The properties and applications of long chain cellulose esters

Pia Willberg-Keyriläinen
The properties and applications of long chain cellulose esters

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Environmental awareness and growing concern about plastic waste and the depletion of non-renewable resources have boosted interest in bio-based polymers in recent years. Although the fraction of bio-based polymers in the global plastics market is still small, the demand and share of bio-based polymers is rapidly increasing. The aim of this dissertation was to prove that fully bio-based long chain cellulose esters have the potential to replace traditional oil-based plastics in selected applications.

In this research, the long chain cellulose esters were synthesized with different side chain lengths (C6-C18) and the influence of side chain length on barrier, mechanical and thermal properties was demonstrated. In order to study the differences in pulp reactivity and properties of cellulose esters, the molar mass of commercial softwood dissolving pulp was decreased in a controlled manner by ozone-hydrogen peroxide treatment. This research proved that decreasing cellulose molar mass enabled the synthesis of long chain cellulose esters with better reaction efficiency than with the original cellulose. In addition, both the cellulose molar mass and the degree of substitution could be controlled. The resulting long chain cellulose esters formed transparent, flexible and heat sealable films with good water vapor barrier and mechanical properties.

Cellulose esters formed smooth and homogeneous coatings with good adhesions when nanocellulose (CNF) films and virgin kraft papers were coated. The long chain cellulose ester coatings also significantly improved the moisture barrier properties of CNF film and kraft paper – these values decreased linearly as a function of ester chain length up to 50% from non-coated values. These coatings also significantly improved the surface smoothness of CNF films by decreasing nano-roughness. The long chain cellulose ester coatings made the material heat sealable and, in addition, the coatings had no antimicrobial activity, and only few microbes adhered to the surface of these films. These results demonstrate that long chain cellulose ester coatings have potential in future packaging applications where surface smoothness, heat sealability and good water vapor barrier properties are required.

Injection molding of long chain cellulose esters and their blends was also studied and the mechanical properties were investigated. The results indicate that thermoplastic long chain cellulose esters are completely processable without any addition of a plasticizer, which is very unusual in the case of cellulose esters. This research proves that these materials have good potential to be used in injection molding applications.

Keywords: cellulose, cellulose esters, thermoplastics, barrier properties, mechanical properties
Tekijä
Pia Willberg-Keyriläinen

Väitöskirjan nimi
Pitkäkätkujisten selluloosaestereiden ominaisuudet ja applikaatiot

Julkaisija
Kemian tekniikan korkeakoulu

Yksikkö
Biotutteiden ja biotekniikan laitos

Sarja
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Biotutetekniikka

Käsikirjoituksen pvm
05.06.2020

Väitöspäivä
06.11.2020

Väittelyluvan myöntämispäivä
26.08.2020

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Englanti

Monografia
Artikkeliväitöskirja

Esseeväitöskirja

Tiivistelmä

Ympäristötietoisuus, kasvava huoli muovijätteistä sekä uusiutumattomien luonnonvarojen ehtyminen ovat viime vuosina kasvattaneet kiinnostusta biopohjaisiin polymeereihin. Biopohjaisten polymeerien kysyntä kasvaa nopeasti, mutta niiden osuus muovien kokonaismarkkinaasta on edelleen pieni. Tämän väitöskirjan tavoitteena oli osoittaa, että täysin biopohjaisilla pitkäkätkuisilla selluloosaestereilla on mahdollisuus korvata perinteiset öljypohjaiset muovit tietyissä sovelluksissa.


Pääälyystettäessä nanoselluloosafilmejä ja käsittelemätöntä videopaperia selluloosaestereilla, muodostui tasainen ja homogeninen pinta, jolla oli hyvä tarttuvuus. Pitkäkätkuiset selluloosaesteripinnoitteet alensiivat myös merkittävästi nanoselluloosafilmin ja videopaperin vesihöyryn läpäisevyyttä; läpäisevyysarvot alenivat lineaarisesti ketjunpituiden kasvaessa. Samalla myös nanoselluloosafilmin pinnankarheus paranu huomattavasti ja pinnoite mahdollisti materiaalin kuumasuamauksen. Selluloosaesteripinnoitteille ei myöskään ollut antimikrobiasta aktiivisuutta. Tulokset osoittivat, että pitkäkätkuisia selluloosaesteripinnoitteita voidaan hyödyntää tulevaisuuden pakkasosuvalle uksessa, joissa vaaditaan sileää pintaa ja hyvää vesihöyryn läpäismäntömyyttä.

Lisäksi pitkäkätkujisten selluloosaestereiden prosessointavuutta ja mekaanisia ominaisuuksia tutkiottiin ruiskuvalun avulla. Nämä termostasit selluloosaesterit olivat täydellisesti prosessoitavissa ilman lisäaineistusta, mikä on selluloosaestereiden tapauksessa harvinaista. Tämän perusteella pitkäkätkuisilla selluloosaestereilla on hyvät mahdollisuudet korvata perinteisiä muoveja esimerkiksi ruiskuvaluaplikaaatioissa.

Avainsanat
selluloosa, selluloosaesterit, termoplastisuus, barrier-ominaisuudet, mekaaniset
ominaisuudet

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I am also deeply grateful to my co-authors Dr. Riku Talja, Dr. Sari Asikainen, M.Sc. Jari Vartiainen, Dr. Jani Pelto, Dr. Hanna-Leena Alakomi and Dr. Hannes Orelma. Without their contribution and support, this thesis would not have been possible. I also want to thank Eija Silvasti, Mari Leino, Vuokko Liukkonen, Nina Vihersola, Mirja Nygård, Upi Anttila and Sini-Tuuli Rauta for their excellent assistance in the laboratory and with the analyses.

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Finally, I want to thank the most important persons in my life. I give warm thanks to my family and friends for all their love and support in my life. My deepest thanks belong to my beloved husband Jukka and to my children Ida and Onni for your endless love, patience and encouragement. You are my everything.

“A bird sitting on a tree is never afraid of the branch breaking, because its trust is not on the branch but on its own wings. Always believe in yourself.”

–Charlie Wardle

Espoo, 6 October 2020

Pia Willberg-Keyriläinen
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<tr>
<td>Abbreviation</td>
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<tr>
<td>--------------</td>
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</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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</tr>
<tr>
<td>AGU</td>
<td>Anhydroglucose unit</td>
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<tr>
<td>AO</td>
<td>Acridine orange</td>
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</tr>
<tr>
<td>C6</td>
<td>Hexanoate</td>
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<td>C8</td>
<td>Octanoate</td>
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<td>C10</td>
<td>Decanoate</td>
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<td>C12</td>
<td>Laurate</td>
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<td>C14</td>
<td>Myristate</td>
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<td>C16</td>
<td>Palmitate</td>
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<tr>
<td>C18</td>
<td>Stearate</td>
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<tr>
<td>CA</td>
<td>Cellulose acetate</td>
<td></td>
</tr>
<tr>
<td>CAB</td>
<td>Cellulose acetate butyrate</td>
<td></td>
</tr>
<tr>
<td>CAP</td>
<td>Cellulose acetate propionate</td>
<td></td>
</tr>
<tr>
<td>CAM</td>
<td>Contact angle measurement</td>
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<tr>
<td>CDI</td>
<td>N,N’-carbonyldiimidazole</td>
<td></td>
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<tr>
<td>CNF</td>
<td>Cellulose nanofibrils</td>
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<tr>
<td>CrI</td>
<td>Crystallinity index</td>
<td></td>
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<tr>
<td>Cuam</td>
<td>Cuprammonium hydroxide</td>
<td></td>
</tr>
<tr>
<td>Cuen</td>
<td>Cupriethylenediamine hydroxide</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Dispersity</td>
<td></td>
</tr>
<tr>
<td>DCC</td>
<td>N,N-dicyclohexylcarbodiimide</td>
<td></td>
</tr>
<tr>
<td>DIM</td>
<td>Diiodomethane</td>
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<tr>
<td>DMAc</td>
<td>Dimethylacetamide</td>
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<tr>
<td>DMAP</td>
<td>N,N-dimethyl-4-aminopyridine</td>
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</table>
DP  Degree of polymerization
DS  Degree of substitution
DSC  Differential scanning calorimetry
FTIR  Fourier transform infrared
H₂O₂  Hydrogen peroxide
H₂SO₄  Sulfuric acid
HCl  Hydrochloric acid
HDPE  High-density polyethylene
ΔHₘ  Melting enthalpy
IL  Ionic liquid
KBr  Potassium bromide
KOH  Potassium hydroxide
LDPE  Low-density polyethylene
LiCl  Lithium chloride
MAS  Magic angle spinning
MCC  Microcrystalline cellulose
Mₙ  Number average molecular weight
Mₙ  Weight average molecular weight
NaOH  Sodium hydroxide
NMMO  N-Methylmorpholine-N-oxide
NMR  Nuclear magnetic resonance
O₃  Ozone
OP  Oxygen permeability
OTR  Oxygen transmission rate
PE  Polyethylene
PLA  Poly(lactic acid)
RH  Relative humidity
Rq  Surface roughness parameter
SEC  Size exclusion chromatography
SEM  Scanning electron microscopy
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ssNMR</td>
<td>Solid state nuclear magnetic resonance</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>$T_{deg}$</td>
<td>Degradation temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>WVP</td>
<td>Water vapor permeability</td>
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<tr>
<td>WVTR</td>
<td>Water vapor transmission rate</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray powder diffraction</td>
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</table>
List of Publications

This doctoral dissertation consists of a summary and of the following publications, which are referred to in the text by their roman numerals:


V. **Willberg-Keyriläinen, Pia;** Orelma, Hannes; Ropponen, Jarmo. 2018. Injection Molding of Thermoplastic Cellulose Esters and Their Compatibility with Poly(Lactic Acid) and Polyethylene. Materials, volume 11, issue 12, page 2358. DOI: 10.3390/ma11122358.
Author’s Contribution

Publication I: The effect of cellulose molar mass on the properties of palmitate esters

The author had the main responsibility for planning the work, interpreting the results and writing the publication under the supervision of Dr. Jarmo Ropponen. The author performed the experimental work and sample analyses. Dr. Riku Talja had the main responsibility for the barrier measurements of the films. Dr. Sari Asikainen had the main responsibility for pretreatments. Prof. Ali Harlin participated in planning the work and writing the publication.

Publication II: The effect of side-chain length of cellulose fatty acid esters on their thermal, barrier and mechanical properties

The author had the main responsibility for planning the work, interpreting the results and writing the publication under the supervision of Dr. Jarmo Ropponen. The author performed the experimental work and sample analyses. M.Sc. Jari Vartiainen performed the barrier measurements of the films and assisted in the interpretation of the results and writing the publication. Prof. Ali Harlin participated in planning the work and writing the publication.

Publication III: Hydrophobization and smoothing of cellulose nanofibril films by cellulose ester coatings

The author had the main responsibility for planning the work, interpreting the results and writing the publication together with Dr. Jarmo Ropponen and M.Sc. Jari Vartiainen. The author performed the laboratory experiments and sample analyses together with M.Sc. Jari Vartiainen. Dr. Jani Peltó performed the SEM and AFM analyses and interpreted the results.

Publication IV: Cellulose fatty acid ester coated papers for stand-up pouch applications

The author had the main responsibility for planning the work, interpreting the results and writing the publication together with Dr. Jarmo Ropponen and M.Sc. Jari Vartiainen. The author performed the laboratory experiments and sample analyses together with M.Sc. Jari Vartiainen. Dr. Hanna-Leena Alakomi had the main responsibility for antimicrobial tests.
**Publication V:** Injection molding of thermoplastic cellulose esters and their compatibility with poly(lactic acid) and polyethylene

The author had the main responsibility for planning the work, interpreting the results and writing the publication together with Dr. Jarmo Ropponen. The author prepared the cellulose esters and carried out the injection molding experiments. Dr. Hannes Orelma assisted in the interpretation of the results and writing the publication.
1. Introduction

Environmental awareness, concern about plastic waste and the depletion of non-renewable resources have driven growing interest towards bio-based polymers in recent years. While bio-based polymers still account for only a small fraction of the global plastics market, this is changing fast and demand for bio-based polymers continues to increase rapidly. Bioplastics, which are made partly or fully from renewable resources, can typically offer a reduction in carbon footprint compared to fossil resources. However, renewable raw material does not automatically mean biodegradability, but there are also bioplastics available, which are suitable for alternative waste management methods such as composting.1–3

Globally, packaging is one of the fastest growing industries and almost half of the material used for packaging is plastics. Thanks to comprehensive media attention, consumers and packaging producers have taken the state of the globe seriously and, as a result of more sustainable thinking, started to shift their preference and attention towards recyclable and non-fossil materials. Nowadays, there are several bio-based alternatives to conventional plastic materials in multiple applications. However, the plastics industry is actively searching for new alternatives and renewable thermoplastic materials. In recent years, sustainable bio-based polymers have been the focus of several studies due to interest in their potential use as bio-based and biodegradable films, coatings and composites.4–8

1.1 Scope of the thesis

This thesis consists of work summarized in five publications (I-V). The aim of this dissertation was to prove that bio-based long chain cellulose esters have the potential to replace traditional oil-based plastics in selected applications. The outline of this research is presented in Figure 1. The first research approach was to demonstrate and understand the effect of cellulose molar mass and side chain length on long chain cellulose ester properties (Publications I and II), and the second research approach was to demonstrate the potential of long chain cellulose esters in a range of applications (Publications III-V).
In Publication I, the effect of cellulose molar mass on cellulose chemical reactivity and cellulose palmitate properties was studied. The molar mass of commercial softwood dissolving pulp was decreased in a controlled manner by ozone-hydrogen peroxide treatment. To examine the differences in chemical consumption, cellulose palmitate esters were synthesized using both native and treated pulps and the effect of molar mass on the barrier, mechanical and thermal properties of cellulose palmitate esters were investigated. This research proved that decreasing cellulose molar mass allowed the synthesis of cellulose palmitate esters with significantly lower chemical amounts than the original cellulose, and it is possible to control both the cellulose molar mass and degree of substitution.

In Publication II, long chain cellulose esters were synthesized with different side chain lengths (C6-C18) using ozone treated cellulose and the effect of cellulose side chain length on barrier, mechanical and thermal properties were demonstrated. By selecting the appropriate side chain length, the properties of the cellulose esters can be tailored as desired.

In Publication III, nanocellulose (CNF) films were coated using long chain cellulose esters with different side chain length and the effect of cellulose ester coatings on CNF film surface smoothness was studied. The barrier and mechanical properties of the formed 3-layer films were also demonstrated. The research showed that long chain cellulose ester coatings can significantly improve the surface smoothness of CNF films by decreasing nano-roughness. According to the results, these 3-layer films have potential to be used in future film and coating applications where good water vapor barrier properties and surface smoothness are needed.
In Publication IV, the coating of virgin kraft paper using long chain cellulose esters with different side chain lengths was described. The effect of cellulose ester coatings on barrier properties, grease resistance and heat sealability of kraft paper was demonstrated. In addition, the antimicrobial activity of the cellulose ester coatings was tested. Standup pouch prototypes were prepared using cellulose C16 ester coated heat-sealed kraft paper with leak-proof seals. The results show that long chain cellulose ester coatings have good potential for future packaging applications.

In Publication V, thermoplastic long chain cellulose esters and their blends were injection molded and the mechanical properties were investigated. The compatibility of cellulose esters with poly(lactic acid) (PLA) and bio-polyethylene (bio-PE) and the effect of cellulose esters on PLA and bio-PE mechanical properties were also evaluated. The results showed that thermoplastic long chain cellulose esters were completely processable without the addition of a plasticizer, which is very unusual in the case of cellulose esters. The publication proved that these materials have potential to be used in injection molding applications.
2. Background

2.1 Cellulose

Cellulose is the most abundant renewable polymer on earth and it can be derived from a variety sources. Cellulose is a structural polymer that provides strength and stiffness to plants; for example, cotton consists ~90% of cellulose, flax and hemp fibers 70-80% of cellulose and wood 40%-50% of cellulose. Cellulose is therefore an important raw material with several applications, from paper and textiles to cosmetics, foods and biomaterials. Cellulose has several benefits, including good biocompatibility, non-toxicity, biodegradability, high chemical modifiability potential, and high mechanical strength. However, in order to be applicable, cellulose solubility and mechanical properties need to be tailored without adversely affecting the natural properties of the material.\textsuperscript{9-14}

Cellulose is a homopolymer consisting of \(\beta\)-D-glucopyranose units (AGU) linked by 1,4-glycosidic bonds to form a linear and unbranched polymeric chain. In native crystalline cellulose, each AGU unit is rotated 180° to each other. This confirmation gives the cellulose molecule a flat, ribbon-like structure. The cellobiose unit consists of two AGU units and is the smallest repeating unit in cellulose with glucose. The molecular structure of cellulose is presented in Figure 2.

Each repeating AGU has three hydroxyl groups: a primary alcohol at the C6 position and two secondary alcohols at the C2 and C3 positions. These hydroxyl groups form a strong hydrogen-bonding network, which makes the crystalline cellulose very rigid and stable and gives cellulose its natural strength and reactivity. Intramolecular hydrogen bonding occurs within the same cellulose chain (between C2-OH and C6-OH and between C3-OH and pyranose ring oxygen) and intermolecular hydrogen bonding occurs between different chains (between C3-OH and C6-OH). Van der Waals forces and hydrophobic interaction hold these planar structures together to form microfibrils, which are arranged parallel to each other.\textsuperscript{11-13,15} A schematic illustration of intra- and intermolecular hydrogen bonds in cellulose is presented in Figure 3.
Cellulose displays six different polymorphs known as I, II, III\textsubscript{I}, III\textsubscript{II}, IV\textsubscript{I} and IV\textsubscript{II}, which can be interconverted from one to another (Figure 4). These different polymorphs can be distinguished by their hydrogen bonding patterns, which affect, for example mechanical properties and cellulose reactivity. Cellulose I, the native form of cellulose, occurs in two allomorphs, I\textsubscript{a} and I\textsubscript{b}. This cellulose I is the most abundant polymorph of cellulose and is the only form found in nature. Cellulose II is obtained from cellulose I either by regeneration of dissolved cellulose or by mercerization (alkali treatment). Although cellulose I is the material that occurs in nature, cellulose II is energetically the most stable form of cellulose. The difference between cellulose I and II is in the orientation of their polymer chains. In cellulose I, neighboring chains are oriented in parallel direction, while the cellulose II has antiparallel chains. Cellulose III can be obtained from cellulose I and II using ammonia or amine treatment. This reaction is also reversible. Cellulose IV is formed by heating cellulose III.\textsuperscript{11,16–20}
Background

The degree of polymerization (DP) describes the number of AGUs in the cellulose chain. DP is highly dependent on the source and treatment of the raw material. For example, wood cellulose has a DP of ~10000 and cotton cellulose of ~15000. After extraction, the DP is reduced significantly depending on the applied treatment. Typically, native cellulose has higher DP values than cellulose processed by pulping or regenerated cellulose. DP greatly influences the physical, biological, mechanical, and solution properties of the polymer. Cellulose is also insoluble in water and common organic solvents even at low DP (DS above 6) due to its hydrogen-bonding network. High DP can significantly reduce cellulose reactivity because the hydroxyl groups may regionally have different levels of accessibility to reagents.

The properties of cellulose-based materials are greatly affected by the DP of the starting cellulose, but also the degree of crystallinity has a major role in the physical, mechanical, and chemical properties of cellulose. For example, cellulose crystallinity directly affects accessibility to chemical derivatizations and swelling properties. The degree of crystallinity is therefore a very important parameter and must be taken into account when considering the applications of cellulose and cellulose-based materials. Cellulose chains aggregate with each other to form elementary fibrils that contain both less ordered amorphous regions and highly ordered crystalline regions. The interchain hydrogen bonds are stronger in the crystalline regions, which provide the fiber with good strength, high axial stiffness, insolubility in most solvents, and prevent the melting of cellulose. The crystallinity index (CrI) describes the relative amount of crystalline material in cellulose. Depending on the origin of the cellulose and the method of separation, the crystallinity index of cellulose typically ranges from 40 to 70%, and the reported crystallinity values vary depending on the measurement techniques applied.
2.2 Methods for cellulose depolymerization

Cellulose can be depolymerized in many ways, for example through chemical and enzymatical hydrolysis.\textsuperscript{31–33} In total hydrolysis, cellulose chains are broken into glucose molecules. In the literature, the focus is primarily in the total hydrolysis. There is only limited literature available on hydrolyzing cellulose to achieve a specific molar mass.

\textit{Acid hydrolysis}

Acid hydrolysis of cellulose is a well-known treatment method to fully degrade cellulose, to adjust its molar mass and to produce microcrystalline cellulose (MCC) by removing amorphous regions.\textsuperscript{34–37} The acid hydrolysis reaction can be controlled by the reaction conditions (acid concentration, reaction time and temperature) and typically hydrochloric acid (HCl) or sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) is used as a catalyst. However, despite the low cost of acid, the acid hydrolysis process has disadvantages, such as the formation of byproducts. In addition, the concentrated acids are corrosive, which means that corrosion resistant reactors must be used and the residual acid is not usually recycled. As a result of these factors combined, acid pretreatment processes tend to be quite expensive.\textsuperscript{38–41}

\textit{Alkaline treatment}

Alkaline treatment is another widely applied method of cellulose pretreatment and typically sodium hydroxide (NaOH) or potassium hydroxide (KOH) are used. Alkaline treatments cause swelling, and result in decreased crystallinity and degree of polymerization, depending on the conditions and prior treatments of the raw material. Alkaline treatment also removes hemicelluloses and lignin from pulp and thus increases cellulose accessibility. In some cases, the advantage of alkaline pretreatment is that reaction conditions can be relatively mild and non-corrosive and typically the residual alkali can be recycled in the process.\textsuperscript{36,39,42,43}

\textit{Enzymatic hydrolysis}

Enzymatic treatment is a common method of hydrolyzing cellulose to soluble sugars for the production of fuels and chemicals.\textsuperscript{35,44,45} In the forest industry, monocomponent cellulases are commonly used to improve some process steps (e.g. refining) or to improve the product quality. Cellulases are also used in the textile industry for finishing textiles.\textsuperscript{46–50}

Cellulases are a group of enzymes with the ability to hydrolyze cellulose and they can be divided into three groups based on their specificity and structure. Endoglucanases hydrolyze arbitrarily accessible glycosidic bonds in the amorphous parts of the cellulose chain, while exoglucanases hydrolyze the cellulose chain from either the reducing or the non-reducing end, producing cellobiose. \(\beta\)-glucosidases complete the hydrolysis by converting the oligosaccharide and cellobiose units to glucose.
Due to the mild conditions (e.g. temperature and pH), enzymatic treatment is an environmentally friendly process in which no solvents or chemical reagents are needed. However, quite dilute reaction mixtures are typically used and therefore large reaction vessels are needed.\textsuperscript{51,52}

\textit{Ozone treatment}

Cellulose pretreatment with ozone has been widely used in several applications. In the paper industry, ozone is used for pulp bleaching due to its high delignification efficiency. Additionally, the pulp viscosity is also adjusted using ozone in dissolving pulp production. Pretreatment with ozone is also identified as an efficient pretreatment method for total enzymatic hydrolysis of agro-based residues and waste papers.\textsuperscript{53–55}

Ozone is an effective oxidizing agent that easily reacts to most organic materials, including lignocellulose.\textsuperscript{56–58} Ozone reacts also with carbohydrates by causing mostly indirect oxidative glycosidic bond cleavage. Ozone oxidize some of the alcohol groups of cellulose to carbonyl groups that then promote both cellulose degradation reactions and color reversion. Color reversion can be minimized if the ozone stage is followed by a peroxide stage.\textsuperscript{59–61} The benefits of ozone treatment are that ozone is relatively easy to generate on site and, therefore, there is no need for chemical transportation and storage. Ozone treatment also occurs at low temperature and does not leave harmful residues in the treated material.\textsuperscript{35,54,62–64}

\subsection*{2.3 Cellulose esters}

Cellulose and cellulose derivatives can provide attractive alternatives as long as their properties are tailored to specific end-use applications. Cellulose chemical modifications can be performed exclusively on its hydroxyl groups, which can participate in all typical reactions, including esterification, etherification, and oxidation reactions. Cellulose esterification is one of the most versatile transformations of cellulose. Cellulose esters of organic and inorganic acids are commercially important cellulose derivatives with a wide range of applications in the field of plastics, films, coatings, fibers, textiles and membranes and also in the cigarette industry.\textsuperscript{10–12,65–70} Examples of commercial cellulose esters are presented in Figure 5. In this thesis, the focus is on organic cellulose esters, which will be discussed in more detail in future sections.
Cellulose acetate (CA), one of the most important commercial cellulose esters, is manufactured by reaction of cellulose with a mixture of acetic acid and acetic anhydride in the presence of sulfuric acid. Typically, cellulose acetate is first esterified to triacetate with a degree of substitution (DS) of 3. Afterwards, the CA is hydrolyzed to the desired DS. Cellulose acetate can be used for a range of applications, such as coatings, filters, films and membranes. \(^{71-74}\)

Cellulose acetate is also a thermoplastic, as are the known mixed cellulose esters cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). However, cellulose esters with short alkyl chains (e.g. CA, CAP, CAB) have a narrow processing window between melt flow temperature and decomposition temperature, and therefore external plasticizers are required for most thermomolding processes.

Long chain cellulose esters are bio-based cellulose esters with a side chain length of C6 or longer. These long alkyl side chains have a high plasticizing effect on the cellulose, which enables melt processing of long chain cellulose esters. In most cases, these esters can be processable without any plasticizers. \(^{75-80}\)
2.3.1 Esterification methods for cellulose esters

The physical and chemical properties of cellulose esters are influenced not only by the DS, but also by the position of the substitution and the distribution of the functional substituent groups in the anhydroglucose units (AGU). Control of regiochemistry in the synthesis of cellulose esters is challenging due to the low reactivity difference between the three hydroxyl groups (especially between the C2-OH and C3-OH groups). This in turn makes regioselective esterification of cellulose quite challenging. Regioselective reactions nearly always require homogeneous reaction conditions in which the cellulose is completely dissolved or, alternatively, regioselectively protected (e.g. tosylation, silylation). However, in cellulose esterification, the reaction occurs preferably in the primary hydroxyl group (C6-OH), which has relatively low steric hindrance. The reaction conditions also affect the relative distribution of the substituent between the C6, C3 and C2 positions. However, in most cases, the substituent distribution of the homogeneously synthesized cellulose esters occurs in the following order: C6 > C3 > C2.81–85

The DS values of cellulose esters also depend on the nature of the reagents; for example, on the size of the acyl group to be introduced. The DS values and the reaction efficiency of cellulose esters decrease as the side chain length increases due to steric hindrance.86,87

Homogeneous and heterogeneous methods

Cellulose esterification can be performed through heterogeneous and homogeneous methods. Due to the fibrous nature of cellulose, its strong hydrogen bond network and crystallinity, cellulose is difficult to dissolve in common solvents. Therefore, cellulose esters are often manufactured under heterogeneous conditions to avoid the challenge of solubilizing the cellulose. However, the main challenge with the heterogeneous method is the accessibility difference between the hydroxyl groups in the crystalline and amorphous regions, resulting in inhomogeneous substitution.10,14,88–90

Under homogeneous solution conditions, the original structure of crystalline cellulose is destroyed. McCormick and Callais91 first published a homogeneous synthesis of cellulose derivatives using lithium chloride (LiCl)/N,N-dimethylacetamide (DMAc) as a solvent system. They concluded that a homogeneous system has many benefits, such as mild reaction conditions, reduced consumption of reagents, selectivity, and high reaction efficiency.67,92 In addition, the homogeneous esterification method allows better accessibility of the reagents to the hydroxyl groups, which results in uniform distribution of the functional groups along the polymer chain and better controllability of the degree of substitution. Although the LiCl/DMAc solvent system is commonly used at the laboratory scale, because it is capable of dissolving even high molecular weight cellulose with negligible degradation, it is not usually applied industrially because the expensive lithium salt is difficult to recycle.93–96
In addition to the LiCl/DMAc solvent system, other non-derivatizing solvents used to dissolve cellulose without chemical modification are, for example, aqueous alkali solutions\textsuperscript{97,98} and alkali/urea systems\textsuperscript{99,100}, inorganic metal complexes\textsuperscript{101,102} (e.g. cuprammonium hydroxide (Cuam) and cupriethylenediamine hydroxide (Cuen)) and N-Methylmorpholine-N-oxide (NMNO)\textsuperscript{103,104}. However, these solvents also have several disadvantages, such as poor dissolving ability, risk of cellulose degradation during the process, and undesired side reactions.\textsuperscript{105,106} Also, low melting point organic salts known as ionic liquids (ILs) have been reported to be effective cellulose solvents.\textsuperscript{107,108}

**Different esterification routes**

Cellulose esterification is usually an acylation procedure that uses carboxylic acids as an acylating agent under acid catalysis or an activated derivative such as an anhydride or acid chloride.\textsuperscript{67} The most common approach to cellulose acylation is reaction with acid chlorides or carboxylic acid anhydrides.

Fatty acid chloride is a powerful reagent for producing long chain cellulose esters. However, during the esterification reaction, hydrochloric acid (HCl) is formed as a by-product and, because HCl gas is corrosive, the materials of reactors are limited. It is therefore important to limit the degradation of cellulose by neutralizing the formed HCl with a base (e.g. pyridine, trimethylamine, DMAP (N,N-dimethyl-4-aminopyridine)).\textsuperscript{90,109–112}

Fatty acids as such do not cause degradation of cellulose, but they have quite low reactivity to cellulose hydroxyl groups. For this reason, fatty acids need to be transformed into more reactive substances. Carboxylic acid anhydrides together with catalysts are considered to be more effective in esterification than free carboxylic acids and, for example, cellulose acetate is usually prepared using a mixture of acetic acid and acetic anhydride. However, the reactivity decreases as the number of carbon atoms increases, and it is challenging to esterify cellulose with long chain anhydrides.\textsuperscript{67,113} N,N’-carbonyldiimidazole (CDI) is a commonly used activating agent for cellulose acylation. In this activation method, CDI reacts with carboxylic acid forming a reactive carbonyl imidazole intermediate, which further reacts with cellulose. The benefits of this activation method are mild reaction conditions, which minimize by-product formation. N,N-Dicyclohexylcarbodiimide (DCC) can be also used as an activation agent, but its disadvantage is high toxicity.\textsuperscript{67,93,109,114,115}

Another process for synthesizing cellulose esters is by transesterification reaction with vinyl esters. During the reaction, the leaving vinyl group immediately tautomerizes to acetaldehyde and, due to its low boiling point, can easily be removed from the reaction system. Transesterification with vinyl esters is usually performed under mild conditions with no need to use hazardous substances.\textsuperscript{90,116–119}
2.4 Applications for cellulose esters

Cellulose esters have been widely used as additives, binders and film formers in coating applications for many years. For example, as an additive in coatings, cellulose esters have many advantages such as viscosity control, improved UV stability and sprayability, and also decreased drying time.\textsuperscript{10,120} A number of studies have been carried out in recent years with the aim of developing new cellulose ester based packaging films as an alternative to materials produced from nonrenewable resources. Cellulose esters form a transparent and rigid film with good barrier and antimicrobial properties and therefore have good potential for use as packaging materials.\textsuperscript{68,121–123} Cellulose esters also have well known thermoplastic properties and they can be processed by conventional processing techniques (e.g. film extrusion, injection molding). Cellulose esters typically have high Young’s modulus, but moderate impact properties.\textsuperscript{124–127} Cellulose esters (especially CA) have also been used in many textile applications due to their properties and good performance in textile processing. Cellulose ester fibers can provide a renewable and recyclable alternative in several technical and hygienic textile applications. Melt spinning is one of the most convenient methods of polymer fiber production at industrial scale for the textile industry, and also the suitability of cellulose esters for melt spinning fibers has been reported.\textsuperscript{128–132} Cellulose esters as a matrix material in fiber-reinforced composites have also been studied\textsuperscript{133,134} and cellulose esters as membranes are also suitable for ultrafiltration applications, in which they have been reported to have good salt rejection and film forming properties.\textsuperscript{135} In addition, cellulose esters have become promising raw materials for 3D printing, offering an attractive pathway for fabricating sustainable structures.\textsuperscript{136–138} Furthermore, most cigarette filters are made of plasticized cellulose acetate.\textsuperscript{139,140} Cellulose esters are also commonly used in pharmaceutically controlled release preparations, such as osmotic and enteric coated drug delivery systems, based on extensive evidence of the low toxicity of cellulose esters having. Thin films of cellulose esters have also been proven to be effective aids for selective protein and biomolecule adsorption.\textsuperscript{141–143}
3. Experimental

In this section, the main materials and experimental techniques used in this work are described. More detailed information can be found in original Publications I-V.

3.1 Materials and methods

3.1.1 Materials

The cellulose material in Publications I-V was commercial softwood sulfite, a dissolving grade pulp produced by Domsjö Fabriker AB, Sweden. Native bleached birch kraft pulp obtained from UPM, Finland, was used for cellulose nanofibril (CNF) production in Publication III. Virgin brown kraft paper (40 g/m², Publication IV) was purchased from Antalis, Finland, PLA (3051D, Publication IV and 3052D, Publication V) from Natureworks, USA, and bio-polyethylene (LDPE SPB681, publication IV and HDPE SHA7260, publication V) from Braskem, Brazil. All other reagents and solvents were obtained from commercial sources (Merck and Sigma-Aldrich, Finland) at the highest purity grade and were used as received.

3.1.2 Ozone and hydrogen peroxide pretreatments

During ozone pretreatment (Z-stage), the pulp (12 wt%) was mixed in a plastic flow-through reactor and ozone flow (190 mg/min) was led into the reactor operating at 25 °C. After ozone pretreatment, the pulp was treated with alkali (E-stage) at 60 °C for 60 min or with hydrogen peroxide (P-stage) at 80 °C for 100 min.

3.1.3 Homogeneous esterification method

Homogenous cellulose esterification (in Publications I-V) was performed using a modified method presented by Ott et al.\textsuperscript{144}, where cellulose was first dissolved in a 5% LiCl/DMAc solution. Anhydrous pyridine (3.6 or 6.6 eq/AGU) was then mixed with the cellulose solution. Finally, fatty acid chloride (3 or 6 eq/AGU) was slowly added to the cellulose mixture. The mixture was then heated to 80 °C and mixing was continued at a constant temperature for 16 hours. The formed
Experimental
cellulose ester was precipitated with ethanol or water, filtered and additionally washed with ethanol and/or acetone.

3.1.4 Heterogeneous esterification method
Heterogeneous cellulose esterification (Publication I) was carried out using a modified method described by Vuoti et al.\textsuperscript{145}. Cellulose and anhydrous pyridine (20 eq/AGU) were mixed together and fatty acid chloride (3 eq/AGU) was slowly added to the cellulose mixture. The mixture was stirred at 100 °C for 5 hours. The formed cellulose ester was then precipitated with ethanol, filtered and additionally washed with ethanol and acetone.

3.1.5 Preparation of CNF films
In Publication III, CNF films were produced with a patented SutCo-concept\textsuperscript{146}. The CNF dispersion, including 30% sorbitol, was first carefully pre-homogenized and then cast onto a plastic substrate using a line speed of 5 m/min. The dispersion formed an even and uniform wet layer. After drying overnight in ambient conditions, the resulting 40 µm thick CNF films were delaminated from the support and cut into A4 sheets.

3.1.6 Long chain cellulose ester films
Films (Publications I-II) were prepared from purified long chain cellulose esters by solvent-casting. The cellulose esters (5 wt%) were dissolved in chloroform and poured into a petri dish (diameter 50-100 mm). The solvent was evaporated under ambient conditions prior to film formation.

3.1.7 Long chain cellulose ester coatings
CNF films (Publication III) and kraft papers (Publication IV) were coated using long chain cellulose esters (2-10 wt% solutions in chloroform depending on the viscosity). First, the surface was treated with LabTEC Tantec corona surface treatment to improve wettability and adhesion. Immediately after corona treatment, each coating formulation was applied to CNF film or kraft paper by Erichsen Coatmaster 510 (Erichsen GmbH, Germany) with a line speed of 1 m/min and a wet film deposit of 100 µm.

3.1.8 Injection molding of long chain cellulose esters
In Publication V, long chain cellulose esters were compounded by a twin screw micro compounder (Vari-Batch™ 15, DSM Xplore, Netherlands) with a screw speed of 100 rpm and screw residence time of 1 minute. The compounding temperature for the different compounds was 130 °C or 180 °C. All materials were dried in a vacuum oven at 40 °C overnight prior to use.
Injection moldings were carried out using a micro injection molding machine (Minijet Type 557-2270, Haake ThermoFisher Scientific, UK) and the standard dog bone shaped samples were molded. In injection molding, the temperature of the mold was 35 °C and an injection pressure of 400 bar for 5 s and post pressure of 200 bar for 15 s were used.

3.1.9 Characterization

**Intrinsic viscosity of the pulp**

The intrinsic viscosity of the pulps was determined by a standard ISO 5351-1.

**Size exclusion chromatography (SEC)**

The relative molar mass of the pulp samples was determined by size exclusion chromatography (SEC) measurements in 0.8% LiCl/DMAc eluent using MiniMix columns equipped with a Waters 2414 Refractive Index Detector (Waters, Milford, USA). The relative molar mass distributions, average molar masses (M_n, M_w) and dispersity (D) were calculated against Pullulan standards.

**X-ray powder diffraction (XRD)**

X-ray powder diffraction (XRD) data of the pulp samples were recorded with a Philips X’Pert MPD diffractometer (Philips Research Laboratories, Eindhoven, Netherlands). The data was collected in a 2θ range of 5° to 40° with a step size of 0.02°.

**Nuclear magnetic resonance (NMR) spectroscopy**

The prepared long chain cellulose esters were characterized using solid state ^13^C CP/MAS NMR spectroscopy (ssNMR) with an Agilent 600 MHz NMR spectrometer (Agilent Technologies, USA) using a 3.2 mm magic angle spinning (MAS) probe head. For all long chain cellulose esters, 10000 scans were accumulated using a 10 s recycle time, 3 ms contact time and a MAS rate of 10 kHz. All ssNMR experiments were carried out at 22 °C.

**Fourier transform infrared (FTIR) spectroscopy**

Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Perkin Elmer FTIR spectrometer (Perkin Elmer Inc., USA) and the potassium Bromide (KBr) method in the range of 400-4000 cm⁻¹.
**Experimental**

*Differential scanning calorimetry (DSC)*

Melting temperatures ($T_m$) and crystallization temperatures ($T_c$) of long chain cellulose esters were determined by a Mettler Toledo Differential Scanning Calorimeter (DSC2 STARe; Mettler Toledo GmbH, Switzerland). The $N_2$ flow rate was 50 ml/min and 40 µl sealed aluminum crucibles were used. The temperature profile was from -60 °C to 250 °C. Heating and cooling rate of 10 °C/min was used in all cases.

*Thermogravimetric analysis (TGA)*

Decomposition temperatures ($T_{deg}$) of long chain cellulose esters were determined by thermal gravimetric analysis (Netzsch STA449F1, Netzsch Gerätebau GmbH, Germany). The TGA measurements were carried out in air atmosphere from 40 to 600 °C with a heating rate of 10 °C/min.

*Scanning Electron Microscopy (SEM)*

Scanning electron microscopy (SEM) analysis of the long chain cellulose ester samples was performed using a field emission SEM (Merlin, Carl Zeiss GmbH, Germany). 2 kV acceleration voltages were used and prior to the imaging the samples were sputter-coated (SCD 050, Balzers AG, Liechtenstein) with a thin gold layer. For cross-section imaging, the samples were freeze-fractured under liquid nitrogen.

*Atomic force microscopy (AFM)*

Surface morphology and roughness of long chain cellulose ester films was analyzed by atomic force microscope (AFM; Park Systems XE-100, Korea). Silicon probe ACTA-905M (Applied NanoStructures, Inc., USA) was utilized, with a nominal resonance frequency of 300 kHz, spring constant 40 N/m and tip radius < 10 nm. AFM images of 10 x 10 µm² representative areas on the samples were acquired with a scan rate of 0.35-0.5 Hz.

*Water vapor transmission rate (WVTR)*

Water vapor transmission rate (WVTR) of long chain cellulose ester films was determined gravimetrically according to a modified ASTM E-96 procedure. Samples with a test area of 5 cm² were mounted on a circular aluminum dish containing water, resulting in 100% relative humidity. The dishes were stored at 23 °C and 50% relative humidity, and periodically weighed until a constant weight reduction was achieved. Water vapor permeability (WVP) was obtained by multiplying WVTR by the film thickness and then dividing by the water vapor difference across the film.
**Oxygen transmission rate (OTR)**

Oxygen transmission rate (OTR) through long chain cellulose ester films was determined according to standard ASTM D3985 using Oxygen Permeation Analyzer Models 8001 and 8011 (Systech Instruments Ltd, UK). Tests were carried out with 50 cm² samples at 23 °C, 80% and 0% relative humidity (RH) using 100% oxygen as a test gas. Oxygen permeability (OP) was obtained by multiplying OTR by the film thickness and then dividing by sea level pressure.

**Grease and oil repellency (KIT test) and grease resistance**

Surface repellency of long chain cellulose esters to grease and oil was determined according to the modified TAPPI T 559 method. Castor oil, toluene, and n-heptane, or mixtures of them in different concentrations, were placed in contact with coated papers and inspected visually. A failure was denoted by a wetting or darkening of the surface due to penetration of the test solution.

Grease penetration was determined according to the modified TAPPI T 507 method. First, standard rapeseed oil was colored with Oil Red O dye and applied to blotting paper. A stain saturated piece of blotting paper was placed against the coated papers and pressed between two plates and kept at 40 °C for 7 days. At the end of the test period, the assembly was removed, and the background of the samples was visually examined.

**Contact Angle Measurements (CAM)**

The contact angles of the long chain cellulose ester films were measured using a CAM200 instrument (KSV Instruments Ltd, Finland) under test conditions of 23 °C and 50% relative humidity using water and diiodomethane (DIM).

**Mechanical properties**

Elastic modulus, tensile strength and elongation of long chain cellulose ester films and 3-layer films were determined at 23 °C and 50% relative humidity using an Instron 4505 Universal Testing machine (Instron, UK) with a load cell of 10 kN. Initial grip distance was 25 mm and rate of grip separation 5 mm/min. In Publications I-III, the film samples of 3 mm width, approximately 50 mm length and 60-70 µm thickness were tested, and in Publication V, the injection molded standard dog bone shaped samples (gauge dimensions 25 mm x 4 mm x 2 mm) were tested.

**Heat sealability**

Heat sealability of long chain cellulose ester films, 3-layer films and coated kraft paper samples were determined using a sealing strength tester (Labormaster HTC 3000, Willi Kopp, Germany). Sealing strength was measured after sealing at 170-200 °C with a sealing force of 850 kPa, sealing time of 3 s, delay time of 20 s, and peeling rate of 12 m/min. The width of the sample strips was 2-5 cm.
Density

Densities of long chain cellulose ester samples were measured according to the Archimedean principle by weighing the sample in air and in ethanol. The ethanol temperature was 22 °C and density 0.7888 g/cm³.

Antimicrobial tests

Antimicrobial activity of long chain cellulose ester samples was analyzed according to modified JIS Z 2801:2000 using a mixture of Staphylococcus aureus VTT E-70045 and Pseudomonas aeruginosa VTT E-96728 cells as the inoculum. The viability of the bacterial cells was monitored with the plate count technique after a contact time of 24 hours at 37 °C. The samples were also examined with acridine orange (AO) staining and epifluorescence microscopy.
4. Results and discussion

4.1 Adjusting the molar mass of the pulps

In this research, the commercial pulp was pretreated with ozone (Z-stage) allowing the molar mass of the pulp to be reduced in a controlled manner. In the first pulp batch, the ozone pretreatment was followed by alkali pretreatment (E-stage). However, the increased content of carbonyl groups caused some coloring effect on the pulp. Therefore, alkali pretreatment was replaced with hydrogen peroxide pretreatment (P-stage) to prevent the coloring effect. Detailed chemical consumptions for the pretreatments, intrinsic viscosities and relative molar masses of the pulp after pretreatments are shown in Table 1.

Table 1. Chemical consumptions in Z-, E- and P-stages, intrinsic viscosity, and relative molar masses of the pulp after treatments (Publication I).

<table>
<thead>
<tr>
<th></th>
<th>Z-stage, (O₃, kg/t)</th>
<th>E-stage, (NaOH, kg/t)</th>
<th>P-stage, (H₂O₂, kg/t)</th>
<th>Viscosityᵃ (ml/g)</th>
<th>Mₘₜ (kDa)</th>
<th>Mₘ (kDa)</th>
<th>Dᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated pulp</td>
<td></td>
<td></td>
<td></td>
<td>490</td>
<td>520</td>
<td>56</td>
<td>9.3</td>
</tr>
<tr>
<td>Treated pulp 1</td>
<td>12</td>
<td>15</td>
<td></td>
<td>200</td>
<td>185</td>
<td>28</td>
<td>5.8</td>
</tr>
<tr>
<td>Treated pulp 2</td>
<td>35</td>
<td></td>
<td>8</td>
<td>110</td>
<td>80</td>
<td>15</td>
<td>6.3</td>
</tr>
<tr>
<td>Treated pulp 3</td>
<td>53</td>
<td></td>
<td>9</td>
<td>110</td>
<td>58</td>
<td>13</td>
<td>4.3</td>
</tr>
</tbody>
</table>

ᵃ measured after ZE or ZP stage

Typically, ozone dosages from 2 to 9 kg/t are used in pulp bleaching processes. However, as the aim of this research was to significantly reduce the molar mass of the pulp, higher ozone consumptions were used, leading to a decrease in viscosity from an initial value of 490 ml/g to 110 ml/g. The used ozone consumptions were also well correlated with the pulp degradation rate and the decrease in pulp molar mass was confirmed by SEC analyzes. The obtained molar masses were reduced from 520 to 185, 80 and 58 kDa respectively, based on the ozone consumption. The more ozone was consumed, the lower the molar mass of the pulps.

The pulps were analyzed both by ssNMR spectroscopy (C4 peak separation method²⁷) and powder XRD (Segal method¹⁴⁷) to study the influence of the ozone pretreatment on pulp crystallinity. According to the powder XRD
analysis, the crystallinity index (CrI) for both untreated and treated pulps was 80%, and based on the ssNMR method, CrI was 56% for both pulps. This suggests that ozone treatment has no effect on crystallinity, and this finding is consistent with the findings reported earlier. The difference in CrI values between the ssNMR and XRD methods is due to the fact that the XRD peaks are often quite wide and vary considerably in width. Therefore, the CrI values determined using the ssNMR method indicate lower and more accurate values than those determined by XRD analysis.

4.2 Preparation of long chain cellulose esters

The main objective of this research was to synthesize long chain cellulose esters with different side chain lengths using both homogeneous and heterogeneous esterification methods. The target was to achieve cellulose esters with good mechanical and barrier properties. The schematic presentation of long chain cellulose esters is shown in Figure 6.

Figure 6. Schematic presentation of long chain cellulose ester synthesis.

The degree of substitution (DS) and purity of synthesized long chain cellulose esters were analyzed by FTIR and ssNMR spectroscopy. In the FTIR spectra, a clear carbonyl (C=O) peak at 1730-1750 cm\(^{-1}\) can be observed, indicating that the fatty acid has reacted with the cellulose. The absorption peak of the cellulose hydroxyl groups at 3360-3420 cm\(^{-1}\) also decreases as the esterification occurs due to the disappearance of the hydroxyl group.\(^{110,150,151}\)

The DS value of long chain cellulose esters was analyzed using ssNMR spectroscopy by comparing the integrals from the cellulose ester carbonyl carbon (173 ppm) with the C1 signal (105 ppm) of cellulose. The ssNMR was used, because all cellulose esters were not soluble in deuterated solvents and therefore liquid state \(^1\)H NMR measurement for characterizing the DS value was not possible. Therefore, all samples were analyzed by the same method to ensure a reliable comparison of DS. It is also earlier reported\(^{152}\) that in case of long chain cellulose esters the \(^1\)H NMR can suffer from poor resolution causing inaccuracies in DS determination. An example ssNMR spectrum is shown in Figure 7. According to the ssNMR analyses, the DS values (Table 2) of the synthesized long chain cellulose esters ranged from 0.3 to 1.3 depending on the used pulp, esterification method, and side chain length.
Results and discussion

Figure 7. ssNMR spectrum of cellulose C16 ester (Publication I).

Table 2. Effect of reaction parameters on DS of cellulose esters (Publications I-II).

<table>
<thead>
<tr>
<th>Esterification method</th>
<th>Pulp</th>
<th>Side chain length</th>
<th>Amount&lt;sup&gt;a&lt;/sup&gt; (molar ratio)</th>
<th>DS&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogenous</td>
<td>Untreated pulp</td>
<td>C16</td>
<td>3:1</td>
<td>0.3</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Untreated pulp</td>
<td>C16</td>
<td>6:1</td>
<td>1.0</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 1</td>
<td>C16</td>
<td>3:1</td>
<td>1.0</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 2</td>
<td>C16</td>
<td>3:1</td>
<td>1.1</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 3</td>
<td>C16</td>
<td>3:1</td>
<td>0.9</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 3</td>
<td>C6</td>
<td>3:1</td>
<td>1.3</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 3</td>
<td>C8</td>
<td>3:1</td>
<td>1.3</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 3</td>
<td>C10</td>
<td>3:1</td>
<td>1.1</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 3</td>
<td>C12</td>
<td>3:1</td>
<td>0.9</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 3</td>
<td>C14</td>
<td>3:1</td>
<td>1.0</td>
</tr>
<tr>
<td>Homogenous</td>
<td>Treated pulp 3</td>
<td>C18</td>
<td>3:1</td>
<td>0.8</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>Untreated pulp</td>
<td>C16</td>
<td>3:1</td>
<td>0.6</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>Treated pulp 1</td>
<td>C16</td>
<td>3:1</td>
<td>1.0</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>Treated pulp 1</td>
<td>C16</td>
<td>6:1</td>
<td>1.2</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>Treated pulp 2</td>
<td>C16</td>
<td>3:1</td>
<td>1.2</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td>Treated pulp 2</td>
<td>C16</td>
<td>6:1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> molar ratio of fatty acid chloride vs AGU,

<sup>b</sup> according to ssNMR analyses, error limit ±0.1
Based on the DS values, it can be concluded that starting pulp molar mass has a major effect on the DS values. When untreated pulp was used in homogeneous esterification as a starting pulp, and with a molar ratio of palmitoyl chloride to AGU of 3:1, the cellulose C16 ester DS was only 0.3, indicating low reaction efficiency. The DS values of cellulose C16 esters were between 0.9 and 1.1 when ozone pretreated pulps with lowered molar masses were used under the same reaction conditions. The treated pulps are more reactive than the untreated pulp, but the steric hindrance of side chains causes that the DSs remain about 1 even though there is a large difference in the molar mass of the starting material. These DS values for cellulose esters prepared from ozone pretreated pulp are higher than those reported earlier. For example, Guo et al.\textsuperscript{153} have reported DS values ranging from 0.1 to 0.4 for cellulose C16 esters in homogeneous systems and Wei et al.\textsuperscript{53} have reported a maximum DS value of 0.7 for cellulose C16 esters. Based on the DS values, it can also be concluded that the side chain length of cellulose esters has an effect on DS. As the side chain length increased from C6 to C18, the DS values decreased from 1.3 to 0.8 under similar reaction conditions due to steric hindrance of cellulose OH-groups and lower fatty acid reactivity.

When heterogeneous esterifications were used, the synthesized cellulose C16 esters resulted in DS values that were much higher than with homogeneous esterifications. The biggest difference was in the case of untreated pulp, where the DS values for the cellulose C16 esters were doubled from 0.3 to 0.6. When the amount of reagent in heterogeneous esterification was doubled from 3:1 to 6:1, the DS of cellulose C16 esters was only marginally higher (1.2-1.3), which seems to be the maximum DS for these long chain cellulose esters under the tested reaction conditions.

### 4.3 Long chain cellulose ester films

Long chain cellulose esters with a DS>0.8 prepared using the homogeneous method and different side chain lengths were soluble in chloroform, and films could be prepared using the solvent casting method. The formed cellulose ester films (Figure 8) were transparent and flexible. In addition, the cellulose esters in this research were able to form films with clearly lower DS values than earlier reported\textsuperscript{79,82,154}. The most probable explanation for this is that long side chains have a greater plasticizing effect on lower molar mass cellulose than on higher molar mass cellulose.

Some small pinholes on the film surface were observed when the microstructure of these films was analyzed using SEM (Figure 9A). These pinholes might be due to air bubbles generated during the high viscous solvent casting process. These pinholes can significantly weaken the mechanical and barrier properties of the films. When the heterogeneous esterification method was used, the cellulose esters were not fully soluble even at a higher DS values. This was due to the uneven distribution of the side chains in the esters, and some insoluble cellulose fibers (5-14 wt\%) were also seen in the films (Figure 9B).
Figure 8. Transparent and flexible films of cellulose esters with different side chain lengths (Publication II).

Figure 9. SEM images of cellulose C16 ester films prepared using the A) homogeneous and B) heterogeneous esterification method (Publication I).
4.3.1 Mechanical properties of films

The mechanical properties, i.e. elastic modulus, tensile strength and elongation at break, of long chain cellulose ester films were analyzed and the results are summarized in Figure 10. The elongation at break value indicates how much the tested film stretched before rupturing, and the elastic modulus measures the material’s stiffness; the higher the elastic modulus, the stiffer the material. According to the results (Figure 10), the elastic modulus of cellulose ester films seemed to decrease when the side chain length of the cellulose esters increased. This observation is in line with earlier published results.\textsuperscript{79} Cellulose C6 ester (600 MPa), cellulose C10 ester (600 MPa) and cellulose C12 ester (550 MPa) achieved the highest elastic modulus values.

In the case of tensile strength and elongation values no similar trend was observed as a function of side chain length. One explanation for this may be that the DS values of the cellulose esters were not the same for all samples. As the side chain length increased, DS values decreased. However, starting pulp molar mass seemed to have a significant effect on cellulose ester mechanical properties; the lower the starting molar mass, the better the mechanical properties. This observation is in contrast to what Park et al.\textsuperscript{155} have earlier reported. Cellulose C12 ester had the highest tensile strength values (35 MPa) and the other measured cellulose esters prepared using the same starting pulp varied at around 20-25 MPa. When a higher molar mass starting pulp was used, the tensile strength values decreased significantly to 10 MPa.

Cellulose C8 ester had very high elongation at break (90%) compared to the other cellulose esters, which had an elongation at break around 50% except for the heterogeneously prepared cellulose ester, which showed only 10% elongation. The cellulose esters, which are prepared by the heterogeneous esterification method, contain residual fibers, which greatly weaken the mechanical properties.

When comparing the mechanical properties of these long chain cellulose ester films with some previously reported\textsuperscript{79,110} results for commercial plastic materials, the elastic modulus and tensile strength values of these films were at the same level as high-density polyethylene (HDPE), low-density polyethylene (LDPE) and cellulose acetate butyrate (CAB). Elongation values were quite low compared to commercial polyethylenes, but in the same range as cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). However, commercial CA, CAB and CAP contain plasticizers that also have an effect on mechanical properties.
Results and discussion

Figure 10. Mechanical properties of long chain cellulose ester films with different side chain length (Publications I-II). Molar masses: pulp1=185 kDa, pulp2=80 kDa, pulp3=58 kDa. *Homogeneous method. **Heterogeneous method.
4.3.2 Barrier properties of films

The barrier properties of long chain cellulose ester films were also analyzed. It has been previously stated\textsuperscript{68,75} that long chain cellulose ester films are typically hydrophobic materials and thus have quite good water vapor barrier properties. Based on the barrier results of long chain cellulose esters in the present research (Figure 11), the water vapor permeability (WVP) values of the films decreased dramatically by increasing the side chain length of the esters. This observation is also in line with the observation reported by Bras et al.\textsuperscript{68}. For example, cellulose C16 and C18 ester films had much better WVP values compared to cellulose C6 ester films. The reason for this is that the percentage of alkyl groups in the film composition increased when the side chain length increased, which increases the hydrophobicity of the films.\textsuperscript{156} This decreases the water absorption into the film, thereby influencing the amount of diffusing water molecules and improving the barrier properties. The molar mass of the starting pulp also has an effect on the WVP values. The WVP values are slightly lower when the starting pulp molar mass is higher. The influence of DS value on the results was difficult to assess because the DS values were not the same for all esters.

The WVP values of long chain cellulose ester films are significantly lower than to some other cellulose based films, such as cellulose acetate, cellophane or cellulose nanofibril (CNF) films.\textsuperscript{157–159} However, the performance is still far from commercial polyolefins.\textsuperscript{160}

![Figure 11. Water vapor permeability (WVP) of long chain cellulose ester films measured at 23 °C, 100/50% RH (Publications I-II). Molar masses: pulp1=185 kDa, pulp2=80 kDa, pulp3=58 kDa. *Homogeneous method. **Heterogeneous method.](image-url)
The most common plastics, such as polyolefins, typically consist of nonpolar hydrocarbon chains. The solubility of nonpolar oxygen molecules in these polymers is proportional to the volume of the amorphous phase.\textsuperscript{161} Measured oxygen permeability (OP) values for long chain cellulose ester films (Figure 12) were comparable to polyethylenes. Based on the analysis, it can be inferred that cellulose C6 ester had the lowest OP value and cellulose C16 ester had the highest OP value. The OP value of one cellulose C16 ester film differed significantly from the other C16 ester values. This may be due to potential pinholes in the film tested, which have a major impact on the OP values. However, no clear correlation between side chain length and OP values was observed, although Bras et al.\textsuperscript{68} have stated that OP values for long chain cellulose esters increased with increased side chain length due to polarity and molecular mobility. The explanation for this finding is that when the side chain length of the cellulose ester is longer the gas moves more easily through cellulose ester film. The crystalline regions in semicrystalline polymers are known to be gas-impermeable, which primarily affects oxygen barrier properties.\textsuperscript{160,162} The molar mass of the starting pulp also seems to have an effect on OP values by reducing OP values at higher molar masses. Bras et al.\textsuperscript{68} and Kulomaa et al.\textsuperscript{163} also found that the OP values of long chain cellulose ester films typically decreased when the WVP values increased. It is therefore challenging to make cellulose ester films that have both good oxygen barrier and water barrier properties.

![Figure 12. Oxygen permeability (OP) of long chain cellulose ester films measured at 23 °C, 80% RH (Publications I-II). Molar masses: pulp1=185 kDa, pulp2=80 kDa, pulp3=58 kDa. *Homogeneous method. **Heterogeneous method.](image-url)
4.3.3 Wetting behavior of films

The contact angle values of long chain cellulose ester films were also analyzed to determine the wetting behavior and hydrophobicity of the films. Contact angles reveal the degree of wetting and surface energy of the cellulose ester film when solid and liquid phases interact. The films have low wettability when the contact angle values are >90°. The contact angle values of water and diiodomethane (DIM) for long chain cellulose ester films are presented in Figure 13. DIM was chosen due to its nonpolar nature and high surface tension. The contact angle values of water ranged between 66° and 90°, and of DIM between 47° and 71°. These values correlate well with the WVP values. Vuoti et al. have reported an increase in cellulose ester film hydrophobicity as the length of the alkyl chain increases, and the results for long chain cellulose esters in this research correlate well with this observation. Cellulose C6 ester film had significantly lower contact angle values than other cellulose ester films, indicating high affinity between both liquids and the surface.

Figure 13. Contact angle values of water and DIM for long chain cellulose esters as a function of time; cellulose esters were prepared using pulp 3 (Mn=58 kDa) (Publication II).
4.3.4 Thermal behavior

Thermal properties of synthesized long chain cellulose esters were analyzed by DSC and TGA. As long chain cellulose esters are an amorphous material, they do not have clear melting temperature. However, some crystallization and melting can be observed (Figure 14) due to the melting and crystallization of side chain crystals. Side chain crystallization and melting can occur when the length of the side chain is C10 or greater. The alignment and orientation of the cellulose backbone can affect the ability of side chains to organize in certain ways and, due to the semiflexible nature of the cellulose backbone, reorganization of side chains can lead to a change in the cellulose backbone packing. The glass transition temperature \((T_g)\) of these materials is too weak to be detected or it possibly overlaps with the side chain melting and crystallization peaks.

![Figure 14. Cooling cycle and 2nd heating cycle of cellulose esters, heating and cooling rate 10 °C/min; cellulose esters were prepared using pulp 3 (M_w=58 kDa) (Publication II).](image)

According to the DSC results (Table 3), the side chain length of the cellulose ester has an effect on thermal properties. The melting and crystallization temperatures and enthalpies of the cellulose esters increased linearly with increased side chain length due to the increase in crystalline thickness, as longer side chain lengths allow more methylene units to participate in the crystallization process. Moreover, the steric effect of longer side chain length causes a loss of substituent mobility. These findings are consistent with previously reported results.
Glasser et al.\textsuperscript{168} have reported that melting temperature ($T_m$) correlated with the DS of cellulose esters: the higher the DS, the lower the $T_m$. For example, in case of cellulose C16 esters (Publication I), the $T_m$ values decreased from 32 °C to 17 °C when the DS rose from 0.7 to 1.1. Correspondingly, side chain melting enthalpies ($\Delta H_m$) increased as the DS values increased. Side chain melting temperatures were slightly higher when homogeneous esterification was used due to the cellulose backbone losing its crystalline structure during the homogeneous esterification reaction, and also because the hydrogen bonds between the backbone and side chains differ to those of heterogeneously produced esters, in which esterification occurs mainly on the cellulose fiber surface.\textsuperscript{169}

Thermal stability of long chain cellulose esters is an important parameter for processability and thus the degradation temperatures ($T_{\text{deg}}$) of cellulose C16 esters were analyzed (Publication I). The $T_{\text{deg}}$ values of all the cellulose esters tested were significantly higher than their processing temperatures (130-150 °C). The molar mass of the starting pulp had an effect on $T_{\text{deg}}$ values. $T_{\text{deg}}$ values for cellulose esters prepared using untreated pulp, were between 210 °C and 236 °C, whereas clearly higher $T_{\text{deg}}$ values were obtained for cellulose esters prepared using ozone pretreated pulps, with $T_{\text{deg}}$ values varying between 250 °C and 310 °C. In addition, when the heterogeneous method was used, the $T_{\text{deg}}$ values were slightly higher. The explanation for this is that heterogeneous esterification has less effect on the cellulose fiber structure than the homogeneous method, where the fibers fully dissolve and, thus, the inter- and intramolecular hydrogen bonds of the cellulose are more disrupted. For unmodified pulp, a $T_{\text{deg}}$ value of about 300 °C has been reported.\textsuperscript{170}

### Table 3. Thermal properties of long chain cellulose esters (Publication II).

<table>
<thead>
<tr>
<th>Side chain length\textsuperscript{a}</th>
<th>$T_m$ (°C)\textsuperscript{b}</th>
<th>Melting enthalpy (J/g)\textsuperscript{d}</th>
<th>$T_c$ (°C)\textsuperscript{c}</th>
<th>Crystallization enthalpy (J/g)\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>C8</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>C10</td>
<td>-22</td>
<td>4</td>
<td>-25</td>
<td>6</td>
</tr>
<tr>
<td>C12</td>
<td>-22</td>
<td>5</td>
<td>-25</td>
<td>6</td>
</tr>
<tr>
<td>C14</td>
<td>4</td>
<td>17</td>
<td>-1</td>
<td>18</td>
</tr>
<tr>
<td>C16</td>
<td>29</td>
<td>37</td>
<td>23</td>
<td>34</td>
</tr>
<tr>
<td>C18</td>
<td>45</td>
<td>49</td>
<td>39</td>
<td>45</td>
</tr>
</tbody>
</table>

\textsuperscript{a} cellulose esters prepared using pulp 3 ($M_w=58$ kDa)

\textsuperscript{b} side chain melting temperature (2\textsuperscript{nd} heating cycle), standard deviation ± 2 °C (DIN 53765)

\textsuperscript{c} side chain crystallization temperature, standard deviation ± 2 °C (DIN 53765)

\textsuperscript{d} standard deviation ± 7.5% (DIN 53765)
4.3.5 Heat sealability

Heat sealability of long chain cellulose ester films was determined using a sealing strength tester. Heat seal strength refers to the maximum force per unit of width required to separate the heat seal and, during the heat sealing process, the polymer chains from each side of the heat seal diffuse into one another. Greater polymer chain diffusion distances result in greater seal strength. According to the results (Table 4), the seal strengths of the films seemed to increase as a function of side chain length when a sealing temperature of 170-200 °C was used. However, when sealing strengths were normalized to film thickness, all values were at the same level. Surprisingly, cellulose C10 and C12 ester films were not heat sealable under the conditions tested; the reason for this is unclear. All tested cellulose ester films failed in tearing mode, because in all cases the seal strength was higher than the strength of the film structure. The adhesive strength of the seal was higher than the strength of the film, indicating the production of an ideal seal.

Table 4. Heat seal strength of long chain cellulose esters (Publication II).

<table>
<thead>
<tr>
<th>Side chain length</th>
<th>Sealing strength (N/m)</th>
<th>Normalized sealing strength ×10^6 (N/m²)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>132 ± 30</td>
<td>2.5±0.6</td>
</tr>
<tr>
<td>C8</td>
<td>183 ± 24</td>
<td>3.7±0.5</td>
</tr>
<tr>
<td>C10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C14</td>
<td>265 ± 170</td>
<td>4.4±2.8</td>
</tr>
<tr>
<td>C16</td>
<td>290 ± 127</td>
<td>3.8±1.6</td>
</tr>
</tbody>
</table>

^a normalized to film thickness.

4.4 Long chain cellulose ester coatings

4.4.1 3-layer films with CNF

Due to their insufficient surface smoothness and moisture barrier properties, CNF films are not competitive with fossil-based films unless additional coatings are applied. Using multilayer film structures, the technical performance of CNF films can, however, be improved and they can be used in high performance film applications (e.g. printed electronics and packaging).

In Publication III, both sides of the CNF films were coated with long chain cellulose esters forming a 3-layer multilayer structures. According to the SEM images (Figure 15), the thickness of the cellulose ester coating layers was 1-5 µm depending on the cellulose ester side chain length (C6-C18) and all coatings had good adhesion to the CNF film. The coatings were quite homogeneous and no pinholes were observed, only some small surface pores could be found.
The heat sealability of these 3-layer films was determined using the sealing strength tester. Pure CNF film cannot be heat sealed, but when coated with cellulose esters quite strong seals were achieved. Seal strength also seemed to increase as a function of cellulose ester chain length. However, the strength of the seals was weaker than the strength of the film structure and the coated cellulose ester layer separated from the CNF film layer during peeling although the cellulose ester coatings had formed well anchored layer on the CNF film.

Figure 15. SEM cross-section images of long chain cellulose ester coated CNF films (Publication III).
Barrier properties of 3-layer films

CNF films are known for their excellent oxygen barrier properties, which are due to their tightly packed polar nanofibrils, which reduce the free volume and thus efficiently prevent the transmission of oxygen and other nonpolar permeants. However, this is true only in dry conditions. Under higher humidity conditions the CNF films begin to swell, which increases oxygen permeation. Because long chain cellulose esters have good water vapor barrier properties but weaker oxygen barrier properties, CNF films were coated with long chain cellulose esters to achieve a 3-layer film structure having both good oxygen and water vapor barrier properties.

All of the prepared 3-layer samples had a very low (<0.1 cc/m²/day) oxygen transmission rate (OTR) in dry conditions (0% RH). Due to the nonpolar nature of cellulose ester coatings, the coating did not affect oxygen barrier values when the RH was raised to 80%. In that case, the OTR values were 40-60 cc/m²/day, which are comparable to those earlier reported\textsuperscript{157,172,173} for pure CNF films at high humidity.

The moisture resistance of CNF film has been found to be low due to the high affinity of cellulose for water. Water molecules can penetrate into the cellulose fibrils, breaking their hydrogen bonds and increasing moisture permeability.\textsuperscript{174} The measured water vapor transmission rate (WVTR) for non-coated CNF film was very high and comparable, for example, to regenerated cellulose films.\textsuperscript{175} When CNF films were coated using cellulose esters, WVTR values decreased significantly from 650 g/m²/day to 300 g/m²/day, clearly as a function of cellulose ester side chain length (Figure 16). The cellulose ester coating layers were very thin, only 1-5 μm; therefore, if the coating thicknesses had been higher, the WVTR values obtained would have been even lower.

![Figure 16. Water vapor transmission rates of 3-layer films measured at 23 °C, 100/50% RH (Publication III).](image-url)
Results and discussion

Mechanical properties of 3-layer films

The mechanical properties (elastic modulus, tensile strength and elongation at break) of prepared 3-layer CNF-films were also determined. According to the results, the mechanical properties of the 3-layer films were close to those earlier reported\textsuperscript{162,175–180} for pure CNF films and regenerated cellulose films. The film properties were thus not weakened by either the cellulose ester coatings or the chloroform used in the coatings, and only some a minor decrease in tensile strength was detected (Publication III).

Surface smoothness of 3-layer films

Surface roughness at the nanoscopic scale (nano-roughness) and the surface topography (micro-roughness) of the 3-layer films were analyzed using atomic force microscopy (AFM). According to the AFM images (Figure 17), all of the cellulose ester coatings covered completely and smoothly the CNF films, and the coatings reduced the surface micro-roughness compared to pure CNF film. The reduction was greatest for cellulose ester coatings with side chain lengths of C8, C10 and C16. Nano-roughness was also very low (1-4 nm) for all cellulose ester coated 3-layer films. These are very low roughness levels, comparable to the length of a single fatty acid chain.

Figure 17. AFM 3D images of coated 3-layer films (Publication III).
4.4.2 Coated kraft paper

Stand-up pouches are one of the fastest growing packaging concepts, where good moisture and oxygen barrier properties and grease resistance are needed. In Publication IV, virgin kraft paper was coated using long chain cellulose esters with different side chain lengths, and the suitability of this material for stand-up pouches was demonstrated.

All of the cellulose ester coatings formed a smooth, homogeneous and well anchored layer on the kraft paper. According to the SEM images (Figure 18), the thickness of the cellulose ester coating layers varied between 6-12 µm. As a reference coating material, bio-LDPE (16 µm) and PLA (65 µm) coatings were used, but the adhesion of these reference materials to kraft paper proved weaker than the adhesion of cellulose ester coatings; this was determined to be because the reference materials were extrusion coated instead of solvent cast.

Figure 18. SEM cross-section images of long chain cellulose ester, bio-LDPE, and PLA coated kraft papers (Publication IV).
The heat sealability of long chain cellulose ester coated papers was determined by sealing samples using the same sealing temperature (200 °C) for all samples, although the used temperature was not optimum for all coatings. For example, for PLA, an optimum heat seal temperature of 110 °C is reported. The achieved sealing strengths of the cellulose ester coated papers varied from 0 N/m to 121 N/m, whereas for the reference materials, bio-LDPE and PLA, the strengths were 228 N/m and 649 N/m, respectively (Table 5). However, coating layer thickness has a significant effect on sealing strength, and when the sealing strengths were normalized to the thicknesses of the coating layers, all values were at the same level. As with the cellulose C10 and C12 ester films, the C10 and C12 coatings were also not heat sealable under the conditions tested.

Table 5. Heat seal strength of long chain cellulose ester, bio-LDPE, and PLA coatings (Publication IV).

<table>
<thead>
<tr>
<th>Coating</th>
<th>Sealing strength (N/m)</th>
<th>Normalized sealing strength ×10^6 (N/m²)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>no coating</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C6</td>
<td>121 ± 12</td>
<td>12.1 ± 1.2</td>
</tr>
<tr>
<td>C8</td>
<td>67 ± 11</td>
<td>6.1 ± 1.0</td>
</tr>
<tr>
<td>C10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C14</td>
<td>98 ± 6</td>
<td>14.0 ± 0.9</td>
</tr>
<tr>
<td>C16</td>
<td>112 ± 18</td>
<td>9.3 ± 1.5</td>
</tr>
<tr>
<td>bio-LDPE</td>
<td>228 ± 17</td>
<td>14.3 ± 1.1</td>
</tr>
<tr>
<td>PLA</td>
<td>649 ± 137</td>
<td>10.0 ± 2.1</td>
</tr>
</tbody>
</table>

*normalized to coating thickness.

**Barrier properties of coated kraft paper**

The primary function of packaging materials is to avoid loss of food quality and give protection against environmental contamination. Therefore, the barrier properties (water vapor, oxygen and grease) of packaging materials are essential. Kraft paper has no measurable barrier properties against oxygen. According to the oxygen permeability (OP) results (Figure 19), all of the cellulose ester, bio-LDPE and PLA coatings significantly reduced the OP of kraft paper. The most effective cellulose ester coatings for OP reduction were found to be cellulose C6, C8 and C16 ester coatings, which achieved similar oxygen barrier levels as PLA coating. The cellulose C10, C12 and C14 ester coatings may have contained some small pinholes, which would have affected their OP values. However, all of the cellulose ester coatings were better oxygen barriers than bio-LDPE, which is a nonpolar polymer and therefore oxygen diffuses easily through it. When the OP values of the ester coatings were compared with, for example, chitosan coatings, the cellulose ester coating values were notably higher.
Nonpolar LDPE consists of high molar mass hydrocarbon chains enabling the most effective barrier against moisture and, for this reason, polyethylene is the most widely used moisture barrier plastic nowadays.\textsuperscript{158} By comparison, all of the tested long chain cellulose ester and PLA coatings showed good potential in significantly reducing the WVP of kraft paper (Figure 20). The WVP values of the cellulose ester coated kraft papers decreased linearly as a function of side chain length from 3080 g×μm/m\(^2\)/day (C6) to 1128 g×μm/m\(^2\)/day (C16) and for all side chain lengths the WVP values were better than PLA. The most effective cellulose ester coating was cellulose C16 ester, which reduced kraft paper’s WVP by 84%. This indicates that long chain cellulose ester coatings have at least as competitive moisture barrier properties as other bio-based barrier coatings\textsuperscript{183–185}. The contact angle values of long chain cellulose ester coatings varied between 66° and 87° depending on side chain length, correlating well with the obtained WVP values. The bio-LDPE coating, which had the lowest WVP value, resulted in the highest contact angle value (98°).
Figure 20. Water vapor permeability (WVP) of long chain cellulose ester, bio-LDPE, and PLA coated kraft paper measured at 23 °C, 100/50% RH (Publication IV).

The grease resistance and grease and oil surface repellency of kraft paper coatings were tested using KIT tests. The “like dissolves like” theory is based on the assumption that a substance dissolves best in a solvent that has a similar polarity to the substance. All of the long chain cellulose ester coatings improved the kraft paper’s resistance against the tested nonpolar compounds (Table 6). Cellulose C16 ester coating had the highest susceptibility, indicating typical behavior of longer hydrocarbon chains. LDPE is a nonpolar polymer and therefore its chemical resistance against nonpolar compounds (e.g. oil and grease) is not optimal. However, while the grease resistance of the bio-LDPE and PLA coatings was better than that of the long chain cellulose ester coatings, the bio-LDPE and PLA coatings were much thicker than the cellulose ester layers, which may have had an effect on the results. CNF films are reported to be impermeable to grease, but the grease resistance and surface repellency values of long chain cellulose ester coatings are comparable with chitosan coatings.
Table 6. Surface grease and oil repellency (KIT test) and grease resistance results of long chain cellulose ester, bio-LDPE, and PLA coatings (Publication IV).

<table>
<thead>
<tr>
<th>Coating</th>
<th>Surface repellency&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Grease resistance&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>no coating</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>C8</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>C10</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>C12</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>C14</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>C16</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>bio-LDPE</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>PLA</td>
<td>11</td>
<td>8</td>
</tr>
</tbody>
</table>

<sup>a</sup> 0 = all penetrated, 12 = no penetration.
<sup>b</sup> 0 = all penetrated, 8 = no penetration.

Antimicrobial properties of coated kraft paper
Antimicrobial properties are also important for food packaging materials for reducing the microbial contamination of different foodstuffs. Antimicrobial materials prevent the growth of microorganisms on food surfaces that are in direct contact with the packaging material. The tested coating samples (cellulose C8 ester, cellulose C16 ester, and PLA) showed no antimicrobial activity and the viability of microbes on the films after a 24-hour contact time with inoculum was the same as at the beginning of testing. In addition, only a few cells were observed on the surfaces of cellulose C8 and C16 esters, whereas microbes strongly adhered to the surface of PLA (Figure 21). As indicated by the antimicrobial action tests, long chain cellulose esters are highly inert to microorganisms, and thus safe to be used in direct food contact.

Figure 21. Images from acridine orange stained cellulose C8 ester, cellulose C16 ester, and PLA film surfaces after 24-hour contact time with inoculum (Publication IV).
4.5 Processability of long chain cellulose esters

In Publication V, the mechanical properties and processability of cellulose C8 and C16 esters were studied in detail. Both cellulose esters were compounded at 130 °C without plasticizers as pure material and as blends, using 25/75, 50/50, and 75/25 wt% ratios in order to study the full range of composition variations. In the case of cellulose esters, processability without additional plasticizers is quite unusual. Both cellulose esters formed a transparent and flexible extrusion strand, indicating that an even distribution of fatty acid branching had been achieved. After compounding, the test specimens were prepared by injection molding.

Cross-sectional surface cuts of the injection molded samples were imaged. According to the SEM images (Figure 22), all samples were well compounded and melted and no significant unevenness was observed. Moreover, cellulose C16 ester seemed to be more porous than cellulose C8 ester and they were also compatible with each other. The largest pores were observed when a 50/50 wt% mixing ratio was used, whereas when the cellulose C8 ester content was increased to 75 wt%, the surface was rather smooth, indicating excellent compatibility.

Figure 22. SEM cross-section images of the injection molded cellulose ester blends (Publication V).
Mechanical properties of injection molded cellulose esters

The mechanical properties (elastic modulus, tensile strength, and elongation at break) of the injection molded long chain cellulose ester samples were also measured. The elastic modulus of all analyzed samples was approximately the same (200 MPa) and no significant differences between cellulose C8 and C16 esters were found.

Tensile strengths of the cellulose C16 and C8 esters were 8 MPa and 6 MPa, respectively (Figure 23). This indicates that the side chain length of cellulose esters has a small effect on tensile strength. The same observation was found with long chain cellulose ester films (Publication II). However, the mechanical properties of these solvent-cast films were slightly better than those of injection molded cellulose esters. This could be due to the possible thermal degradation during the applied injection molding process, although the $T_{\text{deg}}$ of cellulose esters has been reported to be between 230–270 °C (Publication I).

Figure 23. Tensile strength values of injection molded cellulose C8 and C16 ester samples and their blends (Publication V).

The major difference observed between the mechanical properties of cellulose C8 and cellulose C16 esters was in elongation values (Figure 24). Cellulose C8 ester showed four times higher elongation (56%) than the cellulose C16 ester (12%), and the elongations of the specimens increased linearly with increasing amount of cellulose C8 in the cellulose C16/C8 blends. The elongation values obtained for long chain cellulose C8 and C16 esters were also much higher than those reported for commercially available shorter chain lengths CA, CAP, and CAB\textsuperscript{191–193}. However, the tensile strength and elastic modulus values were correspondingly lower. This is consistent with an earlier reported observation\textsuperscript{194} that elastic modulus and tensile strength decreased as elongation values increased.
Results and discussion

Figure 24. Elongation at break values of injection molded cellulose C8 and C16 ester samples and their blends (Publication V).

Compatibility of cellulose esters with PLA and bio-HDPE

Natural fibers are mainly used as reinforcements in polymer composites, and so far, only limited literature is available regarding the use of cellulose esters (shorter chain length CA, CAP, and CAB) in bio-based polymer composites or blends. In Publication V, the aim was also to study the compatibility of long chain cellulose esters (cellulose C8 and C16) with PLA and bio-PE using 25/75, 50/50, and 75/25 wt% ratios. According to SEM analysis (Figure 25), in the cellulose C16/PLA and cellulose C8/PLA blends, spherical-shaped PLA droplets could be observed in the continuous cellulose ester matrix when the PLA contents were 25 wt% and 50 wt%. This indicates that the compounding time (1 minute) and/or compounding temperature (180 °C) used for these samples were not sufficient. Increasing the temperature or time is, however, not desirable due to cellulose degradation, and therefore one way is to use some additives during compounding. The cellulose esters seemed to be more compatible with bio-PE than with PLA and only small unevenness was detected when 25 wt% of bio-PE was added to cellulose ester matrices.
Results and discussion

Figure 25. SEM cross-section images of injection molded cellulose ester blends with PLA and bio-PE (Publication V).

PLA has a very high elastic modulus compared to bio-PE and cellulose C8 and C16 esters (Figure 26). When PLA was blended with cellulose esters, the elastic modulus of the blends decreased linearly as a function of the amount of cellulose ester. Tensile strength values of the PLA blends also showed the same trend, which was expected behavior as the mechanical properties of blends depend on the properties of both components. This trend is common to cellulose-based composites: better interfacial adhesion results in higher strength. PLA droplets were also found in the cellulose ester matrices, which affect the mechanical properties of the blends by decreasing strength values because the droplets act as stress concentrators. The tensile strength and elastic modulus values of bio-PE were also higher than those of cellulose C8 and cellulose C16 esters and, similarly, the mechanical properties were reduced when cellulose esters were compounded with PE.

Both cellulose C8 ester and cellulose C16 ester have significantly higher elongation at break values compared to PLA. However, when cellulose esters were compounded with PLA, the elongation values decreased close to pure PLA values already with a 25 wt% amount of PLA due to weak compatibility. Bio-PE had very high elongation at break, whereas the elongation of the cellulose esters was much lower. However, the elongation of PE at maximum load was the same as that of cellulose C16 ester and much lower than the elongation of cellulose C8 ester. When cellulose esters were compounded with bio-PE, the elongation at break values of PE were significantly reduced in proportion to the added amount of cellulose ester. In the case of elongation at maximum load, even a 75 wt% amount of cellulose C8 ester did not increase the elongation at maximum load of PE. This may be due to the weak interaction between cellulose esters and bio-PE, although this could not be clearly observed in the SEM analysis.
Figure 26. Mechanical properties of injection molded cellulose ester/PLA and cellulose ester/PE blends (Publication V).
5. Conclusions

In this thesis, ozone pretreated pulp is shown be a suitable raw material for preparing long chain cellulose esters. When ozone pretreatment was used, the molar mass of cellulose could be decreased in a controlled manner. The molar mass of the starting pulp was also found to have a significant effect on the DS and properties of long chain cellulose esters. The DS values increased in both homogeneous and heterogeneous processes when the molar mass of the starting pulp decreased and the same reaction conditions were used. Cellulose esters of different side chain lengths (C6-C18) formed transparent, flexible and heat sealable films. Water vapor permeability was found to decrease significantly by increasing the side chain length of the cellulose esters. The water vapor barrier properties of these cellulose ester films were clearly superior to other cellulose-based films such as cellulose acetate, cellophane or CNF films. However, their performance is still far from commercial polyolefins. The mechanical properties of the prepared cellulose ester films were close to polyethylene-based polymers.

CNF films and virgin kraft papers were coated using cellulose esters with different side chain lengths. According to SEM analysis, the cellulose esters formed smooth and homogeneous coatings with good adhesion. These coatings significantly improved the surface smoothness of CNF films by reducing nanoroughness. The cellulose ester coatings also significantly improved the moisture barrier properties of CNF film and kraft paper with WVP decreasing linearly as a function of ester chain length to below 50% of the non-coated WVP value. Also, the resistance of kraft paper against tested nonpolar oil and grease compounds was improved using cellulose ester coatings. The cellulose ester coatings allowed the material to be heat sealable and, in addition, the coatings had no antimicrobial activity, with negligible microbe adherence to the surface of the films.

The prepared long chain cellulose esters were also completely processable without the addition of a plasticizer, which is very unusual in the case of cellulose esters. SEM images showed that materials were uniformly melted and compounded and no large-scale unevenness was observed. Cellulose C8 ester had four times higher elongation than cellulose C16 esters and the values were much higher than those previously reported for shorter side chain length cellulose esters. When cellulose esters were compounded with PLA, some PLA droplets could be observed in the cellulose ester matrix, which indicates that the used compounding time and/or temperature were not sufficient. However, the achieved elongation values of the cellulose esters and cellulose ester/PLA blends were higher than pure PLA.
According to the demonstrated results presented in this thesis, long chain cellulose esters have good potential for a wide range of future applications. Potential demo applications are presented in Figure 27. These 100% bio-based cellulose esters form transparent and clear films with good moisture barrier properties. As a multilayer structure with CNF films, there is good potential to be used for example in bio-based packaging or in printed electronics. Their antimicrobial and grease resistance properties are also optimal for food packaging applications, for example as stand-up pouches. In addition, due to the good processability and mechanical properties of cellulose esters, thermoplastic cellulose materials have very good potential to be used in bio-based plastics applications already in the near future.

Figure 27. Potential future applications for long chain cellulose esters.
Although, these long chain cellulose esters seem to be very promising in several applications, their feasible commercial manufacturing still requires further development. The origin of the raw material is an important factor, but it does not alone ensure the sustainability of the whole value chain. The use of renewable resources instead of fossil-based is an important step in reducing carbon footprint, but also the use of energy efficient reaction methods, “green” chemicals and recyclability of chemicals in production process are as important.

Another point that still requires further investigation is the waste management of these cellulose esters. There are biodegradability tests ongoing for these cellulose esters and according to the preliminary short-term results, these cellulose esters as such seem not to be biodegradable under standard test conditions. This result can be expected due to the fact that even small structural changes to a cellulose molecule may significantly impair the biodegradability. However, according to the unpublished recyclability tests, these cellulose esters can be recycled at least five times without significantly losing their properties. In the future, the material could be recycled either like other plastic products or with a main matrix (e.g. paperboard) in the case of thin film coatings.

From this point of view, the production methods of these long chain cellulose esters presented in this thesis still needs to be optimized and developed. However, the development of these cellulose esters is still proceeding at a rapid pace. The production is no longer on a laboratory scale, but currently cellulose C16 ester has already been produced on a pilot scale. This allows for more extensive application testings (e.g. large scale extrusion film and coating tests) to accelerate the possible commercialization in the near future.
References


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Environmental awareness and growing concern about plastic waste and the depletion of non-renewable resources have boosted interest in bio-based polymers in recent years. Although the fraction of bio-based polymers in the global plastics market is still small, the demand and share of bio-based polymers is rapidly increasing. The aim of this dissertation was to prove that fully bio-based long chain cellulose esters have the potential to replace traditional oil-based plastics in selected applications.