
<td>PS</td>
<td>Poly(styrene)</td>
</tr>
<tr>
<td>RAFT</td>
<td>Reversible addition-fragmentation chain transfer</td>
</tr>
<tr>
<td>RDRP</td>
<td>Reversible-deactivation radical polymerization</td>
</tr>
<tr>
<td>ROP</td>
<td>Ring-opening polymerization</td>
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<tr>
<td>S</td>
<td>Secondary layer of the plant cell wall</td>
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<tr>
<td>SEC</td>
<td>Size exclusion chromatography</td>
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<tr>
<td>Sn(Oct)$_2$</td>
<td>Tin(II) 2-ethylhexanoate</td>
</tr>
<tr>
<td>T</td>
<td>Tertiary layer of the plant cell wall</td>
</tr>
<tr>
<td>TBD</td>
<td>1,5,7-Triazabicyclo[4.4.0]dec-5-ene</td>
</tr>
<tr>
<td>tBMA</td>
<td>tert-Butyl methacrylate</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethyl piperidine-1-oxyl radical</td>
</tr>
<tr>
<td>TFA</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melt temperature</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal microbalance</td>
</tr>
<tr>
<td>$w$</td>
<td>Weight fraction</td>
</tr>
<tr>
<td>$X_c$</td>
<td>Degree of crystallinity</td>
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</table>
Table of contents

Purpose of the study ................................................................. 1

Introduction .............................................................................. 2

Cellulose .................................................................................. 2
  Hierarchical structure of cellulose ......................................... 3
  Cellulose fibers, fibrils and crystals ....................................... 4

Cellulose reinforced composites .............................................. 6
  Surface modification of cellulose ........................................... 6
  Surface modification of cellulose by covalent grafting .......... 7
    Ring-opening polymerization (ROP) ................................. 9
    Atom transfer radical polymerization (ATRP) ................. 11
      PDMAEMA ....................................................................... 13
    Micellization ..................................................................... 14
  Surface modification of cellulose by physical adsorption of
  polyelectrolytes .................................................................. 15
  Micromechanic measurements of cellulose-reinforced composites
  performed with Raman spectroscopy ................................. 18

Experimental .......................................................................... 20

Materials ................................................................................ 20

Characterization methods ........................................................ 21

Experimental procedures ...................................................... 25
  Covalent grafting of cellulose ............................................... 25
    Modification of CNF through SI-ROP ............................. 25
    Modification of CNF through SI-ARGET ATRP ................. 26
  Preparation of block copolymers ........................................ 28
    Di- and triblock copolymers of PCL and PDMAEMA ........ 28
    Triblock copolymers of PB and PDMAEMA or PMAA ...... 28
  Modification of cellulose through physical adsorption .......... 31
  Preparation and evaluation of biocomposites ....................... 32
    PCL-based biocomposites ............................................... 32
    PS-based composites .................................................... 32
    PB-based composites .................................................... 32
Results and discussion ___________________________________________ 33

Part one: Fiber modification and paper-sheet composite preparation
_____________________________________________________________ 35
Covalent grafting of kraft pulp through SI-ROP of ε-CL (Paper 1) _____ 35
Physical adsorption of triblock copolymers to kraft pulp _____________ 37
Paper-sheet composites___________________________________________ 38
  Paper-sheet biocomposites with PCL-grafted fibers ________________ 38
  Lamination of paper-sheet biocomposites__________________________ 40
Paper-sheet composites with adsorbed PB triblock copolymers ____ 43

Part two: Block copolymer adsorption to model surfaces _______ 43
Preparation and evaluation of diblock copolymers of PCL and PDMAEMA
(Paper 2) ______________________________________________________ 44
Preparation and adsorption of triblock copolymers _________________ 49
  ABA- and BAB-type triblock copolymers of PCL and PDMAEMA
(Paper 3) _________________________________ ________________________ 49
  Adsorption of triblocks of PB and PDMAEMAq or PMAA _________ 55

Part three: CNF modification and composite preparation _______ 56
Covalent grafting of CNF through SI-ARGET ATRP of styrene__________ 56
Micromechanic measurements with Raman spectroscopy ____________ 57
Comparative study of covalent grafting and physical adsorption of PCL in
bionanocomposites (Paper 4) ____________________________________ 60

Conclusions __________________________________________________ 70

Future work ___________________________________________________ 72

Acknowledgements _____________________________________________ 73

References ____________________________________________________ 79
Purpose of the study

Fossil-based materials are wide-spread and used in numerous products. However, such materials are not sustainable, and it is, therefore, desirable to replace them with “greener” alternatives in for instance composites. One strong competitor to petroleum-based fibers, as reinforcing element, is cellulose-based fibers. Cellulose fibers and fibrils possess excellent mechanical properties. However, they are by nature not compatible with non-polar matrices, and cannot be used directly to replace fossil-based fibers. On the other hand, their surfaces can be modified, altering the nature of fibers/fibrils, thus providing increased compatibility.

The overall purpose of this study was to expand the toolbox for cellulose modification and characterization and by doing so allow the incorporation of cellulosic fillers in composites. Different types of controlled polymerization techniques were employed to modify the cellulose substrates. The modifications were performed either through covalent grafting, i.e., growing polymers from the surface, or physical adsorption of block copolymers, attaching pre-formed polymers by utilization of charges. Finally, the modified cellulose substrates were used as reinforcing elements in composites and evaluated with respect to material properties.
Introduction

The surface of the planet earth is composed of around 70 % water and 30 % land. Out of the land, approximately 50 % is covered by vegetation including crops, grasslands and forests\(^1\). In Sweden, just the forest covers about 55 % of the land, dominated by pine (42 %), spruce (39 %) and birch (12 %)\(^2\). Independently of which type of tree, the main components are cellulose, hemicelluloses and lignin. Cellulose is the load-bearing constituent, allowing trees to be both tall and thin, and to withstand harsh weather conditions without breaking\(^3\).

Cellulose

The term *cellulose* was first referred to by Anselme Payen in 1838, when he discovered how to make fibers from different plants\(^4\). Since then, cellulose has been studied extensively, and it is now known that cellulose is one of the most abundant natural polymers in the world. It possess many interesting properties, both chemical and physical. In addition, it is not only biobased, but also biodegradable, making it interesting from an environmental perspective\(^5\). Cellulose is the construction material used by nature in plants and trees, and the cellulose crystal in for example ramie fibers, which are plant cellulose fibers, have an elastic modulus of 137 GPa\(^6\). This is well comparable to both synthetic and inorganic fibers, such as aramid and glass fibers, that have elastic moduli of around 65 and 80 GPa, respectively\(^4\). Furthermore, the density of cellulose is around half compared to glass, *i.e.*, it possess high strength in combination with a low weight\(^7\).

The total production of cellulose is estimated to be over \(7.5 \times 10^{10}\) tons/year\(^5\), where the most common source is wood fibers with a world production of \(1.75 \times 10^6\) tons/year\(^4\). Cellulose is used industrially in a wide variety of products including paper, cardboard and textiles\(^5\).
Hierarchical structure of cellulose

The cellulose chain is a natural polymer built up of two anhydroglucose (AGU) rings linked together by β-1,4 glucosidic linkages, as shown in figure 1. The AGU units are oriented towards one another with a rotation of 180° around its molecular axis.

Figure 1: Two anhydroglucose (AGU) rings building up the repeating unit of cellulose, including numbering of the carbons.

Cellulose is a polar macromolecule, where the polarity originates from the three hydroxyl groups per glucose unit; on carbon 6 (C6), there is one primary hydroxyl group and on the C2 and C3 positions, there are two secondary hydroxyl groups. Despite being a polar macromolecule, cellulose does not dissolve in protic solvents, and in addition, it cannot melt. This is ascribed to the strong secondary interactions; van der Waals forces in combination with inter- and intramolecular hydrogen bonds emanating from the hydroxyl groups. Furthermore, the length of the cellulose chain varies depending on the source, e.g., for cellulose in wood the degree of polymerization (DP) can be up to 10 000, while it can be up to 15 000 for cellulose in cotton. In a plant or a tree, cellulose chains are not found as isolated molecules, they grow in the form of fibers within the cell wall. The plant cell wall is built up in different layers: primary (P), secondary (S) and tertiary (T) layer, where the majority of cellulose is found in the thickest part of the S layer, called $S_2$ layer. Fibers, which have a diameter of 10-30 µm and up to a few mm in length, consist of aggregated fibrillar bundles with lateral
dimension of 10-30 nm. These fibrillar aggregates are composed of elementary fibrils, which consist of about 40 cellulose chains, and have a diameter ranging from 1.5 to 3.5 nm. Both elementary fibrils and bundles of fibrils can be up to a few µm in length. The hierarchical structure of a tree is schematically illustrated in figure 2.

![Cellulose chain, Elementary fibril, Fibrillar bundles](Image)

Figure 2: Schematic illustration of the hierarchical structure of a tree adopted from Fengel9, 10.

**Cellulose fibers, fibrils and crystals**

Cellulose fibers are extracted from wood through a process known as pulping, where the wood is disintegrated and fibers can be obtained. Pulping can be performed either mechanically or chemically. In mechanical pulping, the fibers are extracted through grinding and have lower strength compared to other fibers and are, therefore, used in applications that require a lower strength, such as newsprint. However, only around 40 % of wood is cellulose, where the other major constituents are, as previously mentioned, hemicelluloses and lignin. Therefore, to extract fibers with higher purity with respect to cellulose content,
different chemical processes, i.e., chemical pulping, can be applied to remove lignin and part of the hemicelluloses. There are two main processes: the kraft and the sulfite process. The kraft, or sulfate, process, is the dominating process\textsuperscript{12, 13}, while the sulfite process is applied to produce high-cellulose content dissolving pulp\textsuperscript{14}. For the extraction of nanosized fibrils, chemical pulp is preferred over mechanical pulp, due to its higher cellulose content. Since fibrils grow as bundles in cellulose fibers, disintegration of fibers is required in order to obtain individualized fibrils. In the 1980ies, Turbak \textit{et al.}\textsuperscript{15} managed to disintegrate cellulose fibers into cellulose nanofibrils (CNF) through mechanical disintegration. By forcing a water-based fiber suspension through a homogenizer, a CNF suspension with a gel-like consistency was obtained. Noteworthy, it has later been reported that homogenization is a process that is easier to perform on sulfite pulp than kraft pulp\textsuperscript{5, 16}. In addition, different pretreatments can be performed that will separate the fibrils more easily during homogenization, such as enzymatic pretreatment or introduction of charges. Charges can be introduced from for example, carboxymethylation (around 350 µeq/g)\textsuperscript{16} or 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation (around 600 µeq/g)\textsuperscript{17}.

Apart from homogenization, acid hydrolysis can be performed to isolate nanometer-sized cellulose elements. This was first described by Rånby and Ribi\textsuperscript{18, 19}, who treated cellulose fibers with sulphuric acid (H\textsubscript{2}SO\textsubscript{4}), and obtained colloidal suspensions of cellulose. When subjecting cellulose fibers to acid hydrolysis, the amorphous parts of cellulose, the hemicelluloses and the lignin are degraded, leaving the crystalline cellulose intact, in the form of rod-like nanoparticles called cellulose nanocrystals (CNC). Furthermore, different acids can be used to prepare CNC apart from H\textsubscript{2}SO\textsubscript{4}, such as hydrochloric acid (HCl). Depending on the type of acid used for the treatment, surface charges may be introduced. With H\textsubscript{2}SO\textsubscript{4}, a typical charge value of around 40 µeq/g is obtained due to introduction of sulphate groups, whereas with HCl the CNC is produced practically without charge\textsuperscript{20}.
Due to the degradation of constituents, CNC is shorter than CNF with typical dimensions of 3-5 nm in width and 100-200 nm in length if extracted from wood fibers\textsuperscript{21}, as is displayed in the TEM images in figure 3.

Figure 3: TEM images of a) CNF and b) CNC. Reprinted from (Klemm, D. \textit{et al.}\textsuperscript{16}) with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Cellulose reinforced composites**

The attractive mechanical properties of cellulose fibers, \textit{i.e.}, high strength in combination with low weight, are desirable to utilize in more sophisticated applications than conventional paper and board, \textit{e.g.}, in composites. A composite is a material consisting of two, or more, constituents that are combined into a material with preserved inherent properties of the individual components\textsuperscript{22-24}. There are different examples of cellulose reinforced composites, where one common is poly(propylene) (PP) reinforced with saw dust\textsuperscript{25, 26}. However, due to the polar character of cellulose, a modification is often necessary to use it in applications where it is not inherently compatible, \textit{e.g.}, as a reinforcing element in a composite together with a non-polar matrix\textsuperscript{27}.

**Surface modification of cellulose**

The hydroxyl groups present in cellulose can act as anchor points for different types of modifications. Furthermore, due to the poor solubility of cellulose in many both aqueous and organic solvents, modification reactions of cellulose are performed under heterogeneous conditions, \textit{i.e.}, keeping the cellulose undissolved. One alternative to increase the accessibility and, thereby, the
reactivity of the hydroxyl groups, is by disruption of the intra- and intermolecular hydrogen bonds by the treatment with alkaline compounds, e.g., NaOH, that will induce swelling of the cellulose substrate. However, one effect of this can be that the strength decreases, why preservation of the native cellulose structure can be preferred.

**Surface modification of cellulose by covalent grafting**

The most common approach to modify cellulose is by covalent attachment of small molecules, such as alkyl ketene dimer (AKD), 1,2,3,4-butane tetracarboxylic acid (BTCA) and alkenyl succinic anhydride (ASA). Different types of reactions can be applied for covalent modification, for example etherification, acetylation, silylation, amidation and urethane formation.

Apart from small molecules, it is possible to graft polymers on a cellulose surface. Grafting of small molecules allows for increased compatibility between cellulose and a polymer matrix, due to decreased surface energy. This is valid as well for polymers. However, in addition, there can also be increased adhesion between the two components, arising from the possible formation of entanglements between grafted polymers and matrix.

There are two main techniques of grafting, which are the “grafting from” and “grafting to” approach as illustrated in figure 4. In the “grafting from” method the polymer is formed by diffusion of monomer to, and subsequent propagation from, the reactive center situated on the surface. In the “grafting to” approach, a pre-formed polymer with an active chain end is reacted with an active site on the surface to covalently or physically attach the polymer.
The “grafting from” technique is the most commonly used and it presumably yields higher grafting densities, *i.e.*, more polymer grafted per surface area, than the “grafting to” method, where diffusion of the pre-formed polymers to the surface may be sterically hindered from polymers already attached\textsuperscript{40, 41}. On the other hand, the “grafting to” approach allows characterization of the pre-formed polymer with respect to for example molecular weight ($M_w$) and molar-mass dispersity ($D_M$). This is only possible in the “grafting from” approach if the polymer can be detached from the surface, or if the cellulose is afterwards degraded through for example acid hydrolysis, which in turn requires a polymer that does not contain hydrolytically sensitive groups\textsuperscript{39, 42}.

Figure 4: Schematic illustration of the “grafting from” and “grafting to” approaches.
Covalent “grafting from” of polymers from cellulose is performed to a wide extent with conventional free radical polymerization (FRP)\textsuperscript{43, 44}. Initiation takes place through the creation of free radicals on the cellulose surface from for example, chemical initiators, \textit{e.g.,} Ce(IV) ions and Fenton’s reagent (Fe\textsuperscript{2+}-H\textsubscript{2}O\textsubscript{2} system); radiation, \textit{e.g.,} UV-radiation and γ-radiation, or plasma treatment\textsuperscript{40}. However, the control over the polymerization is poor, and therefore controlled polymerization techniques, such as ring-opening polymerization (ROP)\textsuperscript{45, 46} and atom transfer radical polymerization (ATRP)\textsuperscript{47-49}, are of interest to apply as well. “Grafting to” of polymers to cellulose can as well be performed through covalent grafting, but also, through physical adsorption of polymers\textsuperscript{50}, which is described more in detail further down.

\textbf{Ring-opening polymerization (ROP)}

ROP is a controlled polymerization technique that was developed in the 1930ies by Carothers \textit{et al.}\textsuperscript{51}, and since its introduction it has been shown a suitable technique to polymerize a wide variety of cyclic monomers, such as lactones, lactides, cyclic carbonates, siloxanes and ethers. The driving force for polymerization is the inherent ring strain of the monomer, \textit{i.e.,} how thermodynamically unstable the monomer is. If the monomer is a highly strained compound it will be more prone to undergo ROP, \textit{e.g.,} as for seven-membered rings, whereas five and six membered rings, on the other hand, are less strained types, and will not be as easy to polymerize\textsuperscript{52}.

\textit{ɛ}-Caprolactone (\textit{ɛ}-CL) is a seven-membered ring that readily polymerizes with ROP, yielding poly(\textit{ɛ}-caprolactone) (PCL). One common catalyst used for the polymerization of \textit{ɛ}-CL is tin(II) 2-ethylhexanoate (Sn(Oct)\textsubscript{2}). Sn(Oct)\textsubscript{2}-catalyzed ROP of \textit{ɛ}-CL produces PCL with narrow dispersity, high molar mass and well-defined end-group functionality. Furthermore, Sn(Oct)\textsubscript{2} has a reasonably low toxicity and it is approved in food and drug applications (FDA approved)\textsuperscript{53}. The exact mechanism of ROP catalyzed by Sn(Oct)\textsubscript{2} is not known, but it is proposed to be a coordination-insertion mechanism\textsuperscript{54}. In scheme 1, the mechanism
as suggested by Penzcek et al.\textsuperscript{53} is illustrated. It is divided into three different steps: pre-initiation (transformation of the catalyst into a metal alkoxide), initiation (coordination and insertion of the first monomer) and propagation (coordination and insertion of monomers). The metal alkoxide is the active center throughout the polymerization which terminates with a protonation, resulting in a hydroxy-functional PCL\textsuperscript{53, 55}. Noteworthy is that Kricheldorf et al. proposed a slightly different mechanism where both the alcohol containing initiator and the monomer are coordinated to the SnOct\textsubscript{2}-complex during propagation\textsuperscript{56}.

There are some drawbacks with this system; PCL may undergo transesterification reactions during the polymerization, \textit{i.e.}, intramolecular or intermolecular chain transfer reactions. In addition, initiation can take place from water. Hence, the system is needed to be kept dry\textsuperscript{57}.

**Scheme 1:** ROP of \(\varepsilon\)-CL forming PCL through a coordination-insertion mechanism catalyzed by Sn(Oct)\textsubscript{2} and initiated by an alcohol (R-OH) as proposed by Penzcek et al.\textsuperscript{53}.
Intramolecular transesterification, *i.e.*, back-biting, gives rise to cyclic compounds that hinders propagation and, as a consequence, results in shorter chains than aimed for. In intermolecular transesterification, the chain transfer, on the other hand, takes place in between different PCL chains. Independently of which one, the $D_M$ broadens and most likely the aimed/targeted $M_w$ will not be obtained\textsuperscript{53,55}. In addition, it is difficult to fully remove the catalyst after polymerization, which could be a disadvantage for food or biomedical applications even though it is FDA approved\textsuperscript{58}. Therefore, other catalyst systems may be applied, such as the organic catalysts 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU)\textsuperscript{59}.

Once the PCL is formed it is an interesting polymer that has been used in different types of applications, such as biomedical scaffolds\textsuperscript{60}, powder coatings\textsuperscript{61} and biocomposites\textsuperscript{62}. It is a biodegradable\textsuperscript{63} semi-crystalline polymer with a glass transition temperature ($T_g$) around -60 °C and melting temperature ($T_m$) around 60 °C\textsuperscript{64}. Furthermore, PCL can readily be grafted both to\textsuperscript{36,38,65} and from\textsuperscript{46,66-68} cellulose.

**Atom transfer radical polymerization (ATRP)**

For the production of polymers on an industrial scale, FRP has been used to produce large volumes of polymers over a long time due to cost and simplicity in terms of ability to readily polymerize many different monomers. However, FRP lacks control over molecular architecture\textsuperscript{69}. Therefore, other systems suppressing side-reactions are of interest, and in terms of radical polymerization, reversible-deactivation radical polymerization (RDRP) acts, in contrast to free radical polymerization, almost as a true living system\textsuperscript{70}.

In the 1940ies Karasch *et al.*\textsuperscript{71} developed an addition reaction of carbon tetrachloride to olefins, which was later developed into the concept of atom transfer radical addition (ATRA)\textsuperscript{72}. In 1995, Sawamoto *et al.*\textsuperscript{73} and Wang and Matyjaszewski\textsuperscript{74,75}, with the basis in ATRA, independently discovered atom transfer radical polymerization (ATRP), which is an RDRP technique. ATRP has
since then been widely studied together with the other RDRP techniques, nitroxide-mediated radical polymerization (NMP) and reversible addition-fragmentation chain transfer (RAFT). The fundamental behind ATRP is that a dynamic equilibrium between active propagating species and dormant chains is shifted towards the dormant side, keeping the concentration of radicals low. Thereby, the number of side-reactions, e.g., terminations, can be minimized. However, terminations do occur, and ATRP is, therefore, not a “living” polymerization system. The mechanism of ATRP is illustrated in scheme 2.

Scheme 2: The mechanism of ATRP.

\[ \text{P}_n^\text{-X} + \text{Mt}^\text{m/L} \xrightleftharpoons{K_{\text{act}}} \xleftarrow{K_{\text{deact}}} \text{P}_n^* + \text{X-Mt}^{\text{m+1/L}} \]

\[ \text{M} \xrightarrow{k_p} \text{P}_n-\text{P}_n \]

\( P_n^\text{-X} \) is the dormant species, often an alkyl halide where \( X \) is the halide, usually bromide or chloride. \( P_n^\text{-X} \) reacts with a transition metal (Mt), commonly copper, coordinated to a ligand (L). Growing radicals (\( P_n^* \)) are formed, and propagation through addition of monomer (M) occur. At the same time, the transition metal complex is brought to a higher oxidation state (X-Mt\(^{m+1/L}\)) forming a deactivator complex. The number of terminations is kept low due to the increase in concentration of deactivator complex as the concentration of radicals increases, shifting the equilibrium to the dormant side in a phenomenon known as the persistent radical effect. After a limited time, based on the amount of radicals formed according to the equilibrium, the deactivator complex reacts with the propagating species to reform the dormant \( P_n^\text{-X} \) and activator Mt\(^m/L\).

With ATRP it is possible to polymerize a wide range of monomers, including acrylates, methacrylates and styrenics with tailored molecular weights governed by
monomer-to-initiator ratio. Depending on which type of monomer intended to polymerize, the initiator, ligand, temperature and solvent can be varied to optimize the conditions. Furthermore, ATRP can be conducted in the presence of several functional groups, such as cyanides, amines and hydroxyl groups\textsuperscript{91}.

ATRP provides many advantages compared to FRP. However, it should be mentioned that it does suffer from some drawbacks, including the need for relatively large amounts of the transition metal catalyst, and sensitivity to oxygen. Therefore, a modified version of ATRP, \textit{activators regenerated by electron transfer} (ARGET) ATRP was developed\textsuperscript{92}. The system is based on the addition of a reducing agent, \textit{e.g.}, ascorbic acid, which regenerates the active species Mt\textsuperscript{m} from the deactivator Mt\textsuperscript{m+1}. Hence, only a few ppm of copper is needed and, in addition, the reaction is less sensitive to oxygen, which is advantageous when aiming to graft polymers on an industrial scale from, for instance, cellulose\textsuperscript{93}.

**PDMAEMA**

One polymer that is readily polymerized through ATRP, and has gained significant attention due to the fact that it can carry a permanent charge, is poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) with the corresponding monomer, DMAEMA. Introduction of a permanent charge occurs through a \textit{quaternization reaction}, where PDMAEMA is reacted with for example methyl iodide (MeI) forming PDMAEMAQ. Neat PDMAEMA is prone to undergo hydrolysis; however, one effect of the quaternization is that the introduced charge retards the hydrolysis of PDMAEMAQ\textsuperscript{94}. The structures of DMAEMA, PDMAEMA and the permanently charged, quaternized, PDMAEMAQ are seen in figure 5. PDMAEMA can react to external stimuli with respect to both pH and temperature, \textit{i.e.}, it is both pH- and thermo-responsive. When subjected to changes in pH and/or temperature it can switch from a hydrophilic to a hydrophobic character\textsuperscript{95}. Furthermore, PDMAEMA has been evaluated within a wide range of different potential applications,
such as anti-bacterial agent\textsuperscript{96, 97}, waste-water treatment\textsuperscript{98}, and grafted to cellulose as pulp flocculants\textsuperscript{99}.

![Figure 5: Molecular structure of a) DMAEMA, the corresponding polymer b) PDMAEMA, and PDMAEMA in its quaternized form c) PDMAEMAq.](image)

**Micellization**

A block copolymer composed of a hydrophilic block and a hydrophobic block is called an *amphiphilic polymer*\textsuperscript{100}. When an amphiphilic polymer is subjected to a solvent, solubilizing only one of the polymer blocks, the chains of the insoluble segment may self-assemble to form a micelle. This is depending on if the concentration of block copolymers is above the *critical micelle concentration* (CMC), i.e., there is an appropriate hydrophilic/hydrophobic balance and, as a consequence, it is energetically favorable to self-assemble, illustrated in figure 6. Micelles are structures generally 5-100 nm in size\textsuperscript{100-102}. Furthermore, micelles have gained attention since they can be used in different applications, for example to encapsulate, transport, and release compounds, as in drug delivery\textsuperscript{103-105}. In addition, they can also adsorb to surfaces, which allows for alteration of the functionality and/or surface energy of the substrate; an approach which has attracted increasing attention lately\textsuperscript{106, 107}. 
There are several reports describing the ability of PDMAEMA to form micelles in the form of a block copolymer together with different hydrophobic blocks\textsuperscript{108-112}.

Figure 6: Schematic illustration of micelle formation in correlation to CMC of block copolymers of quaternized PDMAEMAp and a hydrophobic block.

**Surface modification of cellulose by physical adsorption of polyelectrolytes**

Polymers carrying charges are called *polyelectrolytes*. A simple polyelectrolyte is a homopolymer where all repeating units can carry a charge, such as a carboxylic group or an amine. Furthermore, there are *weak* and *strong* polyelectrolytes; a weak polyelectrolyte carries a pH-dependent charge, whereas for strong polyelectrolytes, the charge is unaffected by variations in pH. Irrespectively of which type of polyelectrolyte, when charged, it attracts counter-ions, such as Na\textsuperscript{+}, and can consequently adsorb to oppositely charged surfaces, where the driving force for the adsorption is the release of counter ions. Furthermore, the polyelectrolyte is not necessarily a homopolymer, but could also be a copolymer. If the copolymer is random type, it will express an intermediate adsorption behavior of the two corresponding homopolymers. On the other hand, if the copolymer is a block copolymer, particularly large amounts can be adsorbed. When the surface is saturated, only one of the blocks will attach to the surface, acting as an anchor for the other block. In addition, the adsorption can be performed under mild conditions, *e.g.*, in water, which is interesting from an environmental perspective\textsuperscript{113}. 

15
In the pulp and paper industry, adsorption of polyelectrolytes is a well-established method for modification of cellulose fibers. Improvement of properties, such as wet/dry strength, creep and sizing, can be achieved through adsorption of cationic polyelectrolytes, such as poly(acrylamide) and poly(aminoamide)-epichlorohydrin. The adsorption is possible due to the slightly anionic character of a wood cellulose fiber. During regular paper making, carboxyl groups and sulphonic acid groups are the major contributors to the charge. The carboxyl groups originate from either non-cellulosic constituents in wood, e.g., hemicelluloses, or are created during pulping. The sulphonic acid groups, on the other hand, do not come from the wood, but are introduced merely during chemical pulping by the addition of sulphite. Concerning nanocelluloses, i.e., CNF and CNC, additional charges, anionic or cationic, are commonly introduced through chemical treatments during their production, such as: TEMPO-oxidation, carboxymethylation or amination. Furthermore, conventional grafting of polymers regularly requires inert atmosphere, dry conditions and organic solvents. Therefore, the alternative to covalent modification based on polyelectrolytes has attracted interest. The polymer that would have been grafted, is instead prepared in the form of a diblock copolymer, together with a cationic block. The block copolymers can then self-assemble into a micelle, and the cationic block can
act as an electrostatic linker to a cellulose surface. Thus, allowing the adsorption of the block copolymer. The concept of cationic micelle adsorption and subsequent spreading over a cellulose surface is visualized schematically in figure 8. One example of such a cationic block is PDMAEMA in its permanently charged, quaternized, form; PDMAEMAq (figure 5c). PDMAEMAq has, for example, been used as an anchoring polymer for poly(ethylene oxide), that when adsorbed improved paper strength. Furthermore, controlled polymerization techniques can be applied to tailor the different blocks, providing well-defined amphiphilic polymers consisting of water-soluble PDMAEMAq and a suitable hydrophobic block, e.g., poly(styrene), poly(butadiene) or poly(methyl methacrylate). In addition, all these modifications were performed under ambient atmosphere and from water, which are conditions feasible for the pulp and paper industry.

Figure 8: Adsorption of block copolymer micelles and subsequent spreading of the polymer over the surface leading to decreased surface energy and possible entanglements with a matrix polymer.
**Micromechanic measurements of cellulose-reinforced composites performed with Raman spectroscopy**

In 1928 Raman and Krishnan\textsuperscript{120} discovered that when a beam of light was transmitted through a gas, a low-intensity scattering of light appeared. It was shown to be originating from the inelastic scattering of light by the molecules in the gas. Furthermore, utilization of this scattered light as basis for spectroscopy would later be known as *Raman spectroscopy*. In 1977, Mitra *et al.*\textsuperscript{121} observed that when a monocrystalline polydiacetylene fiber was deformed, the peaks in its Raman spectrum corresponding to the backbone shifted. Galiotis *et al.*\textsuperscript{122} later demonstrated that when embedding the same type of fiber in an epoxy matrix, the local axial strain of the fiber could be determined by utilizing Raman spectroscopy in combination with a tensile tester. This was further developed by Young *et al.*\textsuperscript{123} who showed that the shift in Raman of a poly(*p*-phenylene benzobisoxazole) could be related to not only the axial strain, but also to the modulus. In addition, it was demonstrated that a shift in Raman band is a direct reflection of molecular deformation within the fibers.

Based on these discoveries, Eichhorn *et al.*\textsuperscript{124}-\textsuperscript{127} extended the method to include not only synthetic, but also natural fibers, by measuring molecular deformation in a cellulose fiber utilizing Raman spectroscopy. In detail, by observation of the shift for the ether bonds at 1095 cm\textsuperscript{-1} during tensile deformation. The 1095 cm\textsuperscript{-1} Raman signal is corresponding to the C-O stretching motion that is basically parallel to the chain axis\textsuperscript{28}. Furthermore, it could later be shown that measurements of micromechanics of cellulose-reinforced composites, *i.e.*, stress transfer from matrix to cellulose fiber, can be performed with Raman spectroscopy in connection with a tensile tester\textsuperscript{128}, which later also has been applied for nanocellulosic fillers\textsuperscript{20, 129, 130}. A schematic illustration of the method is shown in figure 9.
Figure 9: During tension of a cellulose-reinforced composite the cellulose backbone is strained and the Raman signal for the ether bond at 1095 cm\(^{-1}\) shifts to lower wavenumbers.
Experimental

Detailed information about materials and experimental work can be found in the appended papers and submitted manuscripts.

Materials

All chemicals were purchased from Aldrich unless stated otherwise. 2-(Dimethylamino)ethyl methacrylate (DMAEMA, 98%) was passed through basic Al₂O₃ column, prior to use to remove the inhibitors. ε-Caprolactone (ε-CL, 99%, Alfa Aesar) was dried over CaH₂ overnight, distilled under reduced pressure, and stored under argon at 4 °C. Toluene (HPLC grade, Fischer Scientific) was dried through azeotropic boiling prior to use. Tin(II) 2-ethylhexanoate (Sn(Oct)₂, 95%) was stored over molecular sieves under argon atmosphere 1 week prior to use. ε-Polycaprolactone (PCL, Mₙ 80 000 g/mol), benzyl alcohol (Merck, 98%), (2-hydroxyethyl bromoisobutyrate (HEBI, 95%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), copper chloride (Cu(I)Cl, 99+%), copper bromide (Cu(I)Br, 98%), copper (II) bromide (Cu(II)Br₂, 99%), methyl iodide (MeI, 99%, Lancaster), α-bromoisobutyryl bromide (BiB, 98%), ethyl α-bromoisoobutyrate (EBiB, 98%), sodium ascorbate (NaAsc, 98+%), N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (PMDETA, 99%), propargyl alcohol (99%), sodium azide (NaN₃, 99+%), 4-(dimethylamino)pyridine (DMAP, 99+%), triethylamine (TEA, Merck), trifluoroacetic acid (TFA, 99%), tert-butyl methacrylate (tBMA, 98%), hydroxyl-terminated polybutadiene (HTPB, Mₙ 3000 g/mol, PolySciences) polyethyleneimine (PEI, Mₙ 60 000 g/mol, Acros Organics), Borosilicate glass microspheres 10 µm in diameter (Thermo Scientific, CA) used for AFM force measurements, were all used as received.

Three types of pulps were used. Never-dried sulfite softwood-dissolving pulp, kindly provided by Domsjö, Örnsköldsvik, Sweden that was either carboxymethylated¹³¹ (Paper 1) at Innventia, Stockholm, or TEMPO-oxidized¹⁷ (Paper 4 and Raman
measurements). The modifications were followed by subsequent homogenization according to a previously described protocol\textsuperscript{132} yielding CNF. For paper 3, industrial never-dried kraft pulp (denoted F), kindly supplied by Södra Cell AB and Korsnäs AB, Sweden, was solvent exchanged into toluene and, thereafter, utilized. For adsorption of block copolymers of poly(butadiene) and PDMAEMA/poly(methacrylic acid) (PMAA) and subsequent paper-making, a never-dried kraft pulp (K46) was kindly supplied by SCA, Sweden.

**Characterization methods**

Proton nuclear magnetic resonance (\textsuperscript{1}H-NMR) spectra were recorded on a Bruker AM 400 MHz NMR using deuterated chloroform (CDCl\textsubscript{3}) as solvent. The residual solvent signal was used as internal standard.

Size exclusion chromatography (SEC) systems were used to determine molecular weight ($M_n$) and molar-mass dispersity ($D_M$). For homopolymer PDMAEMA or block copolymers where one of the blocks was PDMAEMA, a SEC system using DMF (0.2 mL·min\textsuperscript{-1}, 50 °C) with the addition of 0.01 M as the mobile phase was used. The SEC was a TOSOH EcoSEC HLC-8320GPC system equipped with an EcoSEC RI detector and three columns (PSS PFG 5 µm; Microguard, 100 Å and 300 Å) ($M_W$ resolving range: 300-100 000 g/mol) from PSS GmbH. Calibration was performed using narrow molecular-weight distribution linear poly(methyl methacrylate) standards ($M_W$ range: 400–300 000 g/mol), toluene was used as a flow rate marker. PSS WinGPC software version 7.2 was used to process the data.

For PCL or poly(styrene) (PS) homopolymers, a SEC system using CHCl\textsubscript{3} (1.0 mL·min\textsuperscript{-1}, 30 °C) as mobile phase was used. The SEC system was a Verotech PL-GPC 50 Plus system equipped with a PL-RI detector and two Mixed-D columns (Varian) calibrated using narrow molecular-weight distribution PS standards ($M_W$ range: 580 to 400 000 g/mol). Toluene was used as flow rate marker.
Experimental

Polyelectrolyte titration (PET) using a 716 DMS Titrino (Metrohm, Switzerland) was performed to measure the charge density of block copolymer micelles in MilliQ water. Potassium poly(vinyl sulfate) (KPVS) and ortho-toluidine blue (OTB) were added as titrant and indicator, respectively. The color change was recorded spectroscopically with a Fotoelektrischer Messkopf 2000 (BASF), and the amount of KPVS needed to reach equilibrium was calculated according to Horn et al.\textsuperscript{133}.

Dynamic light scattering (DLS) (Malvern Zetasizer NanoZS) was used to determine hydrodynamic radii and zeta potentials of block copolymer micelles in deionized water without addition of salt. The concentration of the solutions studied was 100 mg L\textsuperscript{-1}.

Thermal degradation of fibers/fibrils was analyzed with thermogravimetric analysis (TGA). Samples were heated from 40-700 °C at 10 °C min\textsuperscript{-1} in N\textsubscript{2} atmosphere using a Mettler Toledo TGA/DSC1 equipped with a sample robot. STAre software V10.0 was used to analyze the data.

The thermal properties of fibers, fibrils, block copolymers or bionanocomposites were analyzed with differential scanning calorimetry (DSC). The heating and cooling rates were 10 °C min\textsuperscript{-1} in the temperature range of -70 °C to 180 °C under N\textsubscript{2} atmosphere using a Mettler-Toledo DSC with a sample robot and a cryo-cooler. STAre software V9.2 was used to analyze the data, and the degree of crystallinity ($X_c$) was calculated according to:

$$X_c = \frac{\Delta H_c}{w\Delta H_{100}^\circ}$$

where $\Delta H_c$ is the heat of crystallisation of the sample, $\Delta H_{100}^\circ$ is the heat of crystallization of 100 % crystalline PCL, which has a value of 136 J g\textsuperscript{-1}\textsuperscript{134} and $w$ is the weight fraction of PCL in the sample. Furthermore, in a block copolymer with miscible blocks the weight fractions were calculated according to Fox equation\textsuperscript{135}:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

where $T_g$ is the $T_g$ of the block copolymer, $T_{g,1}$, $T_{g,2}$ and $w_1$, $w_2$ are $T_g$’s and weight fractions of the blocks 1 and 2, respectively.
Experimental

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometer (FT-IR) equipped with a MKII Golden GateTM, single reflection ATR system from Specac Ltd, London, UK. The ATR-crystal was a MKII heated Diamond 45 °C ATR Top Plate.

FT-IR images were recorded in attenuated total reflectance mode on a Spectrum Spotlight 400 FT-IR microscope connected to a Spectrum 100 FT-IR spectrometer (Perkin-Elmer Inc.). The area of interest was scanned in ATR image mode by a 16-point dual-array liquid-N₂-cooled MCT detector with a pixel resolution of 1.56×1.56 μm².

Cellulose model surfaces, used for investigation of adsorption behavior of block copolymers (paper 1 and triblock copolymer adsorption), were prepared as described hereafter. Silicon wafers (p-type, MEMC Electronics Materials, Novara, Italy), were oxidized in an air plasma oven (Model PDC 002, Harrick Scientific Corporation, NY, USA), and followed by subsequent adsorption of 2 bilayers of PEI and carboxymethylated CNF using an adopted method136.

Quartz crystal microbalance with dissipation monitoring (QCM-D) (E4, Q-Sense AB, Västra Frölunda, Sweden) was used to study the block copolymer adsorption to the cellulose model surface from a continuous flow of 100 µL/min of block copolymer dispersion. The change in frequency depends on the adsorbed mass according to the Sauerbrey model137:

\[ m = C \frac{\Delta f}{n} \quad \text{eq. [3]} \]

where \( m \) is the adsorbed mass per unit area, \( C \) is a sensitivity constant (-0.177 mg/(m²·Hz), \( \Delta f \) is the change in resonance frequency and \( n \) is the number of the overtone.

Atomic force microscopy (AFM) height images were acquired with either MultiMode IIIa (Veeco Instruments Inc. Santa Barbara, CA) (Paper 2) in tapping mode or MultiMode 8 (Bruker, Santa Barbara, CA, USA) in ScanAsyst mode (Paper 4) on silicon oxide and mica surfaces, respectively. Furthermore, for adhesion
measurements (Paper 2), the colloidal probe technique\cite{33} was applied. A silica particle (Thermo scientific, CA), with adsorbed block copolymers on the surface and a diameter of approximately 10 µm was attached to the cantilever. The measurements were then performed by using AFM tune IT v 2.5 software (Force IT, Sweden), monitoring the thermal frequency spectra of the cantilevers.

Contact angles were measured on a KSV instrument CAM 200 equipped with a Basler A602f camera at 50 % RH and 23 °C, using 5 µL droplets of Milli-Q water. Contact angles were determined using the CAM 200 software.

Optical microscopy was performed on a Leica DM IRM optical microscope.

Peel tests of hot-pressed paper sheet biocomposites were carried with an Instron 4411 with a speed of 10 mm/min with a load cell of 50 N. Prior to testing, the specimens were conditioned at 25 °C, 50 % relative humidity for 96 h.

Tensile testing was performed on PCL-based bionanocomposites with an Universal Material Testing Machine Instron 5944, using a load cell of 50 N, gap length of 10 mm and a cross-head speed of 10 mm/min, which corresponds to an initial strain rate of 100 %/min. Prior to testing All specimens were cut into strips with the dimensions of approximately 4 mm in width and 30-50 µm in thickness. The specimens were conditioned at 23 °C, 50 % relative humidity for 48 hours.

Dynamic mechanical analysis (DMA) was performed on PCL-based bionanocomposites using a TA Instruments Q800 in tensile mode with a gap distance of about 5 mm. Specimens of approximately 5 mm in width and 30-50 µm in thickness were used. Measurements were performed at a constant frequency of 1 Hz, amplitude of 15 µm and a heating rate of 5 °C/min. Temperature scans were performed in a temperature range of -100 °C to 100 °C.

Field emission scanning electron microscopy (FE-SEM) was conducted to study the morphology of cryofractured cross-sections of composites. Samples were attached on metal stubs
with carbon tape, and sputtered with 4 nm Au/Pd in a Cressington 208HR sputter-coater unit, and thereafter studied with a Hitachi S-4800 with an acceleration voltage of 7 kV.

Peeling of laminated paper-sheet biocomposites were studied with a tabletop Hitachi TM-1000 SEM using an acceleration voltage of 15 kV.

Raman measurements were performed with a Renishaw RM-1000 spectrometer using a near infrared laser with a wavelength of 785 nm. The spot size of the laser was around 1–2 μm in diameter, and the power was approximately 1 mW. The laser was focused on the sample using an Olympus BH-1 microscope equipped with a ×50 objective lens. Spectra were recorded in the range 1050-1150 cm⁻¹ with an exposure time of 120 s.

Micromechanic deformations were performed in tension using a Deben microtest rig connected to a 300 N load cell. Tensile increments (0.005 %) were conducted, and at each increment a Raman spectrum was recorded. The spectra were fitted individually using an automated algorithm, a Lorentzian function, based on the work of Marquardt¹³⁹.

**Experimental procedures**

**Covalent grafting of cellulose**

**Modification of CNF through SI-ROP**

ε-CL has been grafted from both kraft pulp fibers (Paper 1) and CNF (Paper 4). Detailed procedures and conditions can therefore be found in the appended manuscripts and hereafter follows only short descriptions.

Cellulose fibers/fibrils were solvent exchanged to toluene from water, followed by subsequent addition of ε-CL, Sn(Oct)₂ and benzyl alcohol (sacrificial initiator), which was added to alter target DP. The reactions were then allowed to proceed under argon atmosphere at 85-110 °C for 4-24 h, according to scheme 3.
Scheme 3: SI-ROP of ε-CL from cellulose fibers (F) or cellulose nanofibrils (CNF) in the presence of benzyl alcohol as sacrificial initiator to give F/CNF-g-PCL.

**Modification of CNF through SI-ARGET ATRP**

Styrene was grafted from CNF for use in composites for micromechanic measurements according to scheme 4. In a first step, TEMPO-oxidized CNF was solvent exchanged into acetone for immobilization of ATRP initiator (BiB) yielding CNF-Br. In a second step, CNF-Br was solvent exchanged into anisole for polymerization by ARGET ATRP of styrene adopted from a previous reported protocol\(^{140}\). CNF-Br in anisole, EBiB, PMDETA, NaAsc and Cu(II)Br\(_2\) were all added to a flask followed by subsequent 3 times evacuation and back-filling of argon. The reaction was then allowed to proceed for 4-24 h at 100 °C, followed by subsequent Soxhlet extraction in DCM overnight, and the product was denoted CNF-g-PS.
Scheme 4: A) Immobilization of ATRP-initiator on CNF, and B) SI-ARGET ATRP of styrene from CNF in the presence of EBiB as sacrificial initiator to give CNF-g-PS.
**Preparation of block copolymers**

**Di- and triblock copolymers of PCL and PDMAEMA**

Detailed information about synthesis for PDMAEMA and PCL block copolymers is described in Papers 2 and 3. Different di- and triblock copolymers of PCL and PDMAEMA have been prepared, and these were: PCL-\(b\)-PDMAEMA, PDMAEMA-\(b\)-PCL-\(b\)-PDMAEMA, PCL-\(b\)-PDMAEMA-\(b\)-PCL, followed by subsequent quaternization of the PDMAEMA block(s) and dispersion as micelles in water. The synthetic procedure is illustrated in scheme 5.

**Triblock copolymers of PB and PDMAEMA or PMAA**

Two types of triblock copolymers with polybutadiene (PB) have been prepared: PDMAEMA-\(b\)-PB-\(b\)-PDMAEMA and PMAA-\(b\)-PB-\(b\)-PMAA, as illustrated in scheme 6. PDMAEMAq-\(b\)-PB-\(b\)-PDMAEMAq was prepared according to similar procedure as PDMAEMAq-\(b\)-PCL-\(b\)-PDMAEMAq, while PMAA-\(b\)-PB-\(b\)-PMAA required the additional step of converting PtBMA to PMAA. The synthetic procedures are illustrated in scheme 6.

Hydroxyl-functional PB, HTPB, was converted into a macroinitiator through acylation with BiB. Thereafter, Br-PB-Br was chain extended by ATRP with either PDMAEMA or PtBMA yielding two triblocks. As final steps, PDMAEMA was quaternized and PtBMA was deprotected to obtain PDMAEMAq-\(b\)-PB-\(b\)-PDMAEMAq and PMAA-\(b\)-PB-\(b\)-PMAA, respectively.
Scheme 5: Preparation of quaternized di- and triblocks of PCL and PDMAEMA starting from the initiator HEBI.
Scheme 6: Preparation of triblocks of PB with either PDMAEMAq or PMAA.
Modification of cellulose through physical adsorption

Block copolymers, both di- and triblocks, were physisorbed to various substrates. Those were: silicon oxide surface, cellulose model surface, CNF and kraft pulp fibers (K46). Table 1 summarizes which polymers that were adsorbed to which substrates.

Table 1: Summary of block copolymer adsorption to various substrates.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Silicon oxide surface</th>
<th>Cellulose model surface</th>
<th>CNF</th>
<th>Kraft pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMAEMAq-b-PCL</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
</tr>
<tr>
<td>PCL-b-PDMAEMAq-b-PCL</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDMAEMAq-b-PCL-PDMAEMAq</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDMAEMAq-b-PB-b-PDMAEMAq</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>✓</td>
</tr>
<tr>
<td>PMAA-b-PB-b-PMAA</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>✓</td>
</tr>
</tbody>
</table>
**Preparation and evaluation of biocomposites**

**PCL-based biocomposites**

Two types of composites including PCL were prepared: paper-sheet biocomposites (Paper 1) and bionanocomposites (Paper 4). Paper-sheet biocomposites were produced by mixing F-\(g\)-PCL, with three different graft lengths of PCL, and unmodified fibers in a Rapid-Köthen equipment, mimicking a paper-making process. Thus, no matrix polymer was added and the amount of PCL was limited to the grafted PCL.

The bionanocomposites, on the other hand, were produced through solvent casting of CNF-\(g\)-PCL or CNF-PDMAEMAq-\(b\)-PCL, both with three different lengths of PCL, and neat PCL. Hence, the amount of CNF was limited to the modified CNF.

**PS-based composites**

Nanocomposites were produced by solvent casting CNF-\(g\)-PS and neat PS from butyl acetate. Nanocomposites with CNF content of approximately 40 wt-% were obtained.

**PB-based composites**

Paper-sheet biocomposites were prepared from fibers modified with PDMAEMAq-\(b\)-PB-\(b\)-PDMAEMAq and PMAA-\(b\)-PB-\(b\)-PMAA produced with the layer-by-layer (LbL) approach. The pulp was washed with 0.01 M HCl for 30 min, rinsed with water and then washed with 0.001 M NaHCO3, followed by subsequent adjustment of pH to 9 through the addition of NaOH.

Micelle dispersion of cationic PDMAEMAq-\(b\)-PB-\(b\)-PDMAEMAq (1.7 wt-% of fiber weight) was added to the pulp and the mixture stirred for 30 minutes, and washed with deionized water. Thereafter, micelle dispersion of anionic PMAA-\(b\)-PB-\(b\)-PMAA (1.7 wt-% of fiber weight) was added and stirred for an additional 30 minutes followed by washing. Paper-sheet biocomposites were then prepared in a Rapid-Köthen equipment.
Results and discussion

To expand the field of application for cellulose-based materials, modifications are often necessary, such as attachment/grafting of polymers. There are mainly two ways to attach polymers to cellulose: either by utilizing the hydroxyl groups present and chemically graft a polymer from/to the surface, or by taking advantage of the charges present on a cellulose fiber/fibril and physically adsorb a polymer. The work of this thesis has been directed to expand the toolbox for cellulose modification by utilizing, and comparing, the two approaches of attaching polymers to cellulose.

In the first part of the thesis, cellulose fiber modification is described. From kraft pulp fibers, \(\varepsilon\)-caprolactone (\(\varepsilon\)-CL) was either grafted by SI-ROP (Paper 1) or modified through adsorption of triblock copolymers based on hydroxyl terminated polybutadiene (HTPB). Thereafter, paper-based composites were prepared and evaluated.

In the second part, the substrates were model-type systems used to investigate the potential in utilizing adsorption of diblock (Paper 2) and triblock (Paper 3) copolymers of PCL and poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) as compatibilizers for cellulose-based materials.

The third and final part, describes modification of cellulose nanofibrils (CNF), their incorporation in a matrix, yielding nanocomposites, and their evaluation. Two types of nanocomposites were prepared; the first one based on poly(styrene) (PS) aiming to perform micromechanics measurements with Raman spectroscopy. The second type was PCL-based bionanocomposites reinforced with CNF compatibilized through either covalent grafting or physical adsorption of PCL (Paper 4), and evaluated with respect to material properties to compare the two approaches of compatibilization of CNF in a non-polar matrix.
Results and discussion

Figure 10: The three parts of the project, modification of: fibers, model surfaces and fibrils. Followed by preparation of composites (Parts 1 and 3).
Results and discussion

Part one: Fiber modification and paper-sheet composite preparation

Kraft pulp fibers were modified through either covalent grafting by SI-ROP of ε-CL (Paper 1), or physical adsorption of triblock copolymers consisting of a middle block of PB and outer blocks of either PDMAEMAq or PMAA. From the modified fibers, paper-sheet biocomposites were prepared.

**Covalent grafting of kraft pulp through SI-ROP of ε-CL (Paper 1)**

Three different lengths of PCL, with target DP: 120, 240 and 480, based on monomer-to-sacrificial initiator ratio, were covalently grafted from kraft pulp fibers denoted: Fiber-g-Short (FgS), Fiber-g-Medium (FgM), and Fiber-g-Long (FgL), respectively. In parallel with the grafting, free PCL was formed from the sacrificial initiator (benzyl alcohol) and denoted: PCL (S), PCL (M) and PCL (L). Molecular weight determinations of the free PCL formed by NMR spectroscopy and SEC are shown in table 2. The molecular weight appears to be limited, i.e., above a certain target DP, longer chains are not obtained.

Table 2: Molecular weight and $D_M$ of free PCL formed during SI-ROP of ε-CL from kraft pulp.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical $M_w$ (g/mol)$^a$</th>
<th>$M_w$ by NMR (g/mol)$^b$</th>
<th>$M_n$ from SEC (g/mol)</th>
<th>$D_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL (S)</td>
<td>13 800</td>
<td>4 600</td>
<td>11 000</td>
<td>1.4</td>
</tr>
<tr>
<td>PCL (M)</td>
<td>27 500</td>
<td>8 400</td>
<td>20 000</td>
<td>1.6</td>
</tr>
<tr>
<td>PCL (L)</td>
<td>54 900</td>
<td>6 800</td>
<td>22 000</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$^a$Based on targeted DP, $^b$estimated from DP calculated from the signals at 4.05 ppm (-CH$_2$O, repeating unit) and at 3.61 ppm (-CH$_2$OH, end group).
Results and discussion

This is hypothesized to be an effect of water initiation, leading to more initiating sites in the system than anticipated, in combination with possible transesterification reactions. This would also explain the somewhat high molar-mass dispersities, which are increasing with higher target DP.

Irrespectively of the molecular weights of the bulk polymer, the grafting was successful, as can be seen in the respective FT-IR spectra (figure 11A). The intensity of the carbonyl peak (1730 cm\(^{-1}\)) increases with higher target DP, and as a consequence, the conclusion can be drawn that when higher DP of PCL is aimed for, more polymer is grafted on the surface, which is in accordance with previous findings\(^{141}\). However, the amount of grafted PCL was, independently of target DP, rather low, as can be seen in the TGA thermograms, figure 11B. One plausible reason of the lower amounts grafted, compared to previous amounts reported for grafting of \(\varepsilon\)-CL from CNF\(^{46}\), could be the higher specific surface area of CNF allowing for more polymer to be grafted per gram of cellulose.

Figure 11: (A) FT-IR spectra and (B) TGA thermograms of unmodified kraft pulp, \(F_gS\), \(F_gM\), \(F_gL\) and free PCL (only TGA).
Physical adsorption of triblock copolymers to kraft pulp

Preparation of triblocks with PB as middle block is described in scheme 6. HTPB was converted into a macroinitiator through acylation with BiB and chain extended with either DMAEMA or tBMA through ATRP. Thereafter, the PDMAEMA blocks were quaternized, and PtBMA blocks converted into PMAA by acidic hydrolysis, yielding cationic and anionic triblock copolymers, respectively. In table 3, a summary of characteristics of the formed triblocks, and the initial homopolymer, is displayed.

Table 3: Characterization in solution and dispersion of homopolymer HTPB and formed triblocks after chain extension, determined by SEC, PET and DLS.

<table>
<thead>
<tr>
<th></th>
<th>In solution</th>
<th>In dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$ (g/mol)</td>
<td>$D_M$</td>
</tr>
<tr>
<td>HTPB</td>
<td>3 000</td>
<td>1.1</td>
</tr>
<tr>
<td>PDMAEMA-b-PB-b-PDMAEMA</td>
<td>11 000</td>
<td>1.2</td>
</tr>
<tr>
<td>PtBMA-b-PB-b-PtBMA</td>
<td>11 000</td>
<td>1.1</td>
</tr>
<tr>
<td>PMAA-b-PB-b-PMAA</td>
<td>8 000</td>
<td>1.2</td>
</tr>
</tbody>
</table>

<sup>a</sup>Assessed from $(M_n$(triblock)$-M_n$(HTPB))/($2 \cdot M_w$(repeating unit of the outer block)).<br><sup>b</sup>cationic charge density, <sup>c</sup>after quaternization of PDMAEMA blocks.
Results and discussion

The $D_M$ is low for all polymers, *i.e.*, the polymerizations were performed in a control manner. Furthermore, DP’s of both types of outer blocks of the formed triblock copolymers are in close vicinity of one another. Concerning micellar properties, both cationic and anionic outer blocks, PDMAEMAq or PMAA, allow formation of micelles.

**Paper-sheet composites**

**Paper-sheet biocomposites with PCL-grafted fibers**

Paper-sheet biocomposites from PCL-grafted fibers were prepared in three different compositional weight ratios, based on dry weight, of modified-to-unmodified fibers: 10:90, 50:50 and 90:10. They were then denoted $Fg(S, M$ or $L)/F$ ($XX:YY$), where $XX$ and $YY$ are amounts of modified fibers and unmodified fibers, respectively. From unmodified kraft pulp fibers, reference sheets were also prepared. The reference sheets, *i.e.*, ordinary paper sheets, and the paper-sheet biocomposites were similar both with respect to appearance and tactility. The resemblance between the two types of sheets was further shown with contact-angle measurements. Both the hydrophobic as well as the oleophilic character, as investigated with water and rape-seed oil, respectively, were the same for all sheets, both reference and biocomposites. Most likely, this is an effect of the low amounts of PCL grafted.

To investigate the compatibility between modified and unmodified fibers two methods were used: FT-IR microscopy of the paper-sheet biocomposites (figure 12) and covalent labelling of the modified fibers with a dye, disperse red 13 (DR13), prior to preparation of the paper sheets (figure 13). In figure 12, the FT-IR images are shown. Note that a different scale bar is used to visualize the fiber structure for the reference material (unmodified pulp). In addition, the papers are non-dense materials, and as a consequence air is present between the fibers. Thus, low-absorbance regions are observed (purple regions for modified fiber-containing papers). Slight differences in between the paper-sheet biocomposites can be noted, such as more polymer grafted.
Results and discussion

for FgL/F (90:10), i.e., higher intensity in the carbonyl region (1760-1700 cm\(^{-1}\)). However, it can be observed that irrespectively of the length of PCL on the fibers, the modified fibers are well dispersed, suggesting that the paper-sheet biocomposites are overall homogeneous at high content of modified fibers, i.e., modified and unmodified fibers are compatible.

Figure 12: FT-IR microscopy images (400x300 µm) of total absorbance over the carbonyl region (1760-1700 cm\(^{-1}\)). The reference sheet is prepared from unmodified kraft pulp.

The compatibility between modified and unmodified fibers was further investigated through labelling the FgS with DR13, yielding FgSgDR13 prior to preparation of paper-sheets.

Figure 13: Photographs (top) and optical microscopy images (bottom) of a (A) reference sheet from unmodified pulp, (B) FgSgDR13/F (10:90) and (C) FgSgDR13/F (90:10).
Results and discussion

By mixing labelled fibers with unmodified fibers in two ratios: 10:90 and 90:10, the homogeneity could be investigated optically. In figure 13, paper-sheet biocomposites produced from labelled fibers and neat pulp are presented both as photographs and optical microscopy images, showing that the modified fibers are homogeneously dispersed within the biocomposites, independently of modified fiber content.

**Lamination of paper-sheet biocomposites**

Interestingly, it was found that when paper-sheet biocomposites composed of 50 or 90 wt-% modified fibers were hot pressed together, they form a laminate structure without the need for any matrix polymer. It is interpreted as, when the fibers are brought close together at a temperature above the $T_m$ of PCL, the chains can interact strongly. Possible interactions of PCL chains are formations of entanglements, or even co-crystallization upon cooling. This would also be in accordance with melt enthalpy of the different paper sheets from DSC measurements, since none of the paper sheets of composition $Fg(S, M \text{ or } L)/F 10:90$ displayed a crystallization/melting transition.

To assess how strongly the sheets adhere, peel test was performed, and the fracture surfaces were investigated by SEM. Images of the peeled specimens obtained are presented in figure 14. Three different regions were observed for the biocomposites $FgS/F (50:50)$ (X), $FgL/F (50:50)$ (Y) and $FgL/F (90:10)$ (Z). Those regions were: (1) non-peeled region, (2) beginning of peel and (3) peeled region (as schematically illustrated in figure 14).
Results and discussion

Figure 14: SEM-images of peeled specimens (X) FgS/F (50:50), (Y) FgL/F (50:50) and (Z) FgL/F (90:10) showing three regions: (1) non-peeled region, (2) beginning of peeling and (3) peeled region, schematically illustrated on top.

In figure 15, the interfacial work of adhesion estimated for the compositions 50:50 and 90:10 are presented. As a reference material, two paper sheets based on neat kraft-pulp fibers were hot pressed, and as expected, it did not result in any adhesion between the sheets. The strongest adhesion was found for samples...
Results and discussion

containing FgL and was so high for the highest content of FgL that the sample broke through a cohesive failure, i.e., within one paper sheet instead of between papers sheets.

![Interfacial work of adhesion from peel test of laminated paper-sheet biocomposites](image)

*Figure 15: Interfacial work of adhesion from peel test of laminated paper-sheet biocomposites. *Only one specimen was possible to peel, the rest broke within one of the layers, through cohesive failure.*

The results from the peel test also supports that longer grafts are indeed formed when higher degrees of polymerization are targeted, since longer polymer chains would easier both entangle and co-crystallize. Noteworthy is, that this is despite that the length of free PCL formed in parallel with the grafting did not seem to increase substantially, table 2. Furthermore, the increasing work of adhesion with supposed increasing PCL length of grafted chains is in accordance with observations from SEM imaging (figure 14).

There was indeed a clear difference when FgL was used instead of FgS. For FgS/F (50:50) an adhesive failure occurred when peeled, and the fracture surface showed no fiber tear (figures 14 X-3). On the other hand, when FgL were used in the biocomposites,
the adhesion increased and for FgL/F (50:50) only one specimen could be peeled. In the peeled specimen, a small amount of fiber tear could be detected (figure 14 Y-3). Furthermore, for FgL/F (90:10) no specimens could be peeled, all samples failed through cohesive failures, illustrated in figure 14 Z-3 where extensive fiber tear is observed. Hence, no interfacial work of adhesion could be estimated, but most likely it is higher than for the other samples since the adhesive joint was shown to be stronger than the paper itself.

**Paper-sheet composites with adsorbed PB triblock copolymers**

Triblock copolymers were adsorbed to kraft pulp fibers as a monolayer, PDMAEMAq-b-PB-b-PDMAEMAq, or bilayer, subsequent adsorption of PMAA-b-PB-b-PMAA. Paper-sheet composites were then prepared and evaluated. However, no significant effect on mechanical properties was obtained, which is ascribed to that the middle block, PB, was most likely too short to effectively bridge fibers together.

The adsorption behavior of triblocks onto cellulose and silicon oxide surfaces is described in detail further down.

**Part two: Block copolymer adsorption to model surfaces**

Model surfaces of cellulose were prepared through plasma treatment of silicon oxide surfaces and subsequent spin-coating of carboxymethylated CNF. In addition, plasma treated silicon oxide surfaces were also used as is. Onto both types of surfaces, block copolymers were adsorbed to study the behavior, formed surface structures and compatibilizing effect.
Preparation and evaluation of diblock copolymers of PCL and PDMAEMA (Paper 2)

Three block copolymers of PCL and PDMAEMA with a constant length of PDMAEMA and different lengths of PCL (DP target: 300, 1200 and 2400) were prepared (Paper 2). The PDMAEMA-block was subsequently quaternized to obtain PDMAEMAq-b-PCL (S, M and L), all according to scheme 7.

Scheme 7: Preparation of diblock PDMAEMAq-b-PCL.

The characterization of the polymers in solution and in dispersion, after quaternization and micellization, is summarized in table 4. All polymers were prepared in a controlled manner, i.e., they had low dispersities. Furthermore, stable micellar structures were formed that were uniform in size and had, as expected, a decreasing charge density with increasing PCL length.

For the comparative study between covalent grafting and physical adsorption, described further down, a longer PCL block was prepared, with DP target 4800, replacing the block copolymer with DP target 1200. This block copolymer will be discussed later (see Comparative study of covalent grafting and physical adsorption of PCL in bionanocomposites, Paper 4) and then be denoted \textit{PDMAEMA-b-PCL (L)}. Consequently, block copolymer with DP target of PCL 2400 will at the later section be referred to as \textit{PDMAEMA-b-PCL (M)}.

The formed block copolymers were adsorbed onto both silicon oxide surfaces and cellulose model surfaces. Silicon oxide surfaces are, apart from anionic, smooth which facilitates imaging of adsorbed structures. Cellulose model surfaces were used as well
since the aim was to understand the compatibilizing effect for cellulose in polar matrices.

Table 4: Properties of macroinitiator PDMAEMA-OH, diblock copolymers of PDMAEMA and PCL in solution and after quaternization, dispersed as micelles, determined by SEC, PET and DLS.

<table>
<thead>
<tr>
<th></th>
<th>In solution</th>
<th>In dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DP target</td>
<td>$M_n$</td>
</tr>
<tr>
<td>PDMAEMA-OH</td>
<td>-</td>
<td>4 700</td>
</tr>
<tr>
<td>PDMAEMA-$b$-PCL (S)</td>
<td>300</td>
<td>9 600</td>
</tr>
<tr>
<td>PDMAEMA-$b$-PCL (M)</td>
<td>1 200</td>
<td>17 000</td>
</tr>
<tr>
<td>PDMAEMA-$b$-PCL (L/M)</td>
<td>2 400</td>
<td>29 000</td>
</tr>
<tr>
<td>PDMAEMA-$b$-PCL (L)$^b$</td>
<td>4 800</td>
<td>58 000</td>
</tr>
</tbody>
</table>

$^a$ Dissolves in water, i.e., no micelle formation, $^b$ Will be discussed later in the section Comparative study of covalent grafting and physical adsorption of PCL in bionanocomposites.

After adsorption, the surfaces were annealed at 160 °C for 2 hours to increase the mobility of the PCL segments and, consequently, allow them to spread out over the surface. AFM images of silica surfaces before and after heat treatment, figure 16, illustrates how the collapsed micellar structures spreads out and covers the whole surface, especially for the long PDMAEMA$q$-$b$-PCL (L). For PDMAEMA$q$-$b$-PCL (S and M), no micellar structures were
Results and discussion

observed, despite that they were detected with DLS. One explanation could be that they are internally weakly bound, and upon contact with the surface, the micellar structure spontaneously unfolds and spreads out.

Figure 16: AFM height images (2x2 µm) of silicon oxide surfaces with adsorbed block copolymer micelles of PDMAEMAq-b-PCL, before and after heat treatment.

The adsorption was monitored with QCM-D and the change in wetting was analyzed with contact-angle measurements. The adsorbed amounts and the contact angles after heat treatment are displayed in table 5. With longer PCL-blocks the amount of both adsorbed polymer and contact angles increased, as expected. However, there was a difference between the two types of surfaces. For the silicon oxide surface, there was a large increase in the amount adsorbed and contact angle, already between short and medium PCL lengths. For the cellulose model surface, on the other hand, this significant increase is shifted to between medium and long PCL length. This is possibly due to that adsorption onto the silicon oxide surface might be enhanced by non-electrostatic
interactions, *e.g.*, Van der Waals forces, in addition to electrostatic interactions.

Table 5: Adsorbed amounts on silicon oxide and cellulose surfaces of block copolymer micelles of PDMAEMAq-\(b\)-PCL, and subsequent alteration in hydrophobicity.

<table>
<thead>
<tr>
<th>Silicon oxide surface</th>
<th>Adsorbed amount (mg/m²)</th>
<th>Contact angle (°)</th>
<th>Cellulose model surface</th>
<th>Adsorbed amount (mg/m²)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMAEMAq-(b)-PCL (S)</td>
<td>4</td>
<td>49 ± 1.5</td>
<td>0.5</td>
<td>38 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>PDMAEMAq-(b)-PCL (M)</td>
<td>13</td>
<td>67 ± 0.6</td>
<td>2</td>
<td>46 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>PDMAEMAq-(b)-PCL (L)</td>
<td>15</td>
<td>68 ± 0.6</td>
<td>10</td>
<td>65 ± 2.1</td>
<td></td>
</tr>
</tbody>
</table>

To investigate whether the block copolymers could act as compatibilizers, *i.e.*, increase the adhesion between a polar surface and a non-polar PCL matrix, AFM colloidal probe measurements were performed. The different block copolymers were separately adsorbed onto a silica probe, and force measurements against a PCL surface at different temperatures were performed, figure 17, top 4.

In these measurements, mainly a combination between two parameters should affect the adhesion. The first one is the surface energy, *i.e.*, a decrease in surface energy should lead to an increase in adhesion\(^{142}\). The second one is physical entanglements between PCL chains on the probe and on the surface. At 60 °C (figure 17, bottom), which is above the melting temperature of PCL a clear increase in pull-off force is observed, especially evident for
Results and discussion

PDMAEMAq-b-PCL (M and L) where the distance in contact is around 0.5-1.5 µm.

Figure 17: AFM force-separation curves for a neat silica probe, and silica probes modified with the three block copolymers PDMAEMAq-b-PCL (S, M and L) against a PCL surface, performed at different temperatures (top 4) and for all 4 samples at 60 °C (bottom).
Hence, they emerge from disentanglements of PCL chains, since a plausible contribution from secondary interactions would act at much shorter distances, up to around 15 nm \(^\text{143}\). Furthermore, the extent of the entanglements is clearly increasing for PDMAEAm\(_b\)-PCL (L) compared to PDMAEAm\(_b\)-PCL (M). In addition, when measuring at temperatures above \(T_m\) (70 and 80 °C), most likely the chain mobility is too high to give rise to strong entanglements. From these measurements it could be concluded that block copolymer adsorption has the potential for increasing interfacial adhesion between two materials with different polarity, especially if processing is performed above \(T_m\) of PCL.

### Preparation and adsorption of triblock copolymers

Triblock copolymers of PCL and PDMAEMA were prepared to study the effects of molecular architecture on different properties, such as morphology and adsorption behavior (Paper 3). Furthermore, adsorption behavior was also investigated for triblock copolymers of PB together with PDMAEAm or PMAA.

**ABA- and BAB-type triblock copolymers of PCL and PDMAEMA (Paper 3)**

Triblock copolymers of PCL and PDMAEMA were prepared according to scheme 8. For triblock PDMAEAm\(_b\)-PCL-b-PDMAEAm, the strategy of combining ROP with acylation with BiB and subsequent chain extension with DMAEMA by ATRP, has been reported previously \(^\text{144}\). The synthetic route for PCL-b-PDMAEAm-b-PCL, on the other hand, has to the authors’ best knowledge not been reported elsewhere. By preservation of the hydroxyl in HEBI and end-group transformation of PDMAEMA, a dihydroxyl functional macrominiator was obtained that could be chain-extended into the desired triblock.

Chain extension of the Br-PCL-Br with DMAEMA by ATRP yielded a polymer giving rise to a clear shift to lower elution volume in SEC (figure 18A) and a \(D_M\) of 1.2 (table 6). A small shoulder can be noted in the macronitiator, which is ascribed to transesterification reactions occurring during ROP.
Scheme 8: Preparation of triblocks PDMAEMAq-b-PCL-b-PDMAEMAq and PCL-b-PDMAEMAq-b-PCL.
Results and discussion

For PCL-b-PDMAEMA-b-PCL, a bimodal trace was obtained after chain extension (figure 18B), indicating that the product was composed of both di- and triblock copolymers. To purify the product, i.e., separate potential diblocks from the desired triblocks, several techniques were attempted, such as: precipitation in different solvents, preparative SEC and ultrafiltration. However, irrespectively of which purification technique that was applied, the SEC trace had the same appearance, i.e., the bimodal appearance remained. This is illustrated in figure 18C, where all fractions from preparative SEC are displayed, plotted with an offset in intensity.

![Figure 18: SEC-traces of: A) Br-PCL-Br (solid line) and PDMAEMA-b-PCL-b-PDMAEMA (dashed line); B) HO-PDMAEMA-OH (solid line) and PCL-b-PDMAEMA-b-PCL (dashed line), and C) fractions of preparative SEC of PCL-b-PDMAEMA-b-PCL.](image)

This suggests that the bimodality in the SEC traces might not be caused by a mixture of di- and triblocks but rather an effect of a physical phenomenon occurring during SEC analysis. PDMAEMA is a thermoresponsive polymer, exhibiting a lower critical solution temperature (LCST) in the range of 38–80 °C in water, depending on pH145, 146. Even though the mobile phase of the SEC system was DMF, the thermoresponsive behavior could cause possible agglomeration since the SEC system was operated at 50 °C and DMF, as water, has the ability to form hydrogen bonds that can interact with PDMAEMA147. DLS measurements were, therefore, performed to elucidate the effect of temperature on the block copolymers in DMF. The temperature was increased from 25 to 50 °C while measuring, and it was observed that the size of the
micellar-type structure varied between 5-5000 nm accordingly. Additionally, it has previously been stated that PDMAEMA can interact with THF SEC columns giving rise to broader $D_m$. It is therefore believed that the bimodal trace is not reflecting the true sample, but rather an effect of a physical phenomena, such as column interactions, possibly enhanced by a temperature-induced association in DMF. Altogether, these findings led us to believe that the triblock PCL-$b$-PDMAEMA-$b$-PCL had indeed been obtained despite the appearance in SEC.

In table 6, molecular weights, $D_M$, $T_g$, and $T_m$ of HO-PDMAEMA-OH, Br-PCL-Br and triblock copolymers determined by $^1$H-NMR, MALDI-TOF, SEC and DSC are displayed. The polymerizations were not run to 100 % monomer conversion in order to suppress side reactions. Therefore, as expected, molecular weights from $^1$H-NMR and MALDI-TOF are lower than theoretical. However, the molecular weight for PCL-$b$-PDMAEMA-$b$-PCL is higher than theoretical molecular weight according to $^1$H-NMR. One explanation may be that there is a slight difference in solubility of of PCL and PDMAEMA in the block copolymers in CDCl$_3$, even though they are visually soluble. As a consequence, the signals for PDMAEMA may be somewhat broadened, and less pronounced in $^1$H-NMR.

The $T_g$'s of PDMAEMA and PCL are around 10 °C and -60 °C, respectively. PDMAEMA-$b$-PCL-$b$-PDMAEMA exhibits a $T_g$ between the $T_g$'s of PCL and PDMAEMA homopolymers indicating that the phases are miscible, and, in addition, no crystalline melting transition can be observed by DSC. This is ascribed to a different packing of chains compared to the homopolymers. If Fox equation (eq. 2) is applied, the weight fraction of PCL is estimated to be 36 %, which is equivalent to a total molecular weight of 22 000 g/mol for this triblock copolymer. This is well in accordance with the molecular weight estimated from $^1$H-NMR, which was 24 000 g/mol (table 6). Triblock PCL-$b$-PDMAEMA-$b$-PCL exhibits two $T_g$'s, i.e., it is phase separating and Fox equation cannot be applied.
Results and discussion

- Based on 100% conversion, determined by MALDI-TOF, SEC, NMR in CDCl3, highest intensity peak from 1H-NMR in CDCl3, determined with DSC, e determined from DMF-SEC, f determined from eq 1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mₚ</th>
<th>Tₚ</th>
<th>Mₙ</th>
<th>Tₙ</th>
<th>M₁</th>
<th>T₁</th>
<th>M₂</th>
<th>T₂</th>
<th>M₃</th>
<th>T₃</th>
<th>M₄</th>
<th>T₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>q-PCL-</td>
<td>28 000</td>
<td>12 000</td>
<td>35 000</td>
<td>1.2</td>
<td>-</td>
<td>42 000</td>
<td>3 100</td>
<td>24 000</td>
<td>4 3</td>
<td>50 000</td>
<td>6 000</td>
<td>5 300</td>
</tr>
<tr>
<td>PDMAEMA-</td>
<td>Br-PCL-</td>
<td>12 000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDMAEMA-</td>
<td>Br-PCL-</td>
<td>29 000</td>
<td>12 000</td>
<td>35 000</td>
<td>1.2</td>
<td>-</td>
<td>42 000</td>
<td>3 100</td>
<td>24 000</td>
<td>6 000</td>
<td>12 000</td>
<td>6 000</td>
</tr>
<tr>
<td>PDMAEMA-</td>
<td>12 000</td>
<td>12 000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO-PCL-OH</td>
<td>28 000</td>
<td>12 000</td>
<td>35 000</td>
<td>1.2</td>
<td>-</td>
<td>42 000</td>
<td>3 100</td>
<td>24 000</td>
<td>6 000</td>
<td>12 000</td>
<td>6 000</td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Molecular weights, Mₚ, Mₙ, Tₚ, Tₙ, of HO-PDMAEMA-OH, Br-PCL-BR, and triblock copolymers determined by 1H-NMR, MALDI-TOF, SEC and DSC.
Results and discussion

Oppositely to the triblock PDMAEMA-b-PCL-b-PDMAEMA, it possesses a crystalline behavior. Hence, the molecular architecture of these types of block copolymers seems to be of high importance when tuning the degree of crystallinity/morphology.

After quaternization of PDMAEMA blocks and dispersion as micelle-type structures in water, charge density, size and Z-potential were measured (table 7). Thereafter, the triblock dispersions were, separately, adsorbed onto silicon oxide surfaces both in a QCM-D and by applying droplets of micellar dispersion.

Table 7: Properties of triblocks of PDMAEMAq and PCL in dispersion and on silicon oxide surfaces determined by PET, DLS, QCM and contact angle measurements.

<table>
<thead>
<tr>
<th></th>
<th>Charge density (meq/g)</th>
<th>$R_h$ (nm)</th>
<th>Z-potential (mV)</th>
<th>Adsorbed amount (mg/m²)</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMAEMAq-b-PCL-b-PDMAEMAq</td>
<td>2.1</td>
<td>190 ± 30</td>
<td>17 ± 5.0</td>
<td>1.1</td>
<td>52 ± 3.5 °</td>
</tr>
<tr>
<td>PCL-b-PDMAEMAq-b-PCL</td>
<td>0.5</td>
<td>50 ± 2.2</td>
<td>28 ± 0.8</td>
<td>0.43</td>
<td>66 ± 2.3 °</td>
</tr>
</tbody>
</table>

The latter surfaces were used for contact angle measurements after annealing at 160 °C for 2 hours. The results from micelle characterization, adsorption and contact angle measurements are presented in table 7. As expected, the triblock with PDMAEMAq as outer blocks had the highest charge. However, the micellar stability was inferior compared to the opposite triblock. Furthermore, with PDMAEMAq-b-PCL-b-PDMAEMAq higher amount of polymer was adsorbed, but the contact angle was somewhat lower. PDMAEMAq is water soluble, and to therefore give rise to a low increase in contact angle, despite higher amount of polymer adsorbed, is expected.
Results and discussion

**Adsorption of triblocks of PB and PDMAEMAq or PMAA**

Adsorption of triblock PDMAEMAq-b-PB-b-PDMAEMAq, and subsequent adsorption of PMAA-b-PB-b-PMAA was observed with AFM imaging (figure 19).

![AFM height images](image)

**Figure 19:** AFM height images (1x1 μm) in the dry state together with corresponding height profile of neat silicon oxide surface, after adsorption of PDMAEMAq-b-PB-b-PDMAEMAq (monolayer) and after subsequent adsorption of PMAA-b-PB-b-PMAA (bilayer).

A monolayer of cationic PDMAEMAq-PB-PDMAEMAq can be adsorbed onto the anionic silicon oxide surface, and a change in surface morphology is detected. Further, when anionic PMAA-b-PB-b-PMAA is allowed to adsorb, it forms uniform micellar structures, confirming both the presence of cationic triblock on the surface and that both types of triblocks can be readily adsorbed to an anionic surface in the form of a bilayer.
Results and discussion

Part three: CNF modification and composite preparation

TEMPO-oxidized CNF was modified either through covalent grafting of PS or PCL (Paper 4), or by physical adsorption of block copolymers of PDMAEMAq and PCL (Paper 4). These were then incorporated as reinforcing elements in composites and evaluated.

**Covalent grafting of CNF through SI-ARGET ATRP of styrene**

Styrene was grafted by SI-ARGET ATRP from CNF and the sacrificial initiator (EBiB) according to scheme 9.

![Scheme 9: SI-ARGET ATRP of styrene from CNF in the presence of EBiB as sacrificial initiator to give CNF-g-PS.](image)

The critical chain entanglement length \( (Z_c) \) is the length of a polymer where network formation through entanglements is possible, and for PS it is ca 38 000 g/mol\(^{151}\). The aim was to graft PS in three different lengths correlated to \( Z_c \), i.e., below, above and high above \( Z_c \). The molecular weights obtained from SEC for the free PS formed in parallel with the grafting are presented in table 8. From the table, it can be concluded that molecular weights were indeed increasing according to the aim. In addition, it has previously been shown that the molecular weight of the free polymer formed from the sacrificial initiator is comparable to the one grafted from the cellulose surface for SI-ARGET ATRP\(^{152}\). Therefore, the molecular weights obtained for the free PS formed can be assumed to be similar to those of the PS grafted from the CNF surface.
Results and discussion

Table 8: \( M_n \) and \( D_M \) of the free PS formed during grafting.

<table>
<thead>
<tr>
<th></th>
<th>( M_n ) (g/mol)</th>
<th>( D_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS (S)</td>
<td>31 000</td>
<td>1.8</td>
</tr>
<tr>
<td>PS (M)</td>
<td>57 000</td>
<td>1.7</td>
</tr>
<tr>
<td>PS (L)</td>
<td>110 000</td>
<td>1.5</td>
</tr>
</tbody>
</table>

In figures 20A and B, FT-IR spectra and TGA thermograms of CNF, CNF-Br, CNF-\( g \)-PS (S), CNF-\( g \)-PS (M) and CNF-\( g \)-PS (L) are shown. From these it can be concluded that the grafting of PS was successful due to appearance of representative peaks of PS in FT-IR, and detection of PS in TGA.

Micromechanic measurements with Raman spectroscopy

Eichhorn et al. previously investigated the micromechanics of composites reinforced with nanocellulosic fillers by utilizing Raman microscopy. By incorporating CNC in an epoxy matrix, the influence of CNC surface charge on micromechanical properties, was determined\(^{20}\). Furthermore, acetylation of TEMPO-oxidized CNF was shown to increase stress transfer from poly(lactic acid)
matrix to CNF under tensile deformation\textsuperscript{129}. Inspired by these studies, an attempt to investigate how polymer-compatibilized CNF in a matrix affect the stress transfer from matrix to CNF in comparison to that of neat CNF was performed.

To be able to perform micromechanic measurements of composites with Raman spectroscopy, some prerequisites needs to be fulfilled. First, the matrix polymer should not have peaks overlapping with the distinct cellulose Raman signal at 1095 cm\textsuperscript{-1}. Second, the sample must be transparent to transmit the laser beam and allow detection. Third, the cellulose content needs to be high enough for detection, which is needed even though that no overlapping peaks are interfering. Fourth, a percolating network of fibrils should be avoided; if a continuous network of fibrils is created, the measurements will not be performed on individual fibrils, but on a network that may have dense and sparse regions and, as a consequence, express a non-uniform local stress transfer.

Photographs of the four PS-based composites are displayed in figure 21. The CNF content is around 30-40 wt-% to allow detection of the cellulose Raman signal. However, it was difficult to produce good quality specimens due to the inherent brittleness of PS in combination with the high amount of CNF incorporated. As can be seen, unmodified, neat, CNF is not compatible at all with PS, as large separated aggregates of CNF are created within the PS matrix. The CNF-g-PS is easier to disperse. Furthermore, for the CNF-g-PS (S) composite the obtained film is not transparent. Interestingly, on the other hand, if the grafted PS is longer than $Z_c$, as for CNF-g-PS (M and L) composites, transparent films can be prepared.
Results and discussion

Figure 21: Photographs of PS composites reinforced with unmodified CNF, and CNF-\textit{g}-PS (S, M and L).

In figure 22, the Raman band shift is shown as a function of strain for composites reinforced with CNF-\textit{g}-PS (medium and long) together with the corresponding linear fits, and 95 % confidence bands. According to theory, the slope of the linear fit is directly proportional to the Young’s modulus, and consequently to the stress, \textit{i.e.}, how much load the reinforcing CNF is bearing during tensile deformation\textsuperscript{126}. However, as can be seen, the data is rather scattered implying that a non-uniform fibril network has been formed. Possibly due to the high content of CNF needed for detection. Therefore, this system appears to be limited, and the induced stress in the CNF-\textit{g}-PS filler could not be determined with Raman spectroscopy.
Figure 22: Raman band shift plotted against strain for PS composites reinforced with CNF-g-PS (L) (black squares) and CNF-g-PS (M) (red squares) together with their respective linear fits (black and red lines, respectively) and 95 % confidence bands (grey and pink lines, respectively).

Comparative study of covalent grafting and physical adsorption of PCL in bionanocomposites (Paper 4)

Three different lengths of PCL were either grafted through SI-ROP of ε-CL or physically adsorbed in the form of the block copolymer PDMAEMAq-b-PCL from/onto TEMPO-oxidized CNF. Two out of the three block copolymers were the same as in paper 1, which were discussed previously in the section Preparation and evaluation of block copolymers of PCL and PDMAEMA. Due to the low adsorption onto cellulose and subsequent minor alteration in contact angle, PDMAEMAq-b-PCL with PCL DP target 1200
was here exchanged for a block copolymer with PCL DP target 4800.

CNF-\textit{g}-PCL (S, M and L), CNF-PDMAEMA\textit{q-b}-PCL (S, M and L), CNF-PDMAEMA\textit{q} or unmodified CNF was incorporated as the reinforcing element in a PCL matrix through solvent casting, and the composites evaluated (Paper 4). Molecular weight, $D_M$ and micelle properties of the block copolymers are shown in table 4. $M_n$ and $D_M$ for free PCL formed in parallel with covalent grafting together with $^1\text{H}$-NMR of CNF-\textit{g}-PCL are displayed in table 9.

Table 9: Molecular weight and $D_M$ as determined by SEC, of free PCL formed in parallel to the SI-ROP of $\varepsilon$-CL from CNF, as well as molecular weight of the mobile segment of PCL in CNF-\textit{g}-PCL determined from $^1\text{H}$-NMR.

<table>
<thead>
<tr>
<th>DP target (PCL)</th>
<th>$M_n$ (g/mol)$^a$</th>
<th>$D_M^a$</th>
<th>$M_w$ (g/mol)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF-\textit{g}-PCL (S)</td>
<td>300</td>
<td>52 000</td>
<td>1.5</td>
</tr>
<tr>
<td>CNF-\textit{g}-PCL (M)</td>
<td>2400</td>
<td>92 000</td>
<td>1.4</td>
</tr>
<tr>
<td>CNF-\textit{g}-PCL (L)</td>
<td>4800</td>
<td>84 000</td>
<td>1.2</td>
</tr>
</tbody>
</table>

$^a$Determined by SEC of free PCL formed in parallel from sacrificial initiator, $^b$estimated from $^1\text{H}$-NMR of CNF-\textit{g}-PCL from DP calculated from the signals at 4.05 ppm (-CH$_2$O, repeating unit) and at 3.61 ppm (-CH$_2$OH, end group).

The molecular weight of PCL formed in the bulk appears to reach a limit, where it, independently of DP target, does not grow any longer. This is the same observation as for the PCL formed in parallel with grafting from kraft pulp. On the other hand, from solvent $^1\text{H}$-NMR of CNF-\textit{g}-PCL, it can be seen that the molecular weight of the PCL grafts indeed increases with higher DP target, which is based on monomer-to-sacrificial initiator ratio. Note, that the part of the PCL grafts closest to the surface, which is assumed to be similar for all grafts, will not be detectable, i.e., most likely it is a large underestimation of the true $M_w$ of the PCL grafts.
Results and discussion

Furthermore, as displayed in figure 23A (FT-IR spectra) the amount of grafted PCL does as well increase on the CNF when higher DP is targeted. These observations are in line with previous results reported elsewhere\textsuperscript{153}.

![Figure 23: FT-IR spectra of (A) CNF-g-PCL (S,M and L) and (B) CNF-PDMAEMAq-b-PCL (S,M and L).](image)

By combining FT-IR spectra (figure 23) and the 1\textsuperscript{st} derivative of the decomposition trace from TGA (figure 24), the amount of CNF in CNF-g-PCL (S,M and L) was estimated.

![Figure 24: First derivative thermograms of CNF-g-PCL (A) and CNF-PDMAEMAq-b-PCL (B).](image)
Preparation of CNF-PDMAEMAq-b-PCL (S,M and L) is a one-step procedure with no work up why the mass loss is negligible. The CNF content can, therefore, be estimated as weight before and after adsorption. Composites were prepared with two CNF contents: ca 0.5 and ca 5 wt-%, denoted low CNF content and high CNF content, respectively.

At first, CNF-PDMAEMAq-b-PCL was dispersed directly after freeze drying with the PCL-matrix in chloroform. This dispersion was thereafter used to solvent cast composite films. The appearance of the dispersion in chloroform is shown in figure 25. Unmodified CNF was as well dispersed according to the same procedure. As expected, it did not disperse at all. Compact flakes are formed, which almost directly settled at the bottom. Compared to unmodified CNF, CNF-PDMAEMAq-b-PCL (S,M and L) were better dispersed in chloroform, as the CNF swell. This was especially evident for CNF-PDMAEMAq-b-PCL (L), where a stable colloidal dispersion was obtained.

![Figure 25: 1.5 mg CNF, unmodified or modified, directly after dispersion (top) and after 30 minutes (bottom). *HT: Heat treatment at 160 °C of CNF for 2 hours prior to dispersion. Note, the white shadow at the bottom of the vials with CNF-g-PCL, visible after both 0 and 30 minutes after dispersion, emerges from the camera flash.](image-url)
The mechanical properties of the formed bionanocomposites (low CNF content) were, thereafter, evaluated with tensile testing. Unfortunately, the properties were inferior to those of neat PCL, as seen in figure 26 displaying the Young’s modulus determined by tensile testing (figure 26A, black bars).

Figure 26: Young’s modulus displayed for all bionanocomposites. (A) with low CNF content and (B) with high CNF content. The average value for neat PCL is marked with a dotted line. *CNF filler was heat treated prior to dispersion in chloroform.
From AFM images of adsorbed block copolymer micelles onto silicon oxide surfaces (figure 16) it was previously observed that the PCL core was spread over the surface after annealing at an elevated temperature. Based on this finding – that heat is required to take full advantage of the compatibilizer – new bionanocomposites were prepared. CNF-PDMAEMAq-b-PCL (short, medium and long) were now heat treated prior to dispersion in chloroform. The effect of the heat treatment was most evident for CNF-PDMAEMAq-b-PCL (L) that could be evenly dispersed in chloroform.

Figure 27: AFM height images (500x500 nm) with corresponding height profiles of: unmodified CNF and CNF-PDMAEMAq-b-PCL (L) before and after heat treatment. Note, that the position on the surface before and after heat treatment is not the same.
Results and discussion

From AFM height images and corresponding height profiles (figure 27), the effect of the heat treatment was visualized by the disappearance of apparent surface structure for CNF-PDMAEMAq-b-PCL (L). Note that the heat treatment was performed outside the AFM, why the images are acquired in different positions.

Bionanocomposites reinforced with heat treated CNF-PDMAEMAq-b-PCL were then prepared through solvent casting. At low CNF content, the Young’s modulus increased compared to the bionanocomposites reinforced with non-heat treated CNF-PDMAEMAq-b-PCL, but not significantly compared to neat PCL. On the other hand, at high CNF content, the Young’s modulus did increase compared to neat PCL. This was especially evident for the longest PCL length that gave rise to a significant increase. CNF-g-PCL as reinforcing element, gave an increase in Young’s modulus with only a small increase with increasing length of the PCL-graft. In addition, the strain at break was higher when CNF-g-PCL was the reinforcing element than when CNF-PDMAEMAq-b-PCL was used. Based on all observations, we propose that physisorbed PCL gives a material with higher Young’s modulus and a lower strain at break, a strong but brittle material; whereas covalent grafting of PCL results in a material with an increased Young’s modulus compared to neat PCL and a preserved strain at break, i.e., a tough material.

This difference is ascribed to be a combination of dispersion of the filler, the interfacial adhesion between CNF and matrix, and the crystallinity of the composite. From the photographs in figure 25, it can be seen that CNF-g-PCL is better dispersed in chloroform than CNF-PDMAEMAq-b-PCL, which tend to form some agglomerations. Therefore, after solvent casting, CNF-g-PCL is most likely better dispersed, as well in the final composites.

The composites were cryo-fractured to gain further information on the interface between CNF and matrix. From SEM images of the cross sections of the biocomposites (figure 28), a high degree of phase separation can be observed for biocomposites reinforced with unmodified CNF, through the presence of many dark
spots\textsuperscript{154}. Biocomposites reinforced with modified CNF, on the other hand, have fewer dark spots, i.e., are less phase separated. Furthermore, CNF-g-PCL was indeed better dispersed, as anticipated from dispersion in chloroform, than CNF-PDMAEMAq-b-PCL in the PCL matrix, especially at high CNF content.

Figure 28: Cryo fractured cross sections of neat PCL and composites reinforced with unmodified CNF, CNF-g-PCL (L) and CNF-PDMAEMAq-b-PCL(L); high and low loading of CNF.
A composite material with high interfacial adhesion between filler and matrix will have higher toughness and strength compared to a composite where the filler and matrix are not compatible\textsuperscript{155}. Due to the higher toughness of CNF-\textit{g}-PCL composites, it is, therefore, suggested that the interfacial adhesion is higher than in CNF-PDMAEMAq-\textit{b}-PCL composites.

From DSC, the crystallinity of the composites was determined according to eq. 1. It was found to vary between 52 and 56\% for CNF-PDMAEMAq-\textit{b}-PCL composites, and between 26 and 48\% for CNF-\textit{g}-PCL composites, depending on PCL length. Thus, a higher crystallinity is obtained for CNF-PDMAEMAq-\textit{b}-PCL composites. One hypothesis is that CNF-PDMAEMAq-\textit{b}-PCL act as a nucleating agent for PCL, which has been observed previously for CNC in a PCL matrix\textsuperscript{38, 156}. As an effect of higher crystallinity for a polymeric material, the Young’s modulus may increase in combination with decreasing elasticity\textsuperscript{157}. Therefore, the higher crystallinity was probably contributing to the lower strain at break, and higher Young’s modulus for CNF-PDMAEMAq-\textit{b}-PCL composites compared to that of CNF-\textit{g}-PCL composites.

However, both types of modification of CNF improved the mechanical properties compared to unmodified CNF, unmodified but heat treated CNF, and CNF-PDMAEMAq-OH, which all gave rise to impaired mechanical properties compared to neat PCL matrix.

From DMA analysis (figure 29), it was observed that over the whole temperature range, the storage modulus (\(E'\)) (figure 29A) was increased for both types of modified CNF fillers. For unmodified CNF filler, on the other hand, already at low amounts of filler, \(E'\) decreased, a decrease that was enhanced with increased amount of CNF filler. Furthermore, the damping (\(\tan \delta\)) (figure 29B) of composites reinforced with modified fillers was lower compared to neat PCL. This suggests that the molecular motion is restricted by the presence of the filler, which could be due to that CNF was compatibilized within the PCL matrix. The \(\tan \delta\) peaks for samples with unmodified CNF, were, on the contrary, higher in intensity. This suggests that the incorporated
unmodified CNF did not act as a reinforcing element. One reason for the poor reinforcement is probably the agglomeration of CNF within the matrix as displayed in SEM (figure 28) due to difference in polarity between CNF and PCL. This displays the importance of a good dispersion of filler within the matrix to obtain a reinforcing effect, which for a nano-sized element is challenging.

Figure 29: Representative graphs of storage modulus (A) and tan δ (B) as a function of temperature of neat PCL and composites reinforced with low and high CNF content of unmodified CNF, CNF-g-PCL (L) or CNF-PDMAEMAq-b-PCL (L).
Conclusions

Surface modifications of different types of cellulose substrates were accomplished either through covalent grafting of polymers or physical adsorption of block copolymers.

Kraft pulp fibers were modified through SI-ROP of \( \varepsilon \)-CL. By combining modified and unmodified fibers, paper-sheet biocomposites that were paper-like with respect to both appearance and tactility were prepared. Despite that the amount of PCL on the modified fibers was rather low; hot pressing of two papers, without addition of matrix polymer, produced a laminate structure with mechanical integrity. In addition, the adhesive joint created from the pressing, could be even stronger than the individual biocomposites, which was ascribed being due to chain entanglements and/or co-crystallization of adjacent grafted PCL chains within the paper sheets.

Triblock copolymers of PB (middle block) and PDMAEMAq (cationic) or PMAA (anionic) as outer blocks were prepared through ATRP. The triblock copolymers were adsorbed to a silicon oxide surface as cationic monolayer or as a bilayer. Thereafter, the different triblocks were adsorbed to kraft pulp fibers and paper-sheet biocomposites were prepared from the modified fibers. However, the mechanical properties of the composites did not improve. Most likely the PB-block was too short to bridge fibers, and both outer blocks physisorbed onto the same fiber.

Di- and triblock copolymers of PCL and PDMAEMA were prepared by combining ROP and ATRP. The diblock copolymers had a constant length of the PDMAEMA-block and four different PCL lengths. The triblock copolymers were composed of a central block of PDMAEMA or PCL in combination with PCL or PDMAEMA as outer blocks, respectively. The morphology/crystallinity of the triblocks was shown to be dependent on the architecture, i.e., both amorphous and crystalline copolymers were obtained by varying block sequence. After quaternization, diblock copolymers were dispersed as stable micelles 40 to 70 nm in size, allowing for adsorption to anionic
silicon oxide and cellulose surfaces under mild conditions. The triblock copolymers also formed micelles, but with lower stability and larger variation in size. Adsorption could be performed, demonstrated by adsorption to a silicon oxide surface. After adsorption, the surface energy of all surfaces decreased. In addition, with AFM force measurements, it was shown that an adhesive interface between block copolymers adsorbed to a silicon oxide probe and a PCL surface was obtained. This demonstrated the possibility of utilizing charged block copolymers as compatibilizers for reinforcing elements in composites.

PS was grafted from CNF by SI-ARGET ATRP of styrene. The modified CNF was thereafter incorporated in a PS matrix yielding a composite. To evaluate stress transfer from matrix to CNF, a combination of Raman spectroscopy and tensile testing was performed. However, probably based on the creation of a fibrillar network, due to the high CNF content, it was not possible to measure on single fibrils, which in turn gave rise to scattered data. Hence, optimization of this system is needed to be able to perform these types of measurements, and to assess the stress transfer.

Grafting and physical adsorption of PCL from/onto CNF as modification procedure was performed and the modified CNFs incorporated in separate PCL matrices yielding bionanocomposites. The two types of modification protocols were compared with respect to material properties of the bionanocomposites. It was concluded that CNF-PDMAEMAq-b-PCL, as well as CNF-\(g\)-PCL, were both better than unmodified CNF in terms of reinforcing capacity. On the other hand, the amount of compatibilizing polymer needed to obtain an effect concerning dispersion of CNF and improved mechanical properties, was higher for CNF-PDMAEMAq-b-PCL than for CNF-\(g\)-PCL. Furthermore, composites reinforced with CNF-PDMAEMAq-b-PCL were strong but brittle, whereas composites with CNF-\(g\)-PCL had high strength and elasticity, \textit{i.e.}, tough materials. The higher toughness indicated that the interfacial adhesion between CNF-\(g\)-PCL and PCL matrix was higher compared to that of CNF-PDMAEMAq-b-PCL and PCL.
Covalent grafting and physical adsorption of polymers are interesting as modification procedures for cellulose-based materials. A discrepancy between increases in molecular weight of free PCL, and of amount of PCL grafted from the fiber/CNF surface was observed during SI-ROP of ε-CL, which would be interesting to investigate, as well as determination of the molecular weight of the grafted PCL. Previously, attempts to degrade the cellulose with enzymes after grafting to obtain the grafted PCL. However, these were not successful, but a strategy in this direction could potentially solve the problem. Another strategy could be to introduce a unit for selective cleavage.

Triblock copolymers of PCL and PDMAEMA could adsorb onto a silicon oxide surface, but it would be interesting to evaluate in detail the effect of the block sequence on adsorption behavior and alteration of surface properties.

The PB block was most likely too short to improve the mechanical properties of paper-sheet biocomposites prepared from modified fibers. It would, therefore, be interesting to utilize a longer PB block, or exchange it for another rubbery polymer.

Data acquired from stress transfer measurements with Raman spectroscopy on CNF-reinforced PS-based composites was of low statistical significance. However, the method works for other CNF-reinforced composites. Therefore, it would be interesting to alter the conditions, obtaining single cellulose fibers/fibrils, and thus allowing for evaluation of stress transfer from the matrix.

Bionanocomposites reinforced with modified CNF were produced by a solvent casting procedure. However, optimization of the processing conditions, including utilization of a more industry-oriented preparation procedure, such as extrusion, would be of interest. In addition, it would be interesting to investigate physical adsorption with an amorphous polymer. Furthermore, differences in other properties than mechanical properties between grafting and adsorption, e.g., barrier properties as well as sensitivity to humidity, would be of interest.
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