

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

An Investigation of Mixed Cellulose Esters and
Acyclic Polyacetates:
Effects of Side-Chain Lengths and Degrees of
Ring-Opening

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Gothenburg, Sweden 2023

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ISBN 978-91-7905-857-9

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Doktorsavhandlingar vid Chalmers tekniska högskola
Ny serie nr 5323
ISSN0346-718X

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I, Robin Nilsson, hereby certify that this thesis is my original work and, to the best of my knowledge, does not contain any material previously published or written by another person, except where due reference or acknowledgment is made.

Cover: An illustration of a polymer film dropped in water.

Printed by Chalmers Reproservice
Gothenburg, Sweden 2023

“All you have to decide is what to do with
the time that is given to you.”

– Gandalf the Grey

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Abstract

Bio-based polymers produced from natural sources are gaining an increased interest as potential replacement for today's conventional fossil-based plastic polymers. Their use is already wide in many large-scale industrial areas such as healthcare, personal care, and food. To widen the potential of biopolymers in new applications such as plastics, their properties need to be tuned by modification to handle factors like relative humidity, which is especially important for gas barriers in food packaging. This thesis explores the effect of two structural variations of cellulose esters, one where the average side-chain length is increased, going from cellulose acetate to cellulose acetate propionate and then cellulose acetate butyrate, and another where the polymer backbone of cellulose acetate is ring-opened. These two modifications affect the glass transition temperature, an important structural factor. The effect of the average side-chain length is explored to a greater extent where they are studied for impact on mechanical properties, water content, water sorption at different RH, the kinetics of water sorption at different RH, mechanical properties at different RH and oxygen permeation at different RH. The focus is on how water interacts with the different esters with regard to the average side-chain length and how water affects their properties. An increase of average side-chain length and the ring-opening were shown to decrease the glass transition temperature. Together with the water sorption and Hansen solubility parameter, it was concluded that longer average side-chain length screens out hydrogen bonding between the polymers. The studies on the average side-chain length and water sorption indicated that water entering the cellulose acetate creates clusters. These formed water clusters create cavities in the polymer which makes the polymer hold more water than before introducing of the water clusters. Oxygen permeation studies on prewetted films prove that these cavities created by water clustering are still present after drying the material at 0% RH and thus resulted in a higher oxygen permeation compared to films that had not been exposed to higher than 50% RH.

Keywords: *cellulose esters, side-chains, acyclic cellulose acetate, ring-opening, water interactions, water sorption, storage modulus, oxygen permeation*

List of Articles

This thesis is based on the following appended papers:

- I. **Screening of hydrogen bonds in modified cellulose acetates with alkyl chain substitutions,**
Robin Nilsson, Martina Olsson, Gunnar Westman, Aleksandar Matic and Anette Larsson
Carbohydrate Polymers, Volume 285, 2022,119188,
DOI: 10.1016/j.carbpol.2022.119188.
- II. **Experimental and simulated distribution and interaction of water in cellulose acetates with alkyl chain substitution,**
Robin Nilsson, Hüsamettin Deniz Özeren, Okky Putra, Mikael Hedenqvist, Anette Larsson
Carbohydrate Polymers, Volume 306, 2023,120616,
DOI: 10.1016/j.carbpol.2023.120616
- III. **Water sorption kinetics and mechanical properties of cellulose esters,**
Robin Nilsson, Anette Larsson
Manuscript
- IV. **Synthesis and Characterization of Acetylated Dialcohol Cellulose,**
Thanaporn Chaiyupathama, Robin Nilsson Nivedhitha Venkatraman, Hampus Karlsson, Lars Evenäs, Ratchawit Janewithayapun, Jakob Karlsson, Anna Ström, Anette Larsson
Manuscript

Contribution Report

My authorship contributions to this thesis are as follows:

- I. Main author. Planned and performed the experimental work, except for the wide-angle X-ray scattering (WAXS) experiments, which were performed by Martina Olsson. Analyzed and interpreted the results in collaboration with the co-authors. Wrote the original manuscript draft and reviewed and edited the article with support from Anette Larsson and the other co-authors.
- II. Main author. Planned the experimental work and wrote the original draft. Hüsamettin Deniz Özeren performed the molecular dynamics simulations and helped interpret these data. Okky Putra performed dynamic vapor sorption measurements. Analyzed and interpreted the results in collaboration with the co-authors. Revision and editing were done with support from the co-authors.
- III. Main author. Planned the experimental work and wrote the original draft. Performed dynamic vapor sorption measurements. Tijana Todorovic performed the M_w measurements. Analyzed and interpreted the results in collaboration with the co-authors.
- IV. Co-author. Performed and planned experimental work with an MSc student under my supervision. Performed acetylation synthesis and postprocessing. Wrote parts of the manuscript and analyzed the results with co-authors. Nivedhitha Venkatraman performed FTIR, DMA, TGA, and DSC. NMR measurement performed by Hampus Karlsson. WAXS performed by Ratchawit Janewithayapun. M_w determination of DALC performed by Jakob Karlsson.

Additionally, this thesis contains unpublished data that were not included in the above-mentioned manuscripts. Following the figure captions, the credits have been referenced.

Publications Not Included in This Thesis

- I. **Influence of Drug Load on the Printability and Solid-State Properties of 3D-Printed Naproxen-Based Amorphous Solid Dispersion,**
Eric Kissi, Robin Nilsson, Liebert Parreiras Nogueira, Anette Larsson, Ingunn Tho, Julian Quodbach
Molecules 26(15):4492, 2021, DOI: 10.3390/molecules26154492
- II. **Mass Transport of Lignin in Confined Pores,**
Roujin Ghaffari, Henrik Almqvist, Robin Nilsson, Gunnar Lidén and Anette Larsson
Polymers 14(10):1993, 2022, DOI: 10.3390/polym14101993
- III. **Morphological analysis of phase separated polymer blends in amorphous solid dispersions for controlled drug release,**
Martina Olsson, Robin Nilsson, Linnea Björn, Ana Diaz, Mirko Holler, Benjamin Watts, Anette Larsson, Polina Naidjonoka, Leonard Krupnik, Yang Chen, Agnieszka Ziolkowska, Marianne Liebi, Aleksandar Matic
Manuscript
- IV. **Molecular Dynamics Simulations of Cellulose and Dialcohol Cellulose in Dry and Moist Conditions,**
Patric Elf, Hüsamettin Deniz Özeren, Per A. Larsson, Anette Larsson, Lars Wågberg, Robin Nilsson, Thanaphon Chaiyupatham, Mikael S. Hedenqvist, Fritjof Nilsson
Manuscript
- V. **Alkyl ketene dimer modification of thermomechanical pulp 2 promotes processability with polypropylene,**
Alkyl ketene dimer modification of thermomechanical pulp to promote processability with polypropylene
Seyedehsan Hosseini, Robin Nilsson, Anna Ström, Anette Larsson, Gunnar Westman
Manuscript

Abbreviations

ADALC	Acetylated dialcohol cellulose
AGU	1,4-anhydro-D-glucose units
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
DAC	Dialdehyde cellulose
DALC	Dialcohol cellulose
DMA	Dynamic mechanical analysis
DO	Degree of oxidation
DSC	Differential scanning calorimetry
DVS	Dynamic vapor sorption
HSP	Hansen solubility parameters
NMR	Nuclear magnetic resonance spectroscopy
PEK	Parallel exponential kinetics
RH	Relative humidity
SEC	Size exclusion chromatography
TGA	Thermal gravimetric analysis
UV-Vis	Ultraviolet-visible spectroscopy
WAXS	Wide-angle X-ray scattering
XRD	X-ray diffraction

Symbols

ΔH_f	Enthalpy of fusion
ΔM_i	The change in moisture content i
C	Concentration
$C_a(t)$	Concentration on the acceptor side at time t
$C_{d,0}$	Concentration on the donor side at time 0
D	Diffusion coefficient
DOH	Degree of hydroxyl groups
DS _A	Degree of substitution of acetyl
DS _B	Degree of substitution of butyryl
DS _P	Degree of substitution of propionyl
DS _{tot}	The total degree of substitution
E'	Storage modulus
E''	Loss modulus
E_d	Dispersive cohesive energy
E_h	Hydrogen bonding energy
E_p	Polar cohesive energy
E_{tot}	Total cohesive energy
F	The rate of transfer per unit area of a section
h	Thickness
$M(t)$	Change in moisture content
M_0	The moisture content at time 0
M_w	Weight average molecular weight
P	Permeability
R_a	Distance between two materials' HSPs
T	Temperature
T_2O	Tritiated water
T_d	Degradation temperature
T_g	Glass transition temperature
$T_{g,mix}$	The glass transition temperature of a mixture
T_m	Melt temperature
V	The volume of the acceptor and donor chamber
V_{molar}	Molar volume
w	weight fraction
δ_d	Dispersive parameter
δ_h	Hydrogen bonding parameter
δ_p	Polar parameter
δ_{tot}	Total Hansen Solubility Parameter
τ	Time constant

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1 | Introduction

One of the significant challenges in our modern time is to achieve a circular economy. With regards to plastics, it means abandoning the production from finite, non-renewable fossil-based resources. The production of these also has a great environmental impact. Instead, one should use renewable bio-based alternatives, which would be able to face the continuing strong demand for plastics. The global plastic production increased from 360 Mt in 2018 to 390 Mt in 2021 [1]. Out of those 390 Mt, only 1.5% were bio-based or bio-attributed plastic, and as much as 44% of the total plastic distribution in 2021 was in packaging. The driving force for renewable plastics is there, which can be seen in an increase of bio-based plastics on the global market, but there is still a long way to go in order to compete with fossil-based plastics [1]. More knowledge is needed in order to tailor renewable bio-based plastics to meet the demands for plastics. One aspect that has gotten a high focus is biodegradation, which is a great property for the usage of plastics in areas like agriculture. On the other hand, in many other areas, biodegradation is not needed where for instance shelf life is essential. When structural integrity is paramount, the ability to make plastics from renewable resources with suitable properties is the key.

1.1. Bio-based Polymers and Water Sensitivity

Renewable sources are natural sources that can regrow, such as trees, annual plants, and animal feedstock. Polymers made from renewable sources are referred to as bio-based¹ polymers, where the most abundant one is cellulose. Cellulose is an example of a biopolymer² that is a good candidate for substituting the high demand for fossil-based polymers in industries, like the plastics packaging industry [2]. Large-scale harvesting of trees for cellulose production as a replacement for fossil-based plastics is appropriate in countries like Sweden, where forests cover more than 70% of the country's surface [3]. 73% of the 28 million hectares of forest is productive, while the others are protected forests. Bio-based polymers can be used for many applications. However, a major disadvantage of cellulose and other bio-based polymers is that many of their properties can be affected by water. This means that applications for these materials where the humidity changes or where they are in direct contact with water are unsuitable [4], [5]. These challenges are found in particular in food packages where the structural integrity and barrier properties, like gas permeance, need to be unaffected by moisture, either present in the package itself or from external factors. Another drawback of bio-based polymers is the processability, which is inferior to many conventional plastics [6], [7]. Both water sensitivity and processability can be addressed by chemically modifying the cellulose. These so-called cellulose derivatives are commonly synthesized by substituting the H in the hydroxyl groups on the cellulose backbone [8]. Many cellulose derivatives currently exist on the market; the most common ones are ethers and esters. Common cellulose ethers include methyl cellulose, ethyl cellulose, hydroxypropyl methylcellulose, and cellulose esters include cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate

¹ IUPAC definition of biobased: "Composed or derived in whole or in part of biological products issued from the biomass (including plant, animal, and marine or forestry materials)." [117]

² IUPAC definition of biopolymer: "Macromolecules (including proteins, nucleic acids and polysaccharides) formed by living organisms". [118]

(CAB), and cellulose acetate phthalate. Cellulose derivatives are used in many areas, such as construction, cosmetics, paints, food, and pharmaceuticals [9]. Chapters 2.1 and 2.2 will dive deeper into cellulose derivatives and cellulose esters.

In order to tailor different types of materials, one can mix bio-based polymers like CA with a plasticizer which can improve the thermal properties, making the chains more flexible and enabling easier processing [10]. A way to increase processability without external plasticizers is chemical oxidation to open up the glucopyranose rings of cellulose [11].

The water sensitivity of bio-based polymers arises because water can interact with their hydroxyl groups by forming strong hydrogen bonding [12]. The presence of water in the materials can act as a strong plasticizer and reduce the glass transition temperature (T_g). In addition, water has itself a T_g of -135°C [13]. In some cases, water can also create stable bridges via hydrogen bonding and cause antiplasticization [14]–[17]. Water has been shown to have a plasticizing effect in relatively hydrophilic polymers like chitosan [18], cellulose [19] and polyvinyl alcohol [20]. It has been discussed by Chen *et al.* that when water enters cellulose, the water breaks the hydrogen bonds between cellulose molecules, creating cellulose-water hydrogen bonding instead [21].

When developing new materials, it is important to be able to predict properties based on the chemical structures. One such tool for polymers is the Hansen Solubility Parameters (HSP) concept, which has mainly been used to investigate the solubility of materials in each other. It has later also been used for other purposes like resin swelling in binary solvents [22] and the dispersibility of crystalline nanocellulose in low-density polyethylene [23]. A study relevant to this thesis was done by Ramanaiah *et al.*, where different CAPs and CABs was studied for temperature induced changes in HSP values [24], [25]. Another study by Ong *et al.* also used HSP to investigate different CAPs and CABs and their influence on salt retention [26].

1.2. Aim and Objective

This thesis aims to provide insights into how specific changes in the chemical structure of cellulose esters alter their properties, how they interact with water, and how water affects their properties. Two different structural changes are investigated, variation of average side chain length and degree of ring-opening. The main study concerns the effect of increased average side-chain length of cellulose acetate with the side groups of acetyl, propionyl, and butyryl. One part of the study includes the effect of different degrees of ring-opening of the cellulose acetate backbone on the thermal properties. The majority of the results focus only on the average side-chain length and goes through water sorption, sorption kinetics, mechanical properties affected by RH, and ends with a permeation study of how water-treatment affects the oxygen permeation of CA at different RH. The main areas of investigation of the thesis can be stated as followed:

- The effect of the average side-chain length on T_g and mechanical properties.
- The effect of the average side-chain length on water sorption and sorption kinetics.

- The effect of the degree of ring-opened cellulose acetate on thermal stability, thermal transitions, and mechanical properties.
- The effect of moisture on CA with regards to oxygen permeation
- The ability of HSP to predict chemical structure-property relationships.

The content of this thesis is based on the content of four studies, the appended Papers I, II, III, and IV. Paper I focuses on how the side-chain length of CA, CAP, and CAB affects their thermal and structural properties, water absorption, and water diffusion. Additionally, it investigates if the value of the materials' HSP can be correlated to their glass transition temperatures, water absorption, and water diffusion. Paper II uses the same materials, studying the sorption isotherms over a wide range of RH (0-80% RH). Paper III investigates the effect of the different side-chains on the sorption kinetics and how the sorption behavior of CA can be directly compared to its mechanical properties at different RH. In Paper IV, acyclic CA is synthesized with three degrees of oxidation, referred to as ADALCI, ADALCII and ADALCIII, and the thermal properties are investigated.

1.3. FibRe VINNOVA Competence Center

This work was financed by FORMAS (2017-00648) and the project is associated to FibRe-Design for Circularity: Lignocellulosic based Thermoplastics (2019-00047) a VINNOVA competence center operating as a research consortium involving Chalmers University of Technology, KTH Royal Institute of Technology, industries, and public organization partners. One of FibRe's vision is "Our vision is a sustainable society where thermoplastic fossil-based plastics are replaced by lignocellulose-based materials". [27]

2 | Bio-based Polymers

There are many different kinds of bio-based polymers, like polymers made from hemicelluloses and lignin, but here we will focus on cellulose and its derivatives. Cellulose, in the form of wood and cotton, has been used for thousands of years as a building material, insulator, and clothing, making a significant historical and modern impact on human society.

2.1. Cellulose and Cellulose Derivatives

Cellulose is a linear homopolymer of 1,4-anhydro-D-glucose units (AGU) linked by β -1,4 glycosidic linkages between carbons C_1 and C_4 . There are two definitions of the cellulose repeating unit, one based on the chemical repeating unit, Figure 1a. The other could be called structural repeating unit with two AGU's are rotated 180° with regard to each other, Figure 1b, which also is referred to as cellobiose. In this thesis, the chemical repeating unit is used in all calculations and discussions. Most modifications to the cellulose are done by replacing the hydroxyl groups with other chemical groups, Figure 1c and 1d, where the examples stated are the substitution focused on in this study, namely acetyl, propionyl, and butyryl. Cellulose itself has been used, and is still used, in many applications, especially its fiber form is used in paper and cardboard. These fibers are manufactured in one of Sweden's largest industrial sectors, the forest industry. The use of cellulose expanded when it was shown that it could be modified to achieve different and new properties. One of the earliest examples is that in 1870 Hyatt Manufacturing Company used nitric acid to modify cellulose into cellulose nitrate, which was used in explosives and plastics [9], [28], [29]. After the successful modifications of cellulose fibers, the interest grew since compared to native fibers the modified celluloses had uses in various technical products. Around 2% of the total cellulose production in 2003 was used for producing regenerated cellulose, which can be synthesis into a large number of different cellulose ethers and esters. In 2022 the market size of regenerated cellulose was 18 billion USD and projected to increase to 27.3 billion USD in 2027 [30], which means that the market is growing and that the starting material for cellulose derivatives is growing.

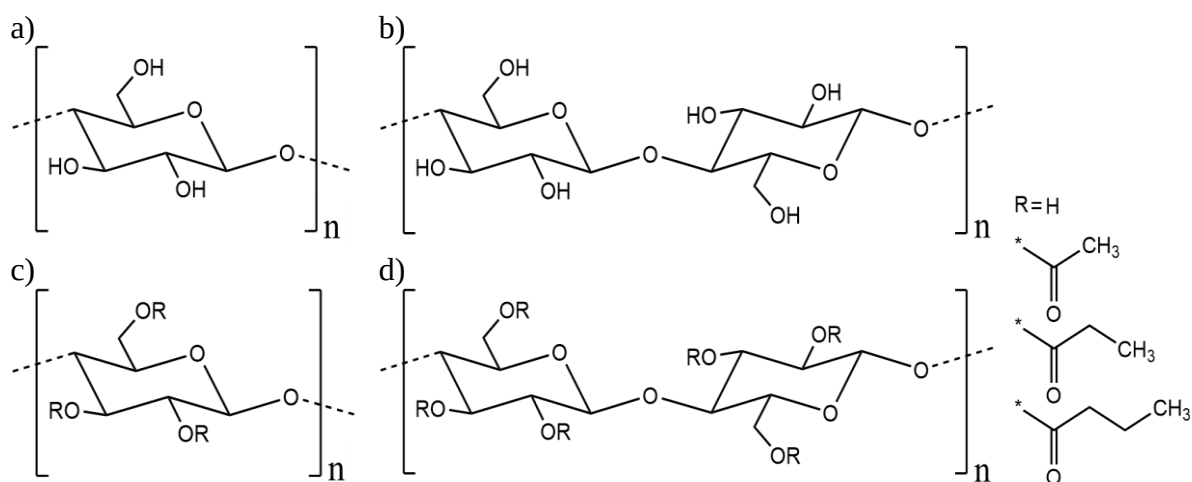


Figure 1. The chemical structure of a) cellulose chemical repeating unit and b) cellobiose. c) and d) show the substituted version of a) and b) where R is either a hydrogen, acetyl, propionyl or butyryl group. cellulose derivative repeating unit where R is either a hydroxyl, acetyl, propionyl, or butyrate group.

2.2. Cellulose Esters

The interest in cellulose esters has increased over the years, Figure 2, with the highest interest during the last 20 years. The simplest ester, cellulose acetate, was discovered in the late 19th century by mixing cellulose with acetic anhydride. The early years were challenging as the production needed specially cleaned cotton, but still patents for photographic film and artificial silk were made. Low substituted CA was found to be soluble in common solvents like acetone and chloroform [31], which enabled the application as a coating for airplanes and the demand grew strongly during the first world war [32]. For some time thereafter, CA was also spun into fiber, cellulose diacetate³ yarn, with new fiber spinning techniques [33], but was phased out by polyester and nylon. A new use as filters in cigarettes increased the popularity of CA, and by 2014 as much as 80% of all the world's cigarette filters contained CA [34]. The global market for CA 2016 was 614 kt [34], where many of the applications use plasticizers or mixed esters to enable injection molding, which enables the production of items like tool handles and toys. CA is also rupturing and splicing resistant, making it a preferred material for photographic film, motion film, but also as security glass in automobiles.

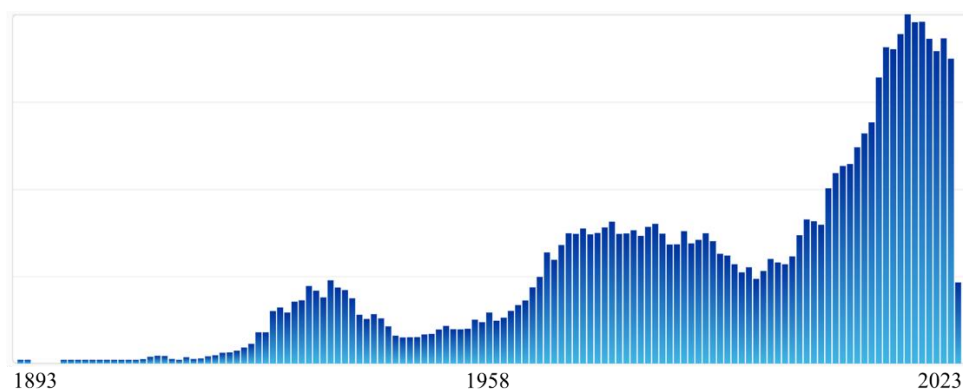


Figure 2. Publications per year on the search “cellulose acetate” according to Scifinder March 2023 [35]

In the literature, the term 'mixed esters' refers to cases where more than one type of side-chain is present as a substituent. For example, a combination of acetyl and propionyl is referred to as CAP, while a combination of acetyl and butyrate is referred to as CAB. They are both commercially available [36], and their ability to dissolve easier than CA favors their usage in many applications. With its toughness, weather resistance, flexibility, and color retention, CAB makes an excellent binder for decorative and protective coatings on human nails, plastic, paper, leather, cars, and other vehicles. CAP is used instead of CAB, when low odor is needed. For example, it can be mixed with plasticizers to make toothbrushes [34]. Cellulose mixed esters have also gained interest in water purification due to their water flux and salt retention, which both can be adjusted by varying the fraction of substituted acetyl, propionyl, or butyryl [26], [37].

³ In literature it is distinguished between cellulose diacetate and cellulose triacetate where diacetate means a DS of 2 and triacetate a DS of 3. In this thesis we use CA to represent cellulose acetate for the full acetylation range.

In the pharmaceutical field, particular CAB has shown to be a promising candidate due to its encapsulation efficiency and its easy processing method, enabling its use in drug delivery systems, medical implants, bone regeneration membranes, and transdermal patches [38]–[40]. In most of these applications, CAB is mixed with biocompatible polymers or plasticizers [39], [41], [42].

2.3 Dialcohol Cellulose and its Acetylation

In recent years, periodate oxidation has gained interest in modifying polysaccharides for material focus after historically mainly being used as an analytical tool for structural characterization [43], [44]. The material produced in this thesis is dialcohol cellulose (DALC), where the modification starts with periodate oxidation of cellulose into dialdehyde cellulose (DAC). This opens the cellulose backbone C₂-C₃ bond in the glucose units of the cellulose polymer, where the principle is viewed in Figure 3. Observe that in reality the ring-opening is not performed in an orderly fashion. The dialdehyde groups are then treated with borohydride to reduce the aldehyde groups into hydroxyl groups, resulting in the structure of dialcohol cellulose, also called acyclic polyalcohol in other studies [45]–[47].

The ring-opening of DALC makes the polymer highly flexible, which enables the possibility of melt-processing [48]–[50]. This can be attributed to the decrease in thermal transitions, where it has been shown that the T_g changes from 160°C to 75°C when the degree of oxidation (DO) increases from 24 to 91% [47]. It has been shown that DALC also exhibits high strain at break and high tensile strength [49].

The potential of DALC is limited due to its moisture sensitivity, where it has been shown to dissolve above 40% DO [47], and thus limiting its applications in areas such as packaging [51]. The manufacturing process of DALC on an industrial scale has been discussed in a review by Nypelö *et al.*, where challenges are stated, especially the need for recycling steps to make the process viable [52]. In order to improve processability, further modification could be done, like replacing the hydroxyl groups with acetyl groups, creating acetylated dialcohol cellulose ADALC. Acetylation of DALC has been performed before by using the conventional acetylation method using acetic anhydride and pyridine [46], [53]. Casu *et al.* showed that 100% acetylated DALC, ADALC could be precipitated in water but was soluble in warm acetone and acetonitrile. Maekawa made a range of ADALC with DO values of 50, 70, 100% and focused on the ability of NMR characterization, which showed to be able to determine the DO and distinguish between DALC and ADALC. Due to the limited number of reports on ADALC, it is an interesting material that may have desirable properties and could serve as a suitable candidate for comparing the effects of acetylation.

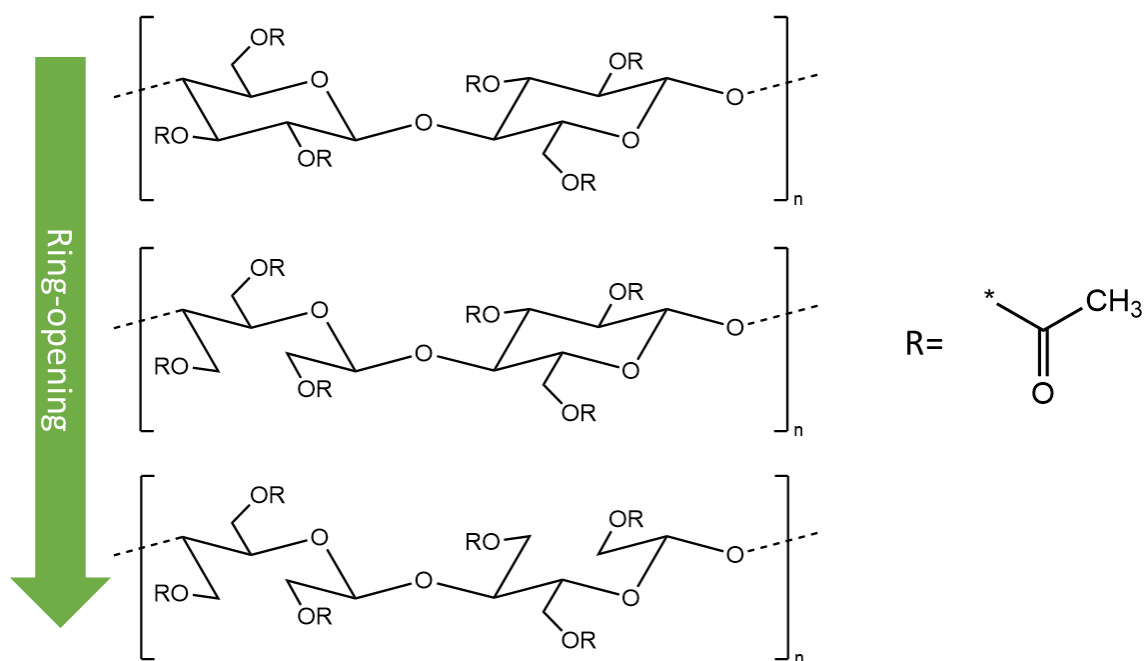


Figure 3. Illustration of different degrees of ring-opening of CA. Observe that the ring-opening performed in the synthesis is not in an orderly manner and is not repeated in a predictable way, this figure simply demonstrated the principle.

3 | Thermal and Mechanical Characterization

Cellulose and its derivatives are naturally semi-crystalline and a unit cell for cellulose of the crystal lattice was proposed in 1928 by Meyer and Mark [54]. A unit cell is “The smallest, regularly repeating material portion contained in a parallelepiped from which a crystal is formed by parallel displacements in three dimensions.” [55]. The crystallinity of cellulose was already suggested in 1858 by Carl von Nageli and later proven by Meyer and Misch in 1937 [56]. Semi-crystallinity means that they have coexisting amorphous and crystalline phases. Assuming dual phases, the IUPAC definition of the degree of crystallinity is “The fractional amount of crystallinity in the polymer sample” [55]. It can be expressed by the volume of the crystalline phase over the total volume. It shall be stressed that crystallinity for cellulose does not have the same distinct uniformity, identical parallelepiped, as there are for inorganic crystals. For crystalline cellulose, or highly organized cellulose fragments, there are slight variations in the distances, which shows up as broader signals in the XRD spectra, compared to the XRD spectra for inorganic materials. However, it is very well accepted in the cellulose community to call it crystalline and amorphous regions. The amorphous and crystalline regions are directly related to a material’s thermal properties. When a molten material is cooled down, a fully crystalline material will only undergo crystallization, while a fully amorphous material are translated to a glassy state, according to Figure 4 [57]. When a molten polymer translates to a glassy state, a stepwise change in the differential heat flow occurs, which is a second-order transition, and the midpoint is by Gedde *et al.* referred to as the glass transition temperature, T_g [57], [58]. During the transition from a glassy to a rubbery state, the mobility of the polymer increases on a long-range segmental scale which is affected by any structural change, such as the backbone and pendant groups [59], [60]. The T_g of the polymer relative to its environment of use is very important. For instance, a rubber with a low T_g is prone to break when the temperatures go below it, because it then becomes stiff and brittle [57]. Similarly, amorphous polymers, at higher temperatures than their T_g , may become too soft for some applications. Due to this, the T_g is a very important parameters to consider when developing polymer for a specific application [61]. The T_g of a polymer is affected by a number of factors: crystallinity, thermal history, symmetry, pendant group mobility and backbone mobility [62]. If one adds pendant groups to a polymer, the T_g is affected differently depending on, for instance, these groups sizes and flexibilities [61]. In this thesis the acetyl, propionyl and butyryl groups are pendant groups. Chain stiffness can also be increased with more rigid and longer groups, such as introducing para-phenyl rings into the backbone or the addition of more bulky pendant groups. For polystyrene, i.e., addition of bulky side-chains, increases the rotation potential-energy barrier, which increases T_g significantly.

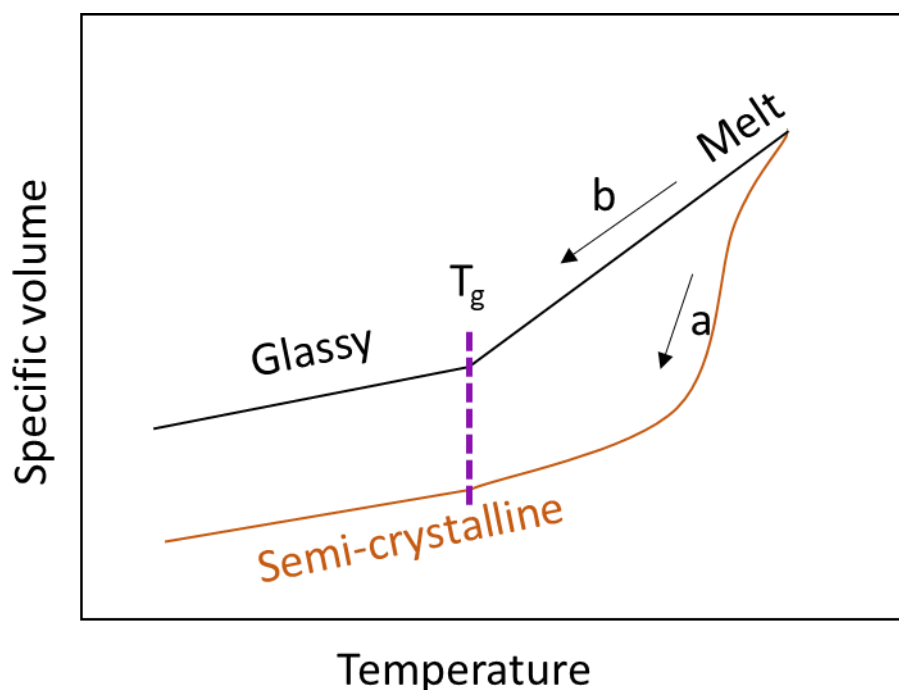


Figure 4. Cooling of a polymer in liquid state by route a) crystallisation or b) forming a glassy state. A T_g is shown in both. Image inspired by Gedde et al. [57]

A purely amorphous polymer has only a T_g , while semi-crystalline material, has both amorphous and crystalline regions, yielding both a T_g and a melt temperature T_m [63]. Examples of semicrystalline polymers are polypropylene and polyethylene. Cellulose is also semi-crystalline, but it has only a T_g in practice since its theoretical melt temperature is above its degradation temperature [64]. Modifying cellulose into CA, CAP, or CAB with a high degree of substitution (DS) brings the T_m down, resulting in a T_m below degradation temperature. Modification (esterification) of the cellulose polymer reduce the inherent intra- and inter-molecular hydrogen bond network of cellulose and consequently the hierarchical structure of cellulose is broken down into a less organized structure, where the cellulose backbones are separated from each other. For instance, CA with DS of 1.75 melts at 245 °C and DS of 2.45 melts at 233 °C [65]. With longer side-chains as for CAP and CAB, the transitions occur at even lower temperatures [66].

Thermal properties are commonly adjusted by, for instance, the addition of plasticizer, which enables easier processability by decreasing the interactions between the polymers. The IUPAC definition for a plasticizer is “a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility” [67]. Plasticizers have different functions depending on the application of the material, for instance in coatings they can give flexibility but also shock resistance or different tactile texture [68], but here we focus on the increased flexibility. Plasticizers are generally used to enhance properties, but there are also cases where undesired plasticization happens. One of the biggest issues for bio-based polymers is water sensitivity, as discussed in Chapter 1.1, where water can act as a plasticizer [69]. Water’s ability to interact with and disrupt hydrogen bonding within a material can greatly impact the internal cohesive energy, and thus also on the T_g , especially in the case of cellulose [68].

The effect of plasticizers on the T_g can be predicted for polymers by several approaches. The simplest is the Fox equation:

$$\frac{1}{T_{gmix}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where w_1 and w_2 are the weight fraction of polymer 1 and 2 in the mixture, similar manner for the T_g as T_{g1} and T_{g2} . The equation assumes that the mixing is random with regards to the two components, meaning that a 50:50 blend gives a T_g of the mean value of the two material's T_g . Another simple model is the Gordon-Taylor equation which is shown in Equation 2 [70], [71]:

$$T_{g,mix} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (2)$$

$$k = \frac{\rho_1 T_{g1}}{\rho_2 T_{g2}} \quad (3)$$

where the variables are the same as for Fox equation, w_1 and w_2 are the weight fraction of polymer 1 and 2, k is defined in equation 3 where ρ_1 and ρ_2 are the densities of components 1 and 2, respectively. Gordon-Taylor equation, similar to the Fox equation, assumes a random mixing. It also assumes ideal solutions, which means that the system allows but the potential energy for interactions between 1-2 should be the average value of those for interactions between 1-1 and 2-2 [58]. Water has been estimated to have a T_g equal to -135°C [13], which, when mixed with polymers according to equation 2 and 3 would greatly impact the blended material's T_g . Equation 2 was intended for mixtures of co-polymers, but has also been used with regard to water in various materials such as poly(lactide-co-glycolide) [69] and poly(vinyl alcohol) [72], and found to match experimental data at low water content. The reason for deviation at higher water contents has been claimed to be due to the formation of binary systems, which in the context of water is water clustering [69].

4 | Water Sorption and Sorption Kinetics

In this thesis, the word sorption will be used for uptake of water, meaning it is the overall uptake of water with no distinction between water surface sorption, commonly called adsorption, and bulk sorption, commonly called absorption.

Since the normal humidity in the air usually ranges from 30-50%, many everyday products are likely to be exposed to water. The water sensitivity of cellulose can easily be observed in newspapers or paper bags outdoors, getting wet and breaking into pieces over time. These are examples of materials with low water resistance, which can be defined as “resistance to the adverse or damaging effects of water” [73]. Water resistance is an important factor in areas like packaging, where properties need to be constant, regardless the humidity [74]. As mentioned in the previous chapter, water has a plasticizing effect on bio-based polymers because of their ability to undergo water sorption, and plasticizing deteriorates the mechanical properties of the materials. However, polymers with less water sorption, i.e. polymers that experience lower plasticizing effect, are more water resistant [75]. One such example is the common polypropylene, which has been shown to only have a small decrease in structural integrity when water is absorbed [76]. In more water-sensitive polymers like cellulose, water is known to absorb and exists in three different forms that interact differently with the materials [77]. Water interacting strongly with the materials is called non-freezing water because it cannot be observed to freeze. Water interacting less strongly with the materials freezes at a lower temperature than bulk water, and lastly, water in pockets does not interact directly with the materials, which is called free water and behaves as bulk water.

How large the water sorption of polymers is depending on the polymer properties and the water vapor pressure, which is connected to the relative humidity (RH). The RH is the ratio between the water vapor actually present in the air and the maximum concentration of water vapor possible at a given temperature [78].

A common investigation of the ability of the material to take up water is to expose them to several RHs and determine the weight of water in the structure at each RH and/or the weight change over time. The response to these conditions on the weight of water in the structure can act as a fingerprint, each material having its unique pattern. In the 1940s Brunauer *et al.* defined five different types of vapor sorption behaviors, also referred to as vapor sorption isotherms, as the investigations are performed at a fixed temperature but with changes of the RH [79]. Figure 5 shows the isotherms classified by Brunauer *et al.*, where different types of materials or material structures have different behaviours. For example, Type II is observed for nitrogen on silica gel and Type V happens for water vapor on charcoal. As can be observed in the figure, Type I is convex upward, Type II an S shape with one inflection point, Type III concave upward, and Type IV has two inflection points. Type V is similar to Type II in having a single inflection point but differs in that it exhibits a gradual increase at the beginning followed by a steep rise and a subsequent gradual increase. In contrast, Type II displays a steep increase at the end.

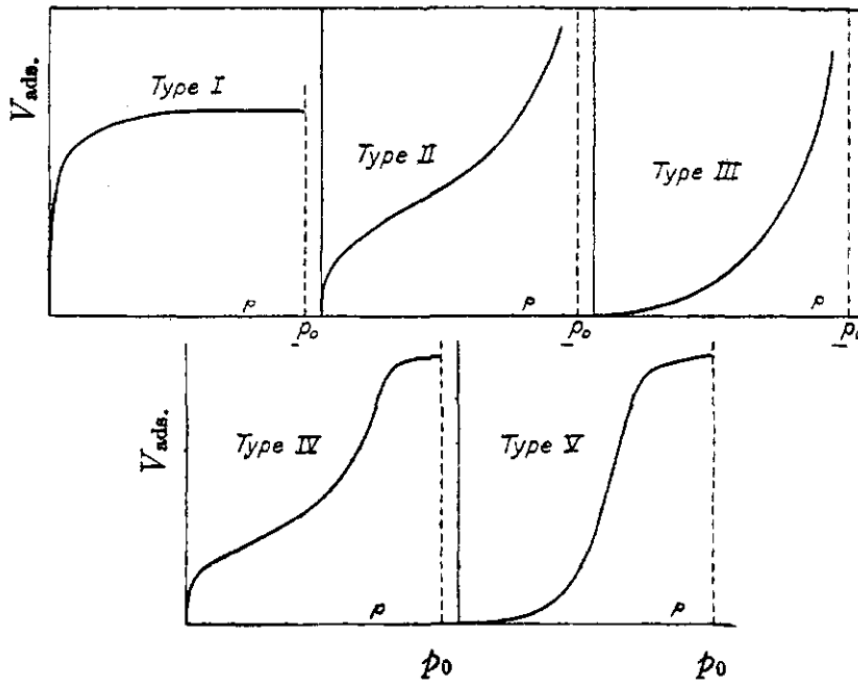


Figure 5. The five sorption isotherms by Brunauer. Volume of sorbed species, V_{ads} versus vapor pressure of the same species p_0 [79], Permission for figure is granted by RightsLink.

Many hydrophilic materials, like cellulose acetate, exhibit a Type II isotherm with regards to water sorption [80], [81]. The behavior of Type II has been explained by a multilayer sorption of water [82].

In studies of water sorption (i.e., increasing relative humidity) followed by desorption (i.e., decreasing relative humidity), it is often observed that the water content during desorption is greater than the corresponding sorption. This difference in water content for sorption and desorption is called hysteresis, and many theories have been proposed to explain it, like induced phase changes or irreversible changes of the structure [83]. For glassy polymers, this has also been explained by the creation of micro-voids in the polymer matrix when the RH increases, which during a decrease in RH collapses at a slower rate and thus results in higher water content than when RH increases for the corresponding RH step. A slow matrix response due to high T_g explains the slow collapse of micro-voids during desorption. [84]. A recent molecular dynamic study by Chen *et al.* on nanoporous cellulose shows that hysteresis originates from different hydrogen bonding networks. They show that cellulose-cellulose hydrogen bonding networks break with increased water content while cellulose-water hydrogen bonding increases, whereas during desorption at the same RH the cellulose-water hydrogen bonding does not break to the same extent [21].

Sorption isotherms, as stated, show the water uptake at equilibrium at each RH condition. In each of these RH steps, the water sorption can be observed dynamically over time, referred to as sorption kinetics. How water is sorbed into a structure over time at a specific condition gives information about the water-structure interactions. Small molecules can diffuse through a material and be described by Fick's diffusion equation in one dimension, Equation 3:

$$F = -D \frac{\partial C}{\partial x} \quad (3)$$

where F is the rate of transfer per unit area of a section, which depends on the diffusion coefficient D , the concentration of the diffusing substance C and the space coordinate x in one dimension [85]. This diffusion model assumes ideal transport without any interaction between the diffusant and the matrix, nor any other interferences. One such interference is if the matrix experience structural relaxation as a result of the presence of diffusant, then referred to non-Fickian diffusion, which is often the case for amorphous polymers below their T_g , [86], [87]. A study on regenerated cellulose by Newns *et al.* showed that the sorption kinetics of water followed a two-stage process, where the deviation from Fickian diffusion arises from chain relaxation due to plasticization by water [88]. Non-Fickian sorption can be described by Equation 4, where the sorbed water in mass at time t ($MC(t)$) can be described by the moisture content at time 0 (MC_0) and a sum of exponentials [89], [90]:

$$MC(t) = MC_0 + \sum_{i=1}^n \Delta MC_i (1 - e^{-t/\tau_i}) \quad (4)$$

where ΔMC_i is the change in moisture content i , and τ_i is the time constant associated with the i^{th} moisture component. A commonly used version of this equation is when i is assumed to be equal to two, also called the parallel exponential kinetics (PEK) model, first used by Kohler *et al.* [89], [90]. The model defines the two exponential components, with one fast and one slow kinetic. They showed that the sorption data for scutched flax with different treatments have a good fit to the PEK model over the tested RH range, and they claim the model offers a better understanding of structural differences between different fiber types. The contribution of the slow kinetic component was observed to increase when the RH increased. The PEK model has also been used to successfully fit sorption data of cotton linter and microcrystalline cellulose by Xie *et al.*, who also suggest that sorption data can be related to matrix viscoelasticity [91]. They assigned the two PEK components to the two Kelvin-Voigt elements, consisting of a spring and a dashpot. They reasoned that the water sorption causes swelling of the materials, which causes deformation, and that the deformation kinetics can be related to Kelvin-Voigt elements.

5 | Hansen Solubility Parameters

Polymer dissolution in solvents is important in many fields, and thus, much research has been performed on “how to study” and “how to predict” the solubility of polymers [92]. In 1916 Hildebrand stated that the internal pressure of the solvent governs the solubility of a solute and, later coined the concept of cohesive energy density [93], [94]. The Hildebrand theories say that the behavior of different solvents can be addressed via the square root of the cohesive energy density, δ . Following the development from Hildebrand theories, Hansen developed the concept Hansen solubility parameters (HSP) in his PhD thesis in 1967 [95], where he related the solubility to interactions arising from dispersive energy, polar cohesive energy, and hydrogen bonding energy. He later wrote a comprehensive book called Hansen Solubility Parameters: A User’s Handbook [96]. This theory builds on the assumption that the total cohesive energy of a pure material is made up of an additive contribution from dispersion, polar and hydrogen bonding energy. As described by Equation 5, which shows that the total HSP (δ_{tot}^2) consists of the total cohesive energy (E_{tot}) divided by the molar volume (V_{molar}). The basis of HSP assumes that the E_{tot} can be divided into three types of interaction energies. The dispersive energy (E_d), also called dispersive cohesive energy, arises from nonpolar interactions and is the most general one. The polar cohesive energy (E_p) originates in permanent dipole-dipole interactions, and the hydrogen bonding energy (E_h) arises from stronger permanent polar interactions, meaning hydrogen bonds.

$$\delta_{tot}^2 = \frac{E_{tot}}{V_{molar}} = \frac{E_d + E_p + E_h}{V_{molar}} = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (5)$$

From this, the three HSPs are the dispersion, polar and hydrogen bonding parameters, δ_d , δ_p and δ_h , respectively, and the square root of the HSPs is assumed to correspond to the dispersive, polar, and hydrogen bonding energy density (where the energy density is E_i/V_{tot}). The primary use of Hansen's solubility parameters (HSP) is to predict solubility by comparing the HSP values of different materials in a three-dimensional space representing dispersion, polar, and hydrogen bonding forces. Material 1 and 2 would then each have a coordinate in this three dimensional plane, where the distance between, Ra (Hansen, 2007; Gårdebjer et al., 2016; Elidrissi et al., 2012), them gives an indication of solubility, see equation 6:

$$(Ra)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \quad (6)$$

where 1 and 2 indicate two different materials, for instance a material and a solvent. A good solvent is close to the material and the further away, the probability of the material dissolving decreases.

The three HSPs can be experimentally determined using a series of solvents, as described by Hansen. In this thesis, however, the HSPs are calculated theoretically by a method of Hoftyzer and van Krevelen [93], which uses an additive method where each chemical group has specific dispersive, polar, and hydrogen bonding components. This is a way of calculating the different HSPs by knowing the chemical structure of the material. For more specific details of how the calculations were done for the esters, see Paper I. HSPs for the ADALC were calculated in a similar fashion.

6 | Experimental Procedures

This section presents the main methods used in this study to make it easier for the reader to grasp the method concepts used. The first section covers the film formation of the ester films, meaning CA, CAP and the three CABI CABII and CABIII, since films are analyzed in the majority of the experimental studies. Thereafter, the different main characterization methods are explained: thermal, water absorption, sorption, sorption kinetics, mechanical analysis, and the acetylation of DALC. For further details regarding experimental methods like FTIR, NMR, and HSP, see Paper I and for density measurements, see Paper II. More details about sorption and desorption kinetics, like PEK model, and the kinetical respond of the mechanical parameters determined by dynamic mechanical analysis (DMA), see Paper III. How the DALC was produced, see Paper IV.

6.1 Film Preparation

Processing conditions of materials can greatly impact their properties, for instance their water permeability [98] and melt temperature [99]. Films for analysis are commonly produced by two methods; In the first method, the solvent casting method, the materials are dissolved in a solution, which then is evaporated in a controlled manner until all solvent is gone and a film is achieved. The second method is melt processing, where the material is melted and pressed into a desired thickness and shape. Solvent casting is very common in research where the polymer is soluble, especially for CA, CAP and CAB, which often are solvent casted using acetone or N-methylpyrrolidone [80], [100], [101]. This study chose melt processing due to many benefits over solvent casting, such as being faster, enabling thicker films, improved uniformity and no risk of layering or trapped solvent [102].

Different films were made for different analyses. Thin films of 0.13 ± 0.02 mm was made for water diffusion, and DMA measurements. In water sorption and density measurements, it is better to use more mass in order to get a better signal-noise ratio, thus 0.49 ± 0.02 mm thick films were made. The film-forming process is explained in Figure 6. A hot-melt press was used, which is simply a hydraulic press with two plates that can be heated. In the method, the sample material was sandwiched between two Kapton films with a steel frame of either 0.1- or 0.5-mm thickness, the Kapton film was, in turn, placed between two steel plates. The whole sandwich was placed in the melt-press at a temperature above the melt temperature of each material, for more specific descriptions see Paper I. The press sequence involved first waiting 2 minutes for the material to melt, followed by a breathing process of low to non-pressure, thereafter, the sandwich was pressed at 15 ± 0.5 t four times, and was rotated 90° at each time. The rotational pressing was used to ensure that the thickness was equal across the whole film. The total time in the press varied from 5-7 min, and afterward, it was cooled in at room temperature with 8.9 ± 0.1 kg weight on top. When they were cold enough to touch, the films were cut into suitable shapes for each type of measurement. Trying to hot-melt press different esters showed that a high molecular weight enables the production of films that do not break easily. Specifically, this was observed for CAB with high substitution of butyryl groups and a number average molecular weight of 15 kDa, which could not form continuous films, while for similar degree of substitution but with 30 kDa made it possible.

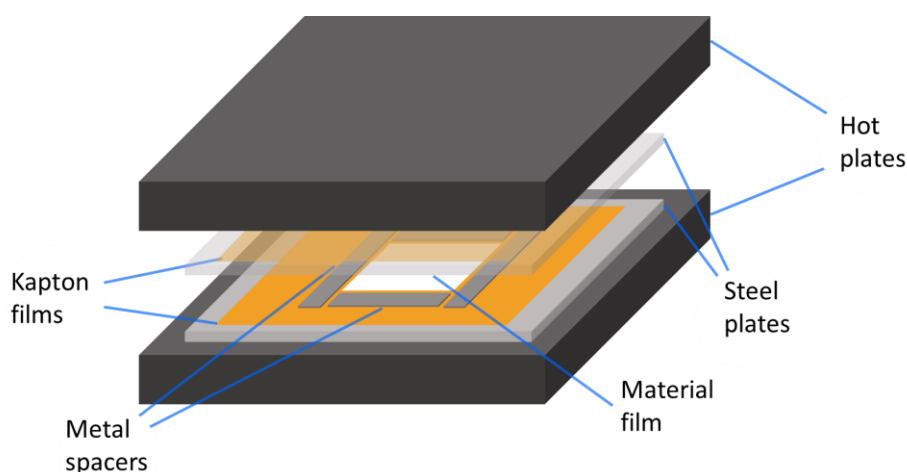


Figure 6. Illustration of the hot-melt pressing sandwich for film production.

6.2 Thermal Characterization

An important parameter in thermal characterization is the degradation temperature, which was determined using a thermal gravimetric analysis (TGA). It was then used as an upper limit in differential scanning calorimetry (DSC), which was the chosen technique for determining the glass transition temperature T_g . The TGA only looks at the weight of the sample, which changes when the sample starts to degrade. As the name implies, the DSC uses calorimetry, which means that it determines the difference in the amount of heat required to increase the temperature of a sample and reference (empty pan) as a function of temperature. The glass transition temperature is a second-order transition, where the material gets a higher energy state with higher mobility above the transition, and this shifts the heat flux to higher values. This can be seen in Figure 7, which shows a typical DSC graph for the materials investigated here. T_g was calculated with the STARE software's midpoint tool, which means the midpoint of a line crossing a tangent line before and after the T_g . The melt temperature, T_m , is identified as the endothermic peak, at which energy goes into the system, increasing the polymer's energy state and mobility, and causing it to melt.

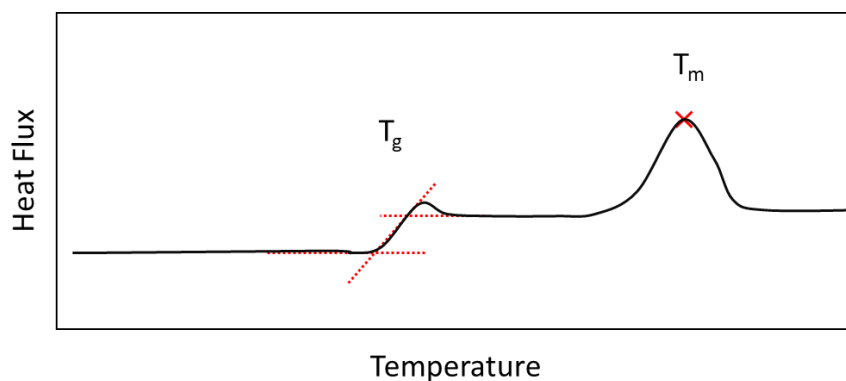


Figure 7. Typical DSC graph with marked T_g and T_m .

6.3 Water Absorption and Water Diffusion

As mentioned in 6.1, 0.5 mm films were produced for water submersion tests for each material. They were dried in an oven for 24 h at 60 °C before the experiment. The films were then submerged in water baths with controlled stirring of 25 rpm for 72 h, see Figure 8. The weights of the films were measured over time in order to be sure of when the maximum weight of water uptake was reached, and also the dimensions were noted for density data.

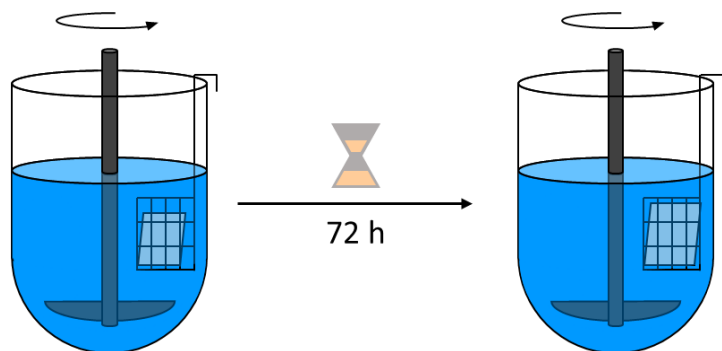


Figure 8. Illustration of water submersion measurements. Note that the increase in the size of the film is for illustration only, in reality there is no visible swelling.

Water diffusion was done by using tritiated water, T_2O , as a tracer and thin 0.1 mm films of each ester. This included two 20 mL chambers with water clamped together and separated by the film of interest, see Figure 9, where T_2O water was added on one side, called the donor side, and the concentration of T_2O was measured over time on the other side of the film, the acceptor side. T_2O was used because its radioactivity makes it easily detectable, and the transport of it over a film can be quantified. This was done by measuring the radioactivity with a PerkinElmer Tri-Carb 2810 TR liquid scintillation analyzer.

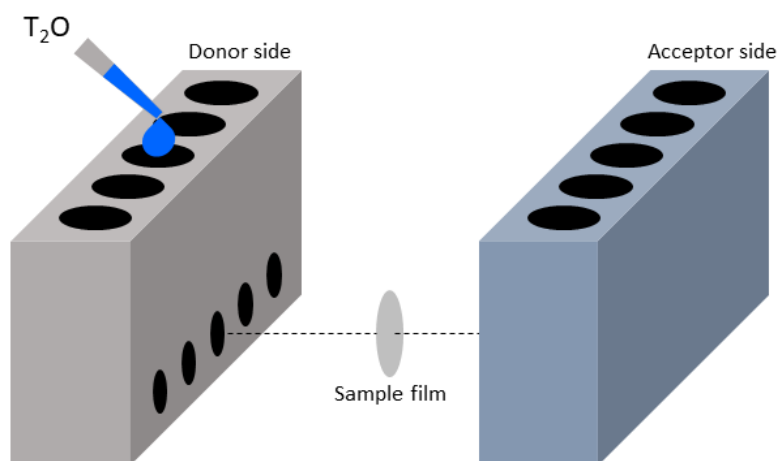


Figure 9. Illustration of the T_2O diffusion chambers. Five films can be measured simultaneously per diffusion chamber set.

The concentration of T_2O acquired from the scintillation analyzer can be used for calculating the permeability, P ($m^2 s^{-1}$), using Equation 7 developed by van den Mooter *et al.* [103]–[105],

$$\frac{2PA}{hV}t = -\ln\left(\frac{C_{d,0} - 2C_a(t)}{C_{d,0}}\right) \quad (7)$$

where h (m) is the thickness of the film, V (m³) is the total volume of the acceptor chamber, t (s) is the time, $C_{d,0}$ (mol m⁻³) is the concentration on the donor side at time 0, and $C_a(t)$ (mol m⁻³) is the concentration on the acceptor side at time t . After rearrangement of eq. 7, P can be calculated. The equation assumes that the chemical potential depends on concentration, no time-dependence on the concentration profile, neglectable stagnant layers in the film, that it is an ideal system, and that the volumes on each side of the film are equal.

6.4 Water Sorption and Water Sorption Kinetics

Water sorption isotherms were achieved by using a dynamic vapor sorption (DVS) instrument. This is an instrument developed by Surface Measurement Systems and can be used to study of the water sorption of materials at different humidities and phasing out the previous popular method of using closed containers with different saturated salts in order to achieve different RH. The basic setup, see Figure 10a, includes a scale holding two measuring baskets, one for the sample and the other for reference [106]. The benefits of the instrument are that only a small amount of a few mg of sample is needed and that it high mass change resolution of 1 part in 10 million, and that it is fully automated and thus can expose the sample to a wide range of combinations of RH and temperatures. Each RH step in the series, see Figure 10b, is held until a steady-state criteria are reached, which in the studies included in this thesis was set to <0.002% min⁻¹ over a 30-min period. The steady-state values for sorption and desorption were used for the hysteresis analysis.

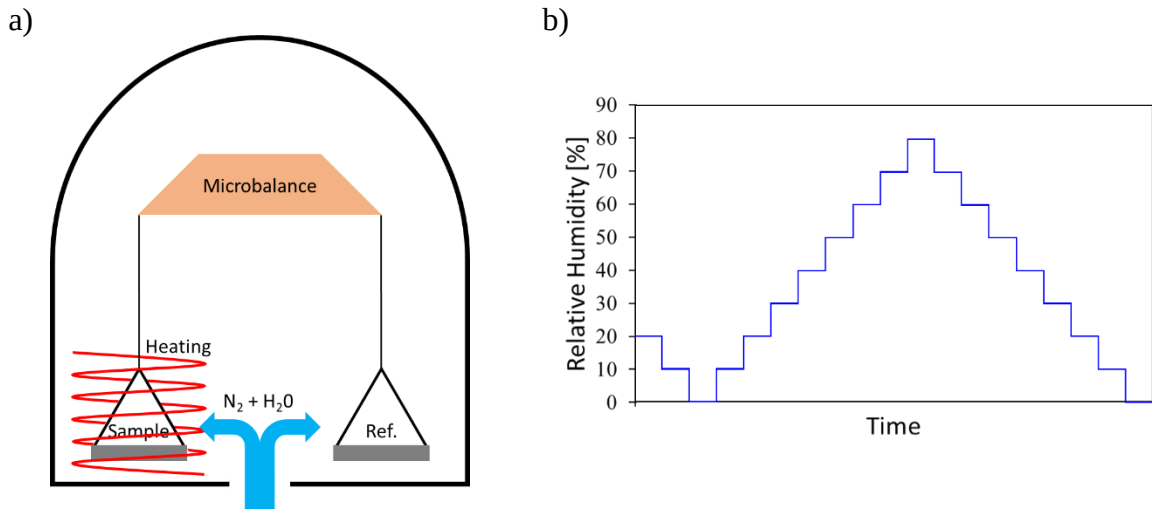


Figure 10. a) the DVS setup principles, b) the used the RH sequence method.

To conduct the water sorption kinetic study, the weight change over time was measured at each RH step before reaching a steady-state condition. The sorption data for each material at each RH step were then fitted to the PEK model using the inbuilt MATLAB[®] curve fitting function “fit” according to Equation 8:

$$MC(t) = a + b(1 - e^{-t/\tau_1}) + c(1 - e^{-t/\tau_2}) \quad (8)$$

where a is the curve intercept with the y-axis, b and c are the contribution coefficient for each exponential term, t is time and τ_1 and τ_2 are the half-time constants of exponent 1 and 2, respectively. As a comparison, a one-exponential model was used, meaning $i=1$ in Equation 4, seen below as Equation 9:

$$MC(t) = a + b(1 - e^{-t/\tau_1}) \quad (9)$$

6.5 DMA measurements at RH

Mechanical analysis for the different esters was done on 0.1 mm films on a dynamic mechanical analysis (DMA) instrument with a tension clamp and an RH accessory. The measurement is done by clamping a film between one stationary holder and one dynamic holder, which deforms the sample at a certain oscillation frequency and strain, Figure 10a. For the esters, the stress-strain properties were investigated over time of exposure to a range of different RH in the linear region of their stress-strain relation. The data obtained were focused on the storage modulus, loss modulus and tan delta [107]. The storage modulus is also called the elastic modulus, and the loss modulus is called the viscous modulus. The two components can easily be understood by the “bouncing ball example”: a bouncing ball is dropped from a certain height, corresponding to an energy state, the ball bounces off the ground and reaches a lower height than before, the storage modulus corresponds to the new height or elastic response (storage modulus E'), and the loss in height, compared to the initial height, corresponds to the energy loss (loss modulus E''). The ratio between E'' and E' is called tan delta. The esters were measured, and their E' , E'' and tan delta were recorded over the range of two different RH methods, one that matched the DVS method by stepping from 0 to 80% RH and down again, see Figure 10b. A second method was developed to look more into details around the RH equal to 60%. The RH in the first cycle first stepped up to 50% and down to 0%, then in the second and third cycles stepped up to 60% and 70%, respectively, see Figure 10b. More details will be covered in the results section.

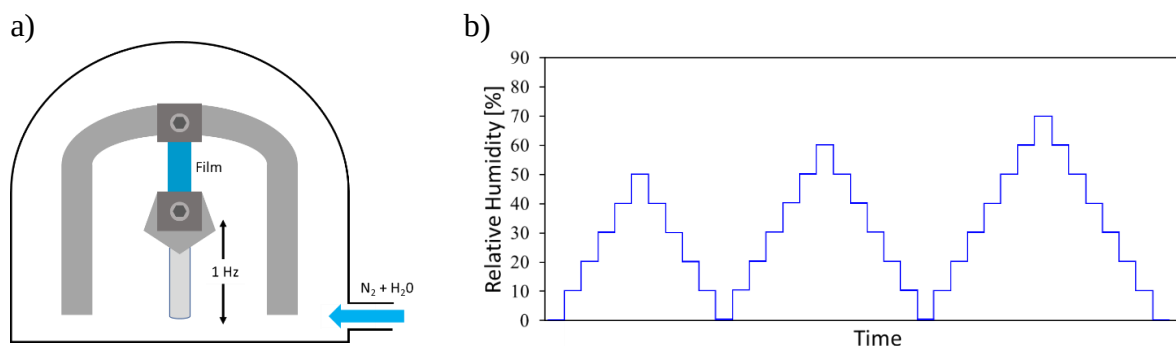


Figure 10. a) Sample tension setup in the DMA instrument and b) RH sequence for the RH 50-60-70 stepping series.

6.6 Acetylation of Dialcohol Cellulose

DAC was prepared from microcrystalline cellulose, specifically Avicel PH101, for more specifications, see Paper IV. Acetylation can be performed in a number of different ways, and

in this project, a method by Ragab *et al.* was used [108]. Instead of the classical use of acetic acid as solvent, acetic anhydride was used by itself as it is in liquid form, with the catalytic assistance of ferric perchlorate. The 55% DO ADALC was precipitated effectively with water and filtrated, while the other 75 and 100%, albeit also precipitating, proved more challenging to filtrate and instead these samples were dialyzed. The three DO are referred to as ADALCI, ADALCII and ADALCIII, where I, II and III corresponds to an increase in DO.

7 | Results and Discussion

This section compiles the major results from the four studies and discusses the results. First, the materials need to be clarified regarding their chemical structure and the HSPs will be used to compare the different results systematically. Section 7.2 goes through the T_g and how it is affected by both the average side-chain lengths for CA, CAP and CAB, and by different degrees of ring-opening of the CA. For the different average side-chain lengths, the mechanical properties are also investigated. The remaining results focus solely on the average side-chain length and examine its impact on various properties, including mechanical strength, water sorption, sorption kinetics, and mechanical properties under varying humidity levels. In the final part of the study, the oxygen permeation of water-treated samples is also addressed.

7.1 Material and Film Properties

As mentioned in the introduction, this study examines two distinct types of structural modifications: changes in the lengths of the side-chains in CA, CAP, CAB, and alterations in the degree of ring-opening of CA, which is referred to as ADALC. Table 1 shows the properties of the CA, CAP and three different CAB: CABI, CABII and CABIII, which have an increasing ratio of butyryl-acetyl. All five materials have a total DS, DS_{tot} , between 2.41 and 2.85, where CA has the lowest of 2.41, while the others have a DS_{tot} between 2.71 – 2.85. As covered in section 1.1 the hydroxyl groups are very important, and thus the lower DS for CA compared to the others should be kept in mind when comparing the different data. Since both CAP and the different CABS have both respective side-group and acetyl, we will instead refer to them as esters with increased average side-chain length. Later on, the difference in effect on the properties of butyryl compared to propionyl will be discussed. The weight average molecular M_w varies between the materials, with 96.7-307 kDa for CA, CAP, CABI, CABII, and CABIII. Going from CA to CABIII, all HSPs and the total HSP decrease as an effect of adding more of the longer side-chains. The reason for this decrease in HSP is that going from acetyl to propionyl and butyryl. The extra methylene groups ($-CH_2-$) add only to the dispersion parameter and the molar volume, and not to the polar parameter nor the hydrogen bonding parameters. The increased molar volume, even if the polar and hydrogen bonding energies are the same, explains why the polar and hydrogen bonding parameters, δ_p and δ_h , decrease with increased average side-chain length. The dispersion parameter δ_d also decreases because the Hoftyzer and van Krevelen model predicts an increase in molar volume is greater than the increase in dispersion energy.

Table 1. Weight average molecular weight (M_w), polydispersity, degree of substitution (DS), degree of hydroxyl groups (OH) and average molar mass (M) for the esters (CA, CAP, and CAB). Table data from Nilsson *et al.* 2022 [109].

Material	M_w [kDa] ¹	Polydispersity	DS _{tot}	DS _A	DS _P /DS _B ²	DOH	Average M of repeating unit [g/mol]
CA	155	4.27	2.41	2.41	-	0.59	263
CAP	245	6.01	2.85	0.21	2.64	0.15	319
CABI	194	5.10	2.85	2.14	0.71	0.15	302
CABII	307	6.33	2.80	1.12	1.68	0.20	327
CABIII	96.5	4.04	2.71	0.14	2.57	0.29	348

¹ M_w measured with SEC, see Paper III.

² DS_P/DS_B mean degree of propionyl and butyryl, respectively. See Paper I for more information about characterization.

Table 2 HSPs for the esters (CA, CAP, CABI, CABII and CABIII). Table data from Nilsson *et al.* 2022 [109].

Material	δ_d (J cm ⁻³) ^{1/2}	δ_p (J cm ⁻³) ^{1/2}	δ_h (J cm ⁻³) ^{1/2}	δ_{tot} (J cm ⁻³) ^{1/2}
CA	19.0	6.2	14.5	24.7
CAP	18.2	4.5	11.3	21.9
CABI	18.4	5.0	11.9	22.4
CABII	18.2	4.3	11.2	21.8
CABIII	18.1	3.9	10.9	21.5

Weight average molecular weights, degree of oxidation, degree of substitution, and HSPs for the ring-opened CA are displayed in Table 3 and Table 4, respectively. The weight average molecular weight is significantly lower than the esters above, while it only decreases slightly from ADALCI to ADALCIII. This decrease arises from the increased oxidation time. The DO was determined with two methods, NMR and UV-Vis, where NMR gives slightly lower DO than UV-Vis. UV-Vis measured how much periodate remains, which means that it is an indirect method to determine DO and therefore could give an overestimation. The risk with UV-Vis to determine DO has been thoroughly discussed by Leguy *et al.* [110].

For NMR, it is the opposite, the signal is from the ppm range where methyl group hydrogen of the acetyl is compared to the signal of the range where the backbone hydrogen usually is located. The results gave a DS_A above 3 for all ADALCI-III, which is impossible for an ideal system with CA since there are only 3 possible sites for substitution, position 2,3 and 6 in the cellulose structure. The high DS_A arises from either the proton signals from the backbone in the NMR being too low, or the proton signal from acetyl groups being too high. One effect to the latter could be that the repeating unit of ADALC has a molecular weight of 288-290 g mol⁻¹ and a weight average molecular weight of 2.86-4.75 kDa, which means that the average number of repeating units is around 12 for ADALCIII and 16 for ADALCII. This means that due to the low number of repeating units the acetylation at the end groups significantly affects the polymer at large compared to larger polymers. It is also possible that acetylation is performed on impurities, like molecules formed during the DALC synthesis. The dark brown color of DALCIII could also indicate the presence of ferric perchlorate, which makes the reaction media almost black during the acetylation reaction, which possibly has reacted with acetic anhydride and thus contributed to a higher content of acetyl groups in the NMR signal. The ADALC reactions will be repeated and re-analysed before submission of paper 4.

Table 3. Weight average molecular weight (M_w), Polydispersity and degree of substitution (DS) for the different ring-opened CA.

Material	M_w [kDa] ¹	Polydispersity	DO [%] UV-Vis	DO [%] NMR	DS _A ATR- FTIR	DS _A NMR
ADALCI	4.75 ± 0.03	1.66 ± 0.08	55	49	2.9	3.7
ADALCII	3.34 ± 0.08	1.54 ± 0.05	75	61	2.9	3.8
ADALCIII	2.86 ± 0.17	1.37 ± 0.15	100	81	2.9	5.1

¹ M_w measured with SEC, see Paper IV.

For the calculations of the HSP, Table 4, it is assumed that the structure is homogenous, and a DS of 3 is used since a higher substitution is not possible with the assumed structure of CA. The different DOs used for HSP calculations were the ones determined by NMR. All HSPs decrease with increased DO, where δ_d and δ_h decrease with 0.1 from ADALCI-II and ADALCII-III. This is because the carbons in the C₂-C₃ bond go from -CHOH- into -CH₂OH, adding an extra hydrogen. In the calculations, the -CH₂OH has a larger dispersion component than -CHOH- (270 vs 80, respectively) and a much larger molar volume (16.1 vs -1). The contribution from the dispersive parameter increases, but the molar volume increases more, resulting in a lowering of the dispersive energy density. The polar and hydrogen bonding energies do not change because the only contribution that change is that of dispersion, and because they stay the same, an increase in molar volume thus decreases the polar and hydrogen bonding energy densities.

Table 4. HSP for the ring-opened CA.

Material	δ_d (J cm ⁻³) ^{1/2}	δ_p (J cm ⁻³) ^{1/2}	δ_h (J cm ⁻³) ^{1/2}	δ_{tot} (J cm ⁻³) ^{1/2}
ADALCI	18.1	5.1	11.7	22.1
ADALCII	18.0	5.1	11.6	22.0
ADALCIII	17.9	5.0	11.5	21.8

Now after the chemical structure of the materials are established and the HSPs are stated, we can start investigating the different experimental results with regards to the chemical structure and HSPs, starting with the T_g .

7.2.1 Glass Transition

Table 5 shows the T_g for all the materials. It is evident that T_g decreases significantly when the average side-chain length increases and when the backbone is ring-opened. From CA to CABIII, the T_g decreases from 193°C to 109°C, which shows that when the average chain-length increases from acetyl to butyryl greatly impacts T_g . One way of explaining this decrease is that an increase in side-chain length pushes the polymers apart, decreasing the possibility for dense packing, and decreasing the interaction forces, which then are directly related to the T_g . For the ring-opened ADALCI-III, the T_g is similar for I and II, while it decreases to -17°C for III. DO for ADALCI and II are 49% and 61%, respectively, and thus possibly too similar to see any difference in T_g . The lack of differences between ADALCI and ADALCII could also

be due to impurities in the samples. Comparing the different ADALCs to CA might not be relevant here, since the M_w for CA and the ADALCs are significantly different, about 30 times higher for CA, the T_g might not be comparable, as the difference probably is a combination of M_w and modification. It should also be noted that ADALCIII appears as a slow-running brownish liquid, possibly due to unintended degradation during the post-treatment of the reaction step. It is evident that despite this uncertainty, the higher ring-opening of ADALCIII decreases the T_g further, indicating that an increase in DO decreases the T_g . In the literature, the ring-opening of cellulose to different DO has shown to decrease the T_g [47]. The observed decrease in T_g in Paper 4 for increased ring-opening was thus expected and can be explained by the fact that the ring-opening makes the backbone less bulky and thus increases the possibility of movement.

Table 5. The T_g for all esters and ring-opened CA. Table data from Nilsson et al. 2022 [109].

Material	T_g [°C]
CA	193
CAP	143
CABI	154
CABII	136
CABIII	109
ADALCI	64
ADALCII	63
ADALCIII	-17

In order to make it easier to compare the different materials to each other, the chemical structure can be translated into the mentioned HSPs. Here it is assumed that the difference in M_w has a minimal effect on the T_g of the materials. Figure 11 shows how the T_g relates to the different HPSs. For all parameters, the T_g increases with the HPSs, which are the same as energy densities, thus in other words, T_g increases when the energy density increases. T_g is generally accepted to be related to the attractive forces within the material [111], and hence this makes sense. The average-side chain has a smaller change in T_g over a wider range of energy densities compared to the ring-opening, which changes drastically over a narrow change in energy density. For the dispersive parameter, δ_d , the T_g decreases with an increase in average side-chain length, decreasing the energy density, where the T_g appears to decrease exponentially. Observe this means going from right to left in Figure 11a. Figure 11 shows the significant difference between the ring-opened and non-ring-opened polymers. Due to the increased degree of ring-opening, the flexibility of the chain increases, leading to a decrease in T_g . However, this increase in chain mobility is not reflected in the HSP, which have been calculated using the additive method and therefore show only a small change.

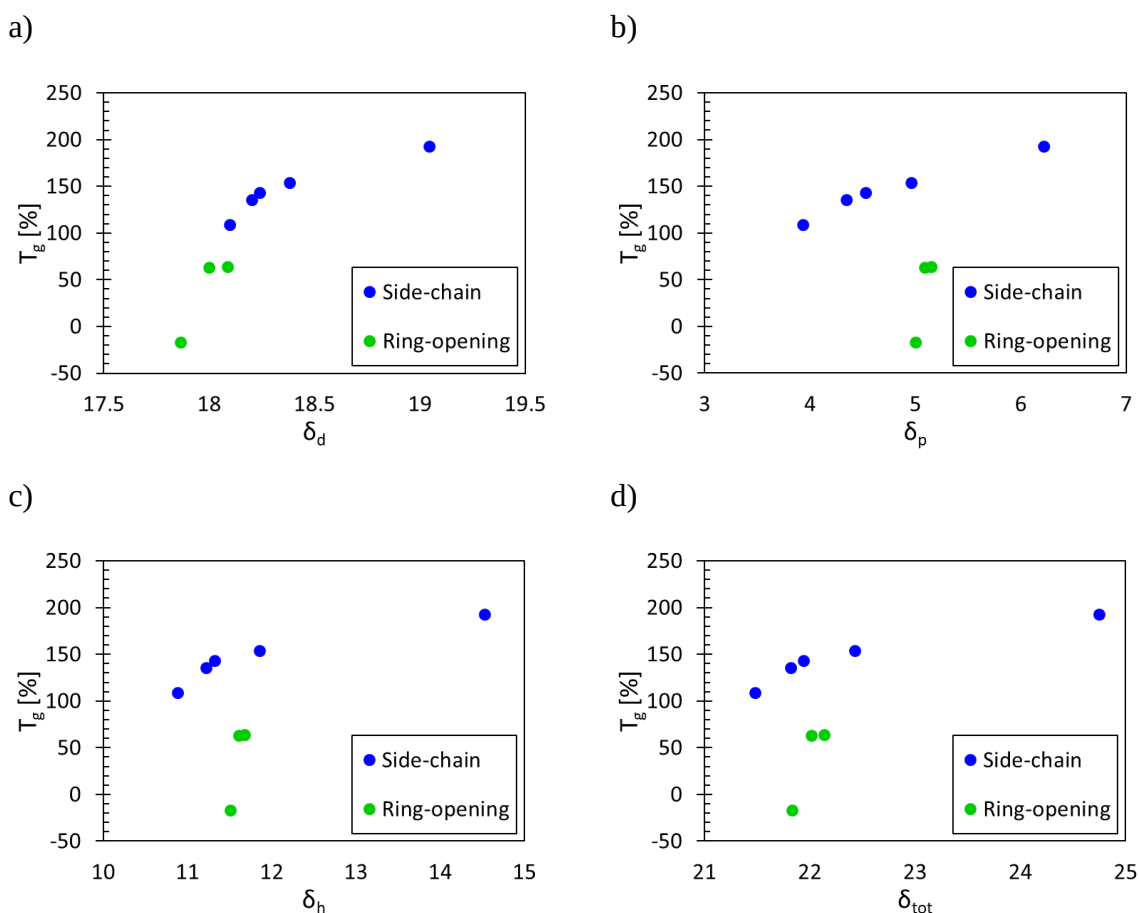


Figure 11. T_g plotted against a) δ_d b) δ_p c) δ_h , and d) δ_{tot} for increased average side-chain (blue) and increased DO (green).

7.2.2 Mechanical Properties

From this point on, there is only a focus on the average side-chain increase of CA, CAP, CABI-III. Figure 12 shows how the storage modulus of the esters is related to their HSPs. Observe that these data are not from the papers but included here. These measurements are performed similar to the DMA methods described in the method section, but without humidity control. The relation between the storage modulus and the HSPs appears to be like that of T_g in Figure 11 for the different average side-chain lengths, where an increase in energy density increases the storage modulus. This indicates that T_g and storage modulus is similarly affected by the change in average side-chain length. This could be explained by the fact that T_g is well tied to mechanical properties since they both depend on the strength of the intermolecular interactions.

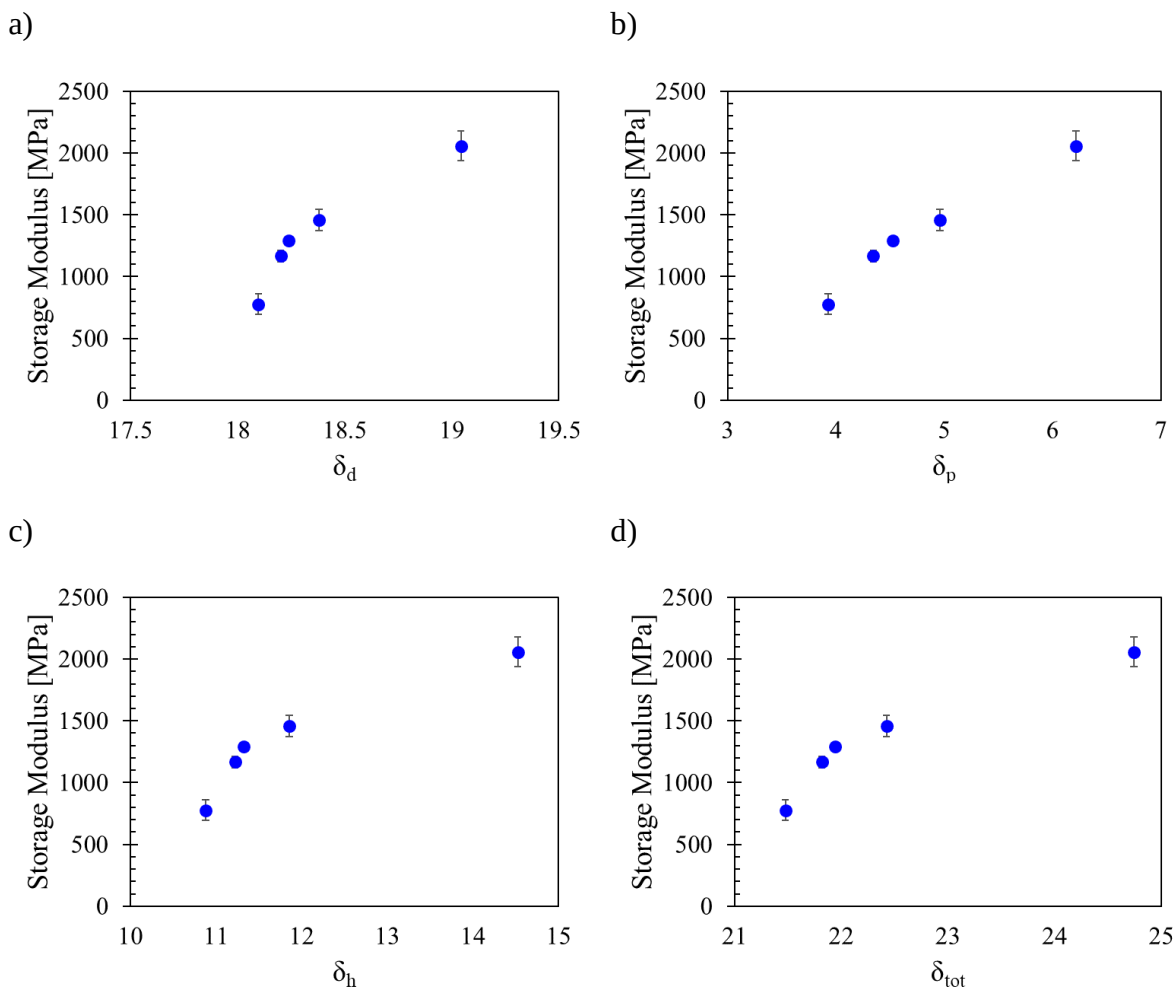


Figure 12. Storage modulus of the esters as a function of the HSPs. This is not included in any of the papers.

7.3 Water Absorption, Sorption and Sorption Kinetics

This section covers how the side-chain lengths of the different esters affect the water interaction by first investigating what happens when hot-melt pressed films are submerged in water, how much water is taken up, and how it affects density and the storage modulus. Submerging an object in water is considered an extreme case, and therefore a more comprehensive analysis could be conducted by subjecting it to varying levels of water immersion, such as different relative humidity conditions. Therefore, we studied how the sorption of water behaves in the different esters, both equilibrium values and kinetics. After that, the same RH conditions are mimicked while investigating the mechanical properties, how storage modulus changes during one RH cycle, and the effect of a series of RH cycles. In the last part, the oxygen permeation of CA is studied for how it is affected at different RH after being pretreated with 50% RH and submerged in water.

Starting with water submersion, Table 6 shows that the weight increase in water for CA is 12%, followed by a decrease to CABIII with 1.8%. Note that CAP has a lower weight increase than CABI and slightly higher than CABII, which means that a high substituted CAP ($DS_p=2.64$) is

similar to CABII, which is medium substituted ($DS_B=1.68$). This show that butyrate has a greater effect on water sorption than propionyl, which is expected. A similar observation can be done for the water permeation, although here, CABIII is higher than CAP and CABII. If water sorption is directly related to water permeation, that would not be the case. It could also be that the CABIII is the deviation, possible related introduction of cracks due to its brittle nature, which was noticed during processing and handling. For CA, CAP, CABI and CABII the hot-melt pressing resulted in films of the desired size without any issues, while for CABIII the resulting film after cooling easily cracked when removed from the Kapton film and from general handling of the film, making it more difficult to make desired film sizes. The water uptake is only looking at weight increase of the material, but it is known from Table 1 that the different esters have a wide range of average molar masses of the repeating unit, 263-348 g/mol. Thus, if the water uptake instead is translated to how many water molecules there are per repeating unit, it can be observed that CA has almost two water per repeating unit. The rest of the esters have much lower, closer to a half water per repeating unit. The trend is similar to the weight increase.

Table 6. Water uptake after water submersion, water permeation and the number of water molecules per monomer repeating unit for the esters CA, CAP, CABI, CABII and CABIII. Table data from Nilsson et al. 2022 [109].

Material	Water uptake [wt%]	Water permeation [$10^{-12} \text{ m}^2 \text{ s}^{-1}$]	Water molecules per repeating unit according to Figure 1b.
CA	12.0 ± 2.0	5.0 ± 0.6	1.75
CAP	3.8 ± 0.2	1.2 ± 0.2	0.67
CABI	4.4 ± 0.2	1.9 ± 0.5	0.74
CABII	3.3 ± 0.1	0.8 ± 0.1	0.61
CABIII	1.8 ± 0.5	1.5 ± 0.2	0.35

If the water uptake for films submerged in water is compared to the dispersion parameter δ_d in Figure 13, it is observed that, similar to T_g and the storage modulus, a decrease in water uptake is observed when the energy density decreases. In all these three parameters, T_g , storage modulus and water uptake, a large jump exists between CA and the other esters in the dispersion parameters. If the total parameter δ_{tot} is observed, the CAP and CABs are in the range of 21.5-22.4 while CA shows up much higher at 24.8, and similar for the water uptake around 1.8-4.4 % for the CAP and CABs compared to CA's 12%. This large jump could be explained by a higher amount of hydrogen bonding of CA, which is screened out effectively by replacing a few acetyl groups with butyryl groups, going from CA to CABI, which is closest. The reason CAP is not the closest to CA, despite having only one extra ethyl group compared to the two in CABI, is that CABI has a lower DS, which can be seen by looking at the average molar mass for its repeating unit, which is 302 g/mol for CABI and 319 g/mol for CAP. Any further increase in modification from CABI, or increase in average side-chain length, follows a similar decreasing trend with decreased energy density but smaller steps in both property and parameter. Hydrogen bonding is a short-range interaction, around 200 pm nanometer [112], and a standard carbon-carbon bond is 154 pm [113]. Given this, it is easy to correlate the effect of longer average side-chains. At the same time, the range from CABI and CA is large, for instance, a CAP with a similar substitution as CABI might have given a more precise indication

of where the hydrogen bonding is affected with regards to, for example, the energy density or average side-chain length.

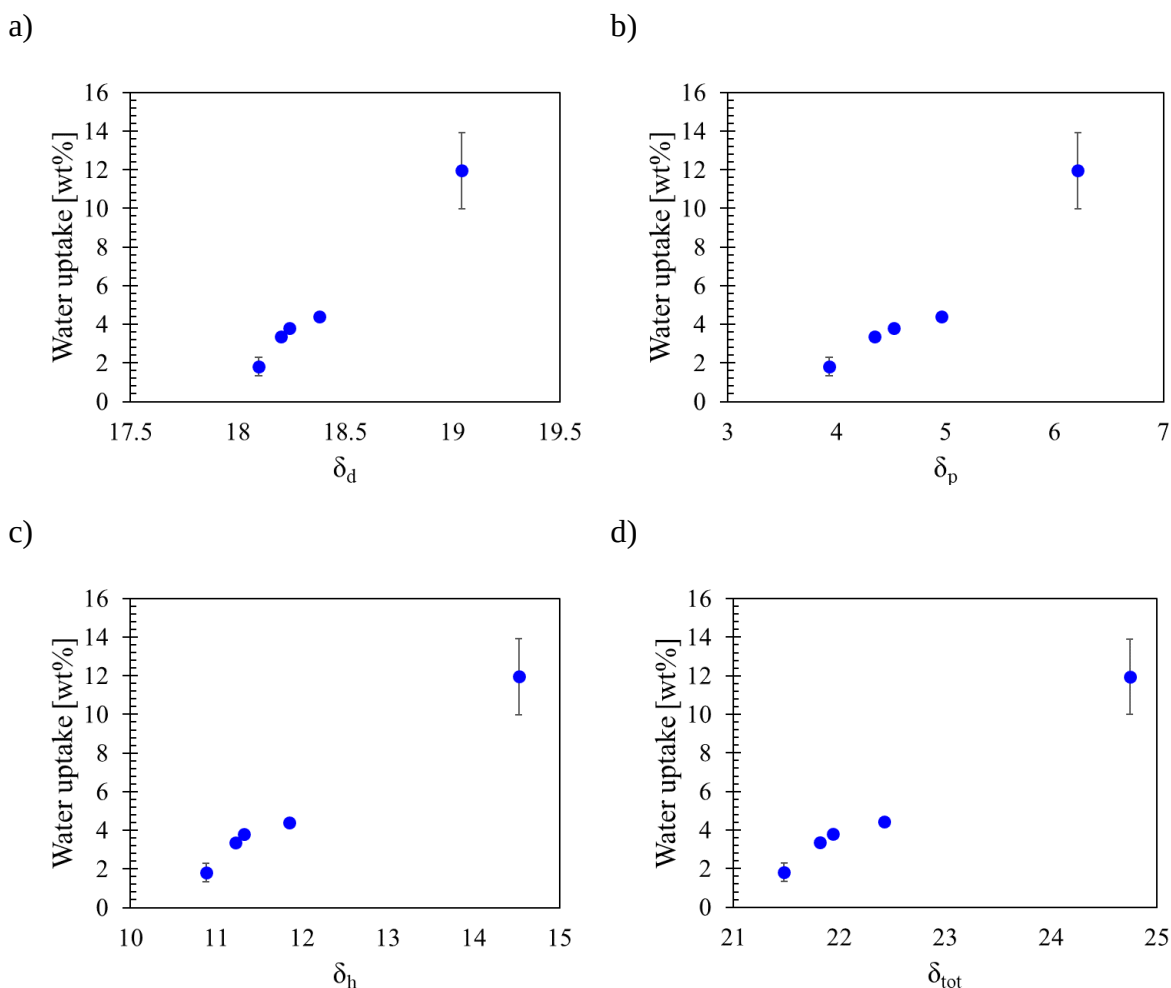


Figure 13. Water sorption of samples submerged in water over the different HSPs.

Figure 14 also shows the water uptake, but now together with the density increases for the same sample. The density increases for all esters, indicating that water occupies empty spaces inside the films rather than swelling. If swelling were the dominant effect of the water, the density would go to an average combined density of the esters and water, meaning decreasing towards the water's density of 1 g cm^{-3} . If the density increase for the esters is compared to the water sorption, it is evident that CA has a much higher weight increase than density increase. This indicates that for CA, the polymer system softens by the water, causing the polymer chains to move and relax, and thus accommodating for more water, i.e., swelling. The higher swelling of the system could indicate that clusters of water are formed. However, it does not necessarily mean the other esters do not get water clusters, only to a much less extent than CA.

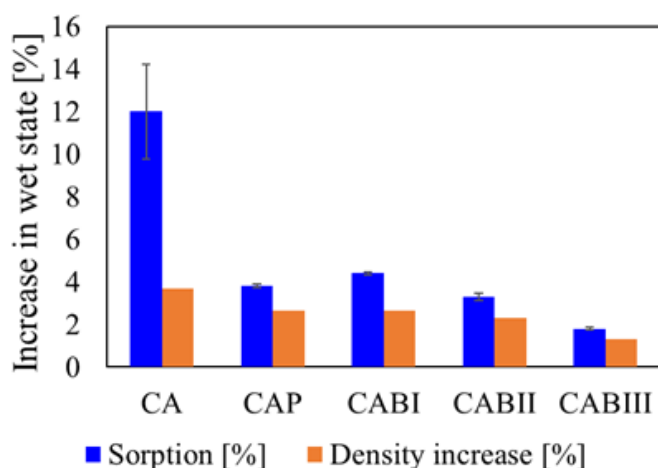


Figure 14. Water sorption and density increase after submersion in water of the esters.

So far it has been about full submersion in water, Figure 15a and 15b instead shows the weight increase of moisture in films of esters at different RH, starting from 0, going to 80, and down again with 10% increments. Also, it is clear that CA takes up more moisture, and a decrease is observed in a similar order as fully submerged films with CA, CABI, CAP, CABII, and CABIII in decreasing order. It can be seen in Figure 15a that in sorption and desorption, meaning increasing and decreasing RH, the weight of moisture differs at each step, and the weight of moisture increases slightly more for each sorption step at high RH. Then when RH decreases, the materials are holding more moisture in each step than for corresponding sorption event, an effect like this is called hysteresis. CA exhibits a larger hysteresis than the other esters, and Figure 15b, shows a difference in the weight of moisture in each RH step, and displays more clearly that the hysteresis effect decreases with the average side-chain length, with CABIII having the lowest. Together with the density increase, this supports the claim that moisture is taken up in the structure and forms clusters, preferably in CA. These clusters deform the structure and the water in them is the first to leave during desorption. The reason could be explained by that water in direct contact with water has lower interaction energy than water interacting with cellulose [114], and thus the cluster water has easier to leave the polymer compared to the water that interacts directly to the polymer. Based on the existing hysteresis, the other esters might also exhibit water clusters, but the cluster formation is less than for CA. The hysteresis happens because it is assumed that at the higher moisture content, the structure accommodates more moisture and thus deforms more but does not return to the original polymer structure. Stepping down from 80% to 70% RH is even slower than the rest of the desorption. In other words, the contraction of the polymer matrix is slower than the leaving of water. The weight increase from moisture appears to go back to the original weight when the RH is back at 0% RH, indicating that the moisture content is reversable. This does not directly explain if the cavities created from the water clustering is still there after water has left, or not.

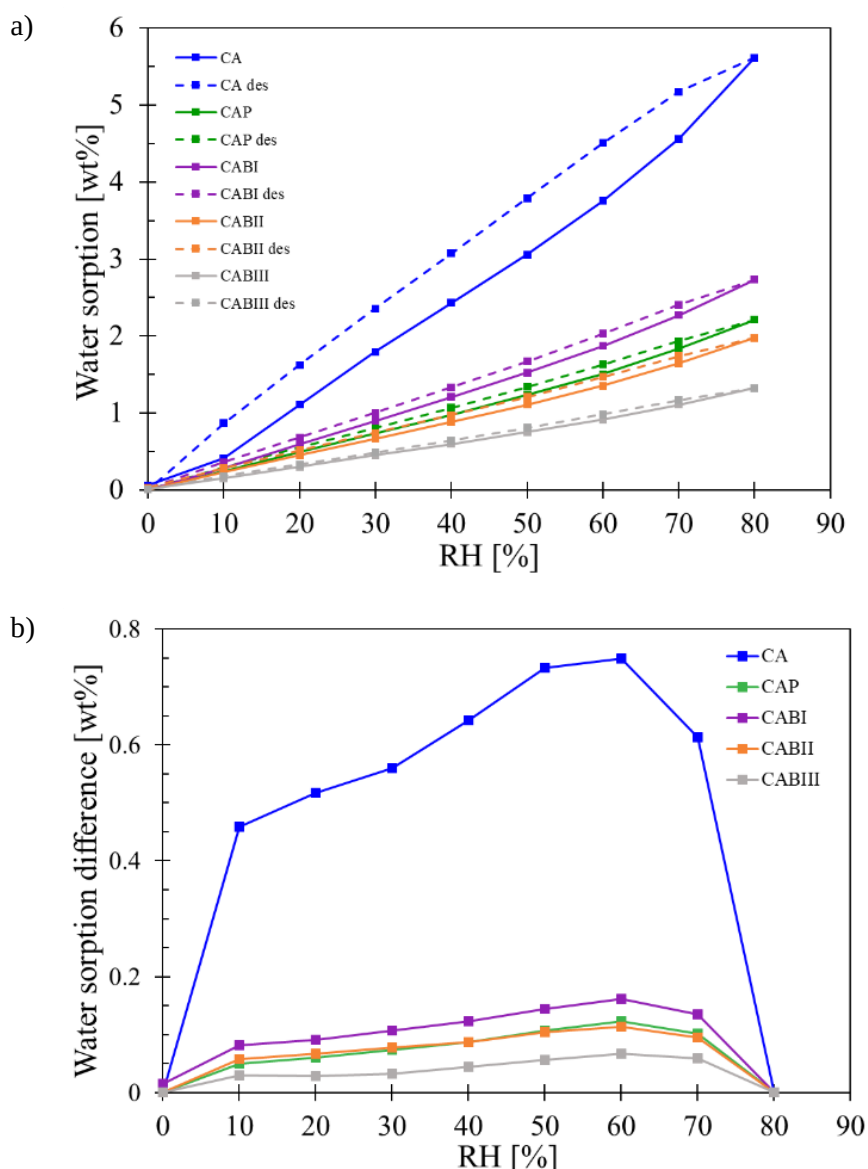


Figure 15. a) Sorption and desorption curves for all esters b) the difference between sorption and desorption.

The RH studies so far have been on moisture content at equilibrium in each RH-step. Figure 16 shows how water sorption happens over time in each RH step going up for the sorption and for each RH step going down for the desorption. For CA in particular, it is more evident that as the RH is stepping up, the sorption kinetics appears to get slower, where the sorption step 0-10% RH takes around 100 min and the 70-80% RH step takes around 240 min. The explanation behind the much longer sorption time for CA's 70-80% RH is probably related to the structural changes of the polymer when it accommodates more water and forms water clusters. The duration of the sorption steps is getting slower for the increased average side-chain length going CA-CABI-CAP-CABII-CABIII, matching the also decreased total amount of moisture that is taken up in each step. The relatively similar sorption times of the CAP and three CABs could indicate no structural change; thus, no clustering is likely to happen.

As described in the theory part, the kinetic for the sorption data can be analysed using the PEK model to see if the kinetics of the esters could be divided into two kinetic components and to try to link the kinetics components to actual structural phenomena. One observation is that, indeed, as the literature has shown on CA, also holt-melt pressed films of CA in this study, appears to be able to be fitted to the PEK model. This is evident in Figure 17, where CA sorption from 30-40% RH and 70-80% RH have both a slow sorption (solid lines) and fast sorption (dashed line). Comparing RH step changes at low to high RH values shows that sorption is slower for both the kinetical components in the PEK model, the slow and fast components. Due to the large difference in time scale, they should be compared with caution. The desorption for 30-20% RH and 70-60% RH appears to be relatively similar, and thus the desorption kinetics appear less affected by RH.

For the other esters, when the average side-chain length increases, the PEK model is not valid to the same extent. Even though the PEK model gives solutions for the esters CAP, CABI-III, the confidence interval increases significantly going from CA to CAP and CABI-III, see Paper III Supporting information. While the R² and root mean square error suggest a good fit of the PEK model to all esters and RH, the sorption and desorption curves for CAP starting at RH 70% show an almost linear slow component (Figure 17 b and d, and Paper 3), which, together with the large 95% confidence intervals indicate that the PEK model provides unreliable data for CAP. For example, desorption data starting at 70% RH give values of *b* ranging from -1.3 to 1, and ranging from -55 to 101 min. Therefore, the model appears to fail for CAP, but also for CABI-III, which is further discussed in Paper III. Instead of the PEK model, they can instead be well described by a one exponential component.

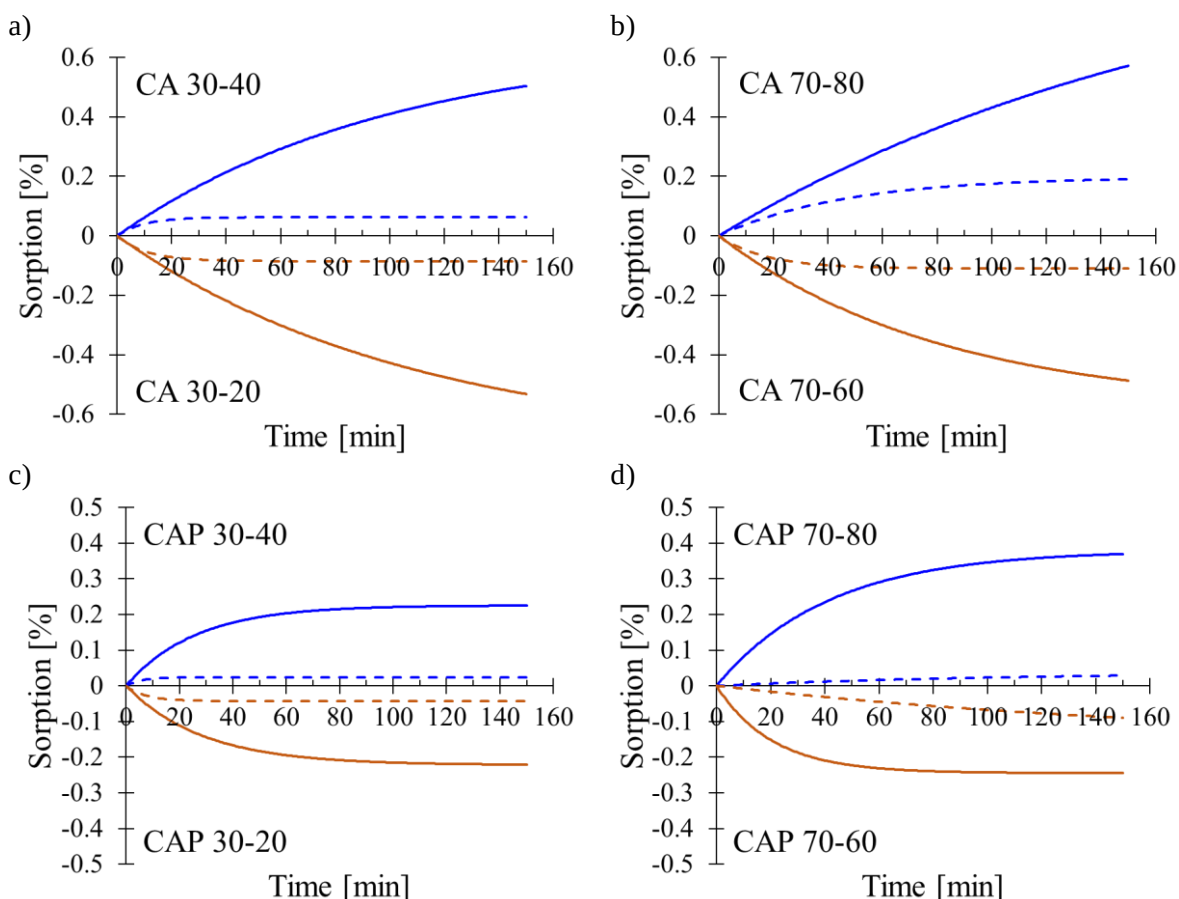


Figure 17. PEK model's two components for CA and CAP are plotted separately, solid line=slow component, dashed line=fast component. a) and b) show sorption of CA going in RH steps 30-40 and 70-80% RH in blue and desorption 30-20 and 70-60% RH in brown. c) and d) show the same but for CAP instead.

7.4 Mechanical properties at different RH conditions

It was previously shown that the mechanical properties decrease with an increased average side-chain length. The mechanical properties are expected to behave differently for different average side-chain lengths, even when exposed to water. Figure 18 shows the storage modulus of films dried in an oven (orange) and films submerged in water for 24 h (blue). The storage modulus decreases when the films are treated with water, with CA changing the most and CABIII changing the least. That CA is mechanically most affected supports the previous observation that the structure is directly affected by water sorption, which for examples softens the structure.

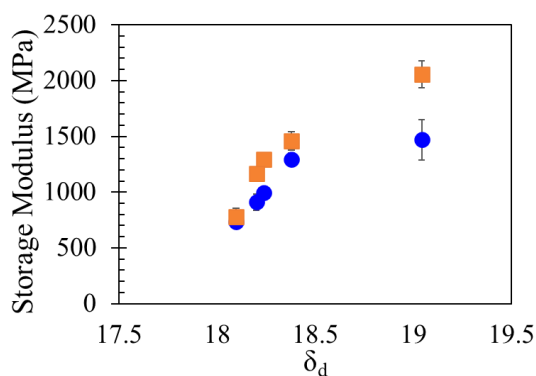


Figure 18. Storage Modulus of the esters as dry films (orange squares) and wet films (blue circles) as a function of the total HSPs.

Let us look into closer detail of the water interaction by conducting the mechanical analysis at different RH conditions for CA due to its higher water sorption and mechanical response. The first method that was performed followed the same RH increase and decrease in 10% increments similar as the DVS, see Figure 19. Observe that the RH for the DMA measurements goes from 5% RH and then 20% RH before the RH ramping in 10% RH increments. When the RH increases, the storage modulus is observed first drastically to decrease, followed by a slow increase. It can be assumed that the first steep decrease could be related to water entering the structure and softening it. A similar observation could be done for the loss modulus and tan delta. Since the loss modulus is directly related to how much energy the system loses, each RH step starts with an increase in energy loss, which could be the effect of an increase in the chain mobility. The following decrease in loss modulus is slightly higher than the previous step, for 30% up to 80% RH. This can be connected to Figure 19d, the length of the sample film, which appears to be elongated with an inverse exponential growth, meaning it elongates first fast and then slows down. The film softens from water sorption, the force from the clamps holding the film in the DSC instruments elongates the film. This elongation causes the polymer to form more oriented polymer chains and decreases the cross-section area, which gradually increases the strength of the sample film in the direction of the elongation. This could explain the slow secondary increase in storage modulus at each RH step going up in RH. The elastic modulus shows a ramping pattern for the stepwise increases in RH, but for the decreases in RH, no clear ramping behaviour is observed. This could be related to the structure not reaching any equilibrium, which is more discussed in detail in Paper III. Observing the data in Figure 19d, it is clear that the length of the sample film increases progressively with the maximum elongation occurring at 80% RH. Upon desorption, the length decreases, but not to its initial value. This behaviour can be attributed to the presence of irreversible length changes due to energy dissipation, while the elastic portion of the deformation causes the sample to contract during the desorption.

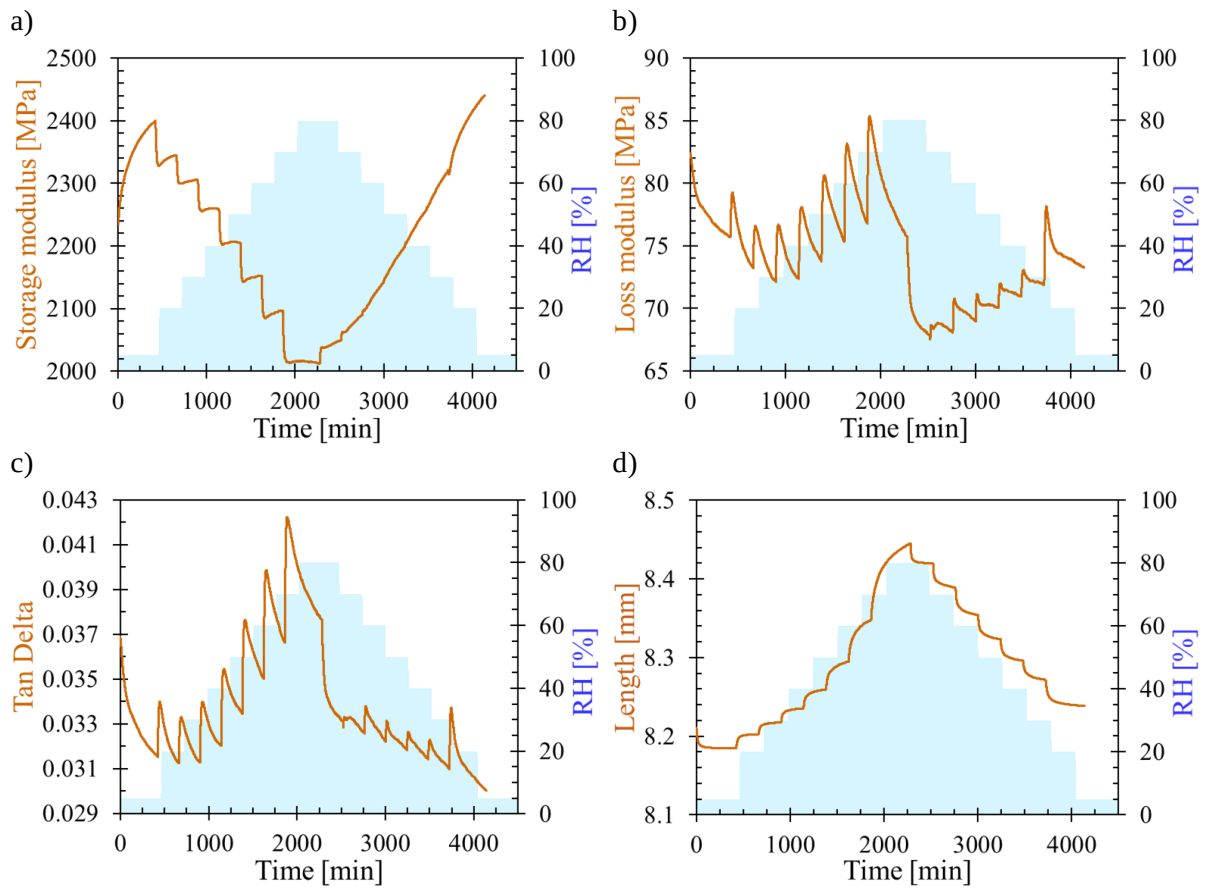


Figure 19. DMA measurement of CA using a RH method similar to that of DVS, stepping up to 80 % RH and down again.

Now the question is how does the change in storage modulus relate to the water sorption? As stated, the time frame of the changes in storage modulus is on a larger scale than for the DVS, 4400 min compared to 2700 min, respectively. Figure 20 focuses on one step 30-40% RH and compares the two PEK curves plotted on the same time axis as the storage modulus and the length of the sample film. Now it is more obvious that the initial fast drop in storage modulus matches the initial fast increase of the film length, and the slow length increase after 50 min could be related to the storage modulus increase. In Figure 21, the higher humidity step of 70-80% RH is displayed, there the storage modulus decreases fast, just as at the 30-40% RH step. The length elongation during the 70-80% RH step appears to be larger and more prolonged than during the 30-40% RH step, as reflected by the sorption curves, where the fast sorption is more prolonged in time in the 70-80% RH step compared to 30-40%. The storage modulus also stops decreasing at a longer time. The storage modulus does not appear to increase as significantly as the 30-40% RH step, but this could be because the length is still changing relatively much per time unit, and the moisture content is still increasing. The same connection as the 30-40% RH step can thus be made, that the fast sorption appears more linked to the fast decrease in storage modulus. This indicated that the moisture sorption as two components can be connected to physical events. It can be assumed that the fast sorption component is related to water that goes in between the polymer chains and thus has a strong impact on the mechanical properties. The slow sorption component is more like connected to the formation of water clusters, which appears to have a less significant effect on the mechanical properties.

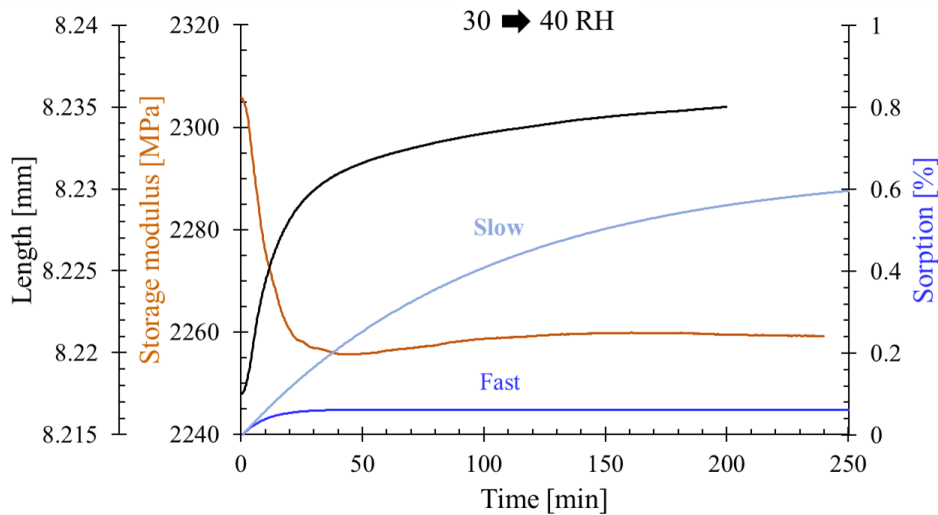


Figure 20. CA sorption step 30 to 40% RH showing length in DMA, storage modulus and the slow and fast component from the PEK model.

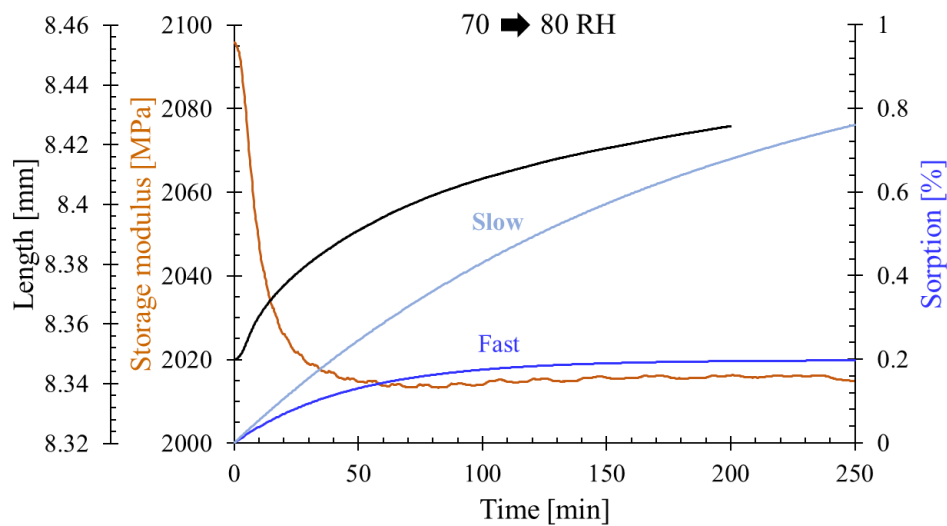


Figure 21. CA sorption step 70 to 80% RH showing length in DMA, storage modulus, and the slow and fast component from the PEK model

In the DVS measurements, it was observed that the water sorption appears reversible in the sense that the water content was cycled to the same weight value as the beginning. Although, a second cycle following the first one would have been more optimal to perform and is suggested for future work. Cycling of RH was performed, Figure 22, but with the DMA instead, looking at the mechanical properties. The cycling was performed as 0-50-0-60-0-70-0 both to see the effect of RH cycling and if the effect would change from reaching a higher maximum RH in the cycle. The storage modulus appears to return to the same value at 5% RH for each cycle, indicating that cycling to 50, 60, and 70% RH does not change the dry strength of the material. Keep in mind that the first data point in the first DMA cycle is ignored because of a difference in equilibration time. The length of the film appears to increase at the end of each cycle. This strengthens the observation that when the RH increases, the sample film is stretched irreversibly. In Figure 22a the storage modulus is compared to the RH, if instead one would

compare to the moisture content, Figure 22b, it is evident that the storage modulus is linearly related to the moisture content, as predicted by Chen *et al.* [21].

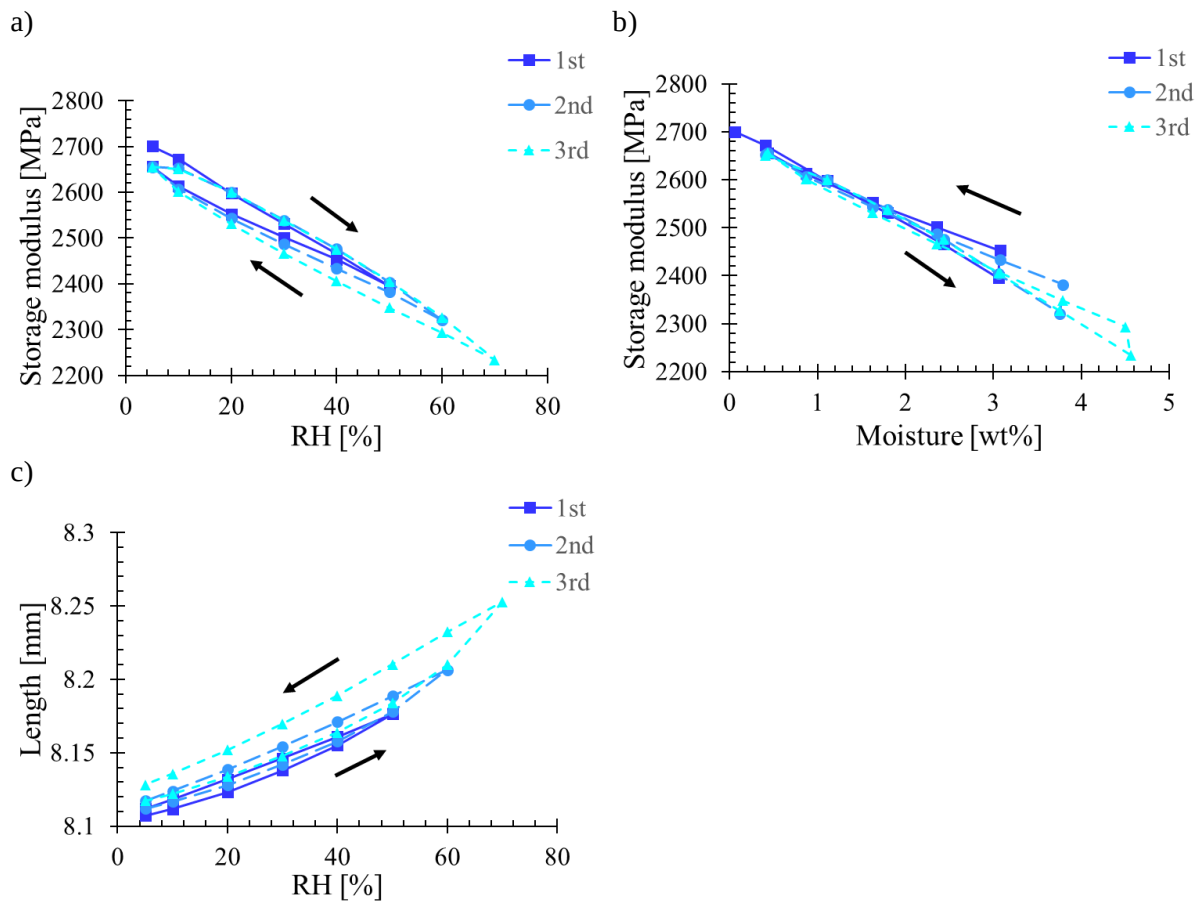


Figure 22. a) Storage modulus of CA cycled in RH to 50, 60 and 70% RH in 10% steps, b) Storage modulus for same cycle translated to moisture content, c) Length during the same RH cycling.

7.5 Oxygen Permeation and Humidity

An important parameter for packages is the oxygen permeation, as explained at the beginning of this thesis, and thus a CA film was investigated, as shown in Figure 23. This study aimed to answer the question: what happens with the oxygen permeation at different RH if the film has been prewetted? The sorption and desorption measurements show that it is likely that water forms clusters, but if the film goes back to its initial structure and the cavities disappears the oxygen permeability should be the same for a prewetted film and a film that has not been prewetted. The experiment was performed as following: one set of films was conditioned at 50% RH directly after hot-melt pressing, and the other set (referred to as prewetted) was after hot-melt pressing submerged in water at room temperature for 24 h followed by storage at 50% RH before the oxygen permeation measurement. These measurements were kindly provided by Tetra Pak and are not included in the Papers. The measurement starts at 50% RH, decreases to 0%, increases to 50%, and ends at 80%. When exposed to 0% RH, the oxygen permeation increases slightly for the unwetted film and almost doubles for the wetted film. Returning to

50%, the oxygen permeation decreases for both, with the non-wetted one staying lower. At 80% RH, the oxygen permeation is almost similar for both films. In contrast, the oxygen permeability increases with increased moisture content has been observed in for example microfabricated cellulose films [115] and chitosan films [116]. The increase in oxygen permeation for the chitosan film is explained by a plasticizing effect from water. Interestingly, a dried prewetted film has higher permeation than a non-wetted film, this could possibly be related to cavities creased by water clusters that do not disappear when the water is removed at 0% RH. The oxygen permeation values at each RH are taken at equilibrium after 60 hours. This would support the previous observations of water cluster formation that were discussed for high RH and the reason for the desorption curve containing much more water at each RH step for decreased RH. At 80% RH, both films exhibit similar permeability, which may be attributed to the fact that the films which were not pre-wetted start to adsorb moisture and create water clusters, while the pre-wetted films begin to fill the pre-existing cavities, leading to comparable structures in the polymer systems. Thus, the conclusion is that pre-wetting of the films leads to the formation of water clusters, which appear to increase the oxygen permeation at lower humidity, particularly below 50% RH. However, at higher RH values such as 80%, the structures of the pre-wetted and the moisture-exposed films become more alike, and thus more similar oxygen permeabilities are observed.

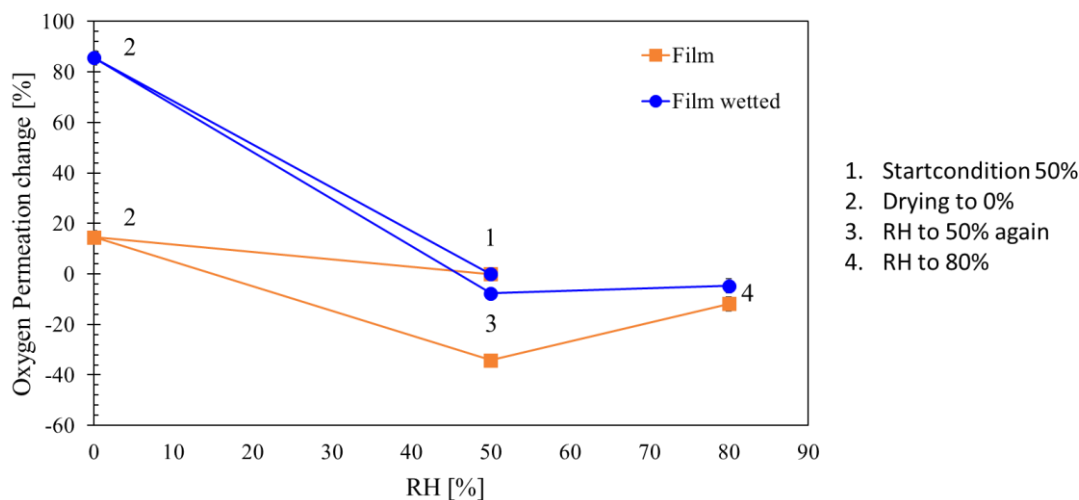


Figure 23. Oxygen permeation at series of RH, 50-0-50-80, of one set of CA films pre-treated at 50% RH and one set submerged in water for 24 h. Measurements provided by Tetra Pak, Lund.

8 | Conclusion

From thermal and chemical structure investigation of the esters it was found that by increasing the average side-chain length of CA with propionyl and butyryl, the T_g decreases significantly, which, together with the HSPs could be related to a screening of hydrogen bonding as the side-chains side-chain lengths increased. The T_g also appears to decrease significantly for a CA structure that has an increased ring-opening, which, based on the small changes in HSP might be more due to the increased mobility of the polymer backbone. T_g of esters appear thus to be able to be tailored with both a change in average side-chain length and degree of ring-opening of the backbone, where the ring-opening appears to have a much greater effect on T_g and thus on the intermolecular forces. The same was observed for the mechanical properties, such as storage modulus, as they are strongly connected to the materials T_g . The water sorption for films submerged in water was shown to give a large change in weight for CA compared to the other esters. This supports that CA has a high degree of hydrogen bonding to water which promotes water sorption, while the longer average side-chain lengths of CAP and CABI-III have a lower degree of hydrogen bonding. The increased side-chain length appears thus to cause a screening of the available hydrogen bonding site and thus result in less water sorption. In summary, the HSPs appears to be a good tool when looking at properties like the T_g for the small change in side-chain length from for CA to CABIII, whereas when comparing to large changes such as introduction of ring-opening of the backbone, the HSPs show a lower ability to predict the effects. This means that for a minor change in the chemical structure, the HSPs could be used as a prediction tool.

When submerged in water, the density of all cellulose esters increases, which indicates that the water that is taken up is entering empty voids. However, by comparing the weight increase in water and the density change, it was observed that CA appears to have swelling, where more water enters the structure than available voids, pushing the matrix apart and creating water clusters. This observation is strengthened by looking at water sorption at different RH conditions, where a hysteresis happens between sorption and desorption. One explanation for the hysteresis is that water clusters are created at high moisture content, which upon desorption, resulting in higher moisture content than the corresponding sorption step. The other esters, CAP and CABI-III also show a hysteresis effect but much less than CA, indicating that the hysteresis gets less significant with increased average side-chain lengths and decreases in the order CABI, CAP, CABII, and CABIII.

By looking at the kinetics of the sorption curves, it is evident that CA is the only of the esters that can be well described, or rather well fitted, to the PEK model, having one slow and one fast sorption component. The other esters could be described by one exponential component. The stated creation of water clusters for CA, and to a lesser extent for the other esters, could indicate that the slow sorption component of CA is related to water clustering. The PEK model could thus only describe systems that have water molecules entering the system and both soften and deform the structure.

When CA is exposed to an increased RH, the storage modulus initially decreases fast, followed by a slow and low increase. The fast decrease in storage modulus in each RH step is linked to the fast sorption component of the PEK model. This means that such fast entering water has a direct effect on the storage modulus. The secondary phase of the storage modulus with a slow increase could be an effect of the sample film getting stretched during the measurement, where

the elongation increases with increased RH. The slow sorption component of the PEK appears to not be directly related to the mechanical properties, but it could cause further elongation of the film. The slow sorption could be related to the water clustering, which could mean that water clusters in CA have a minor effect on the mechanical properties. It is likely that the clustering is created simultaneous as the deformation of the polymer matrix. Cycling to different RH shows that the length of the film increases with each cycle, which means that the film experience irreversible deformation.

Studies of oxygen permeation confirm the water clustering that happens in CA at exposure to high RH. After being fully wetted once and then exposed to drying conditions, the oxygen permeation becomes significantly higher, even doubled, compared to a non-wetted film. This gives a strong indication that water creates clusters, which upon drying, leave cavities behind that do not recover or do not recover fully, resulting in an easier pathway for oxygen to permeate through the structure.

To conclude, this work has investigated cellulose esters and the effect of changes to their chemical structure, and how these changes affect their thermal and water permeability. The impact of this work shows the importance of knowing how small changes in the ester structure affect its properties and thus adds to the knowledge base on how to design esters for specific uses. The importance of previous water exposure for CA is also shown as important and encourages carefulness with conditioning and awareness of the history of materials when they are used in everyday products.

9 | Future outlook

This work showed that there is a large difference in properties between CA and the rest of the esters CAP, CABI, CABII and CABIII, and that the structural influence on this could be due to the screening of hydrogen bonding. CABI is the closest in structure and properties to CA due to the low ratio between butyl and acetyl, but still the difference to CA is large. Based on the observed range for CABI to CABIII and that CAP with its high propionyl to acetyl ratio it is similar to CABII, it can be assumed that a medium or low propionyl to acetyl ratio similar to CABI and CABII could possibly partly cover the big gap between CABI and CA. This could give greater insight into where exactly the average side-chain length is high enough to screen out hydrogen bonding.

Both DVS and DMA measurement were performed going from 0% RH up to 80% and down again. The oxygen permeation studies of wet films suggest that more information about both moisture uptake and mechanical properties could be obtained by cycling more than once up to 80%. Possibly the still existing cavities observed at dry condition for the oxygen permeation would cause a higher moisture content at the beginning of a second DVS RH cycle.

As stated for the ADALC, there appears to be some uncertainty about the synthesized material's chemical structure, with the DO being low in NMR compared to UV and the DS being higher than possible in NMR. Further studies are needed. One thing that could be done for DO is to break the glycosidic bonds of DALC by hydrolyzation with sulfuric acid and then run a carbohydrate analysis. Only the intact glucose rings would be detected and thus give the ratio of AGUs that are not ring-opened. Further analysis with NMR could also possibly give a deeper insight into the high DS of the ADALC.

Future research on the topics presented could give more insight. Especially with the ADALC, which is an interesting material and still relatively unknown. Even if it was discovered 50 years ago it has not been studied much further over the years. Further study of the degree of acetylation and the degree of ring-opening could give promising materials as it provides a large tuning of the T_g which is related to many other properties. Expanding the analysis to how other properties are affected would be very interesting, for example, the water sorption and water permeation, as it is observed during synthesis that they precipitate in water, but that only indicates some water resistance. If an application such as in packaging could be interesting, it would demand forming the materials into films and studying those films. The future for modified DALC could be exciting.

10 | Acknowledgements

The financial support from FORMAS is gratefully acknowledged.

I would like to express my gratitude to the following people, who have supported me and without whom this thesis would not exist:

Professor Anette Larsson, my main supervisor, for her wisdom, positiveness, and excellent guidance, which have made me into the scientist I am today.

Professor Gunnar Westman and Professor Christian Müller as co-supervisors, for their support and guidance, when I needed it.

My co-authors for Paper I-IV are acknowledged for all their contributions.

My reference group in Vinnova competence center FibRe, for all the feedback on my work.

Martin Gunnarsson, Katarina Jonasson and Hanna Eliasson at Tetra Pak for providing oxygen permeation measurements.

Treesearch, which has provided me with a necessary scientific network and collaboration opportunities.

My fiancée, Louise Samuelsson, who has supported me throughout my work.

Ms. Roujin Ghaffari, for all the support and friendship for being my go-to colleague.

All my office mates and colleagues with whom I have created many memories.

Ms. Rydviha Govender, for providing an excellent linguistic review of the manuscripts.

Last, but not least, my family and friends who have inspired me and formed me into the person I am today.

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