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Preparation and Characterization of Composite Films Consisting of Poly(Lactic Acid) and Nanocrystalline Cellulose

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ABSTRACT

There is a growing need for materials from a renewable feedstock. As a consequence, the biodegradable polymer poly(lactic acid) (PLA) has gained extensive attention. In order to improve the properties of PLA, composite films consisting of PLA and nanocrystalline cellulose (NCC) has been produced via solvent casting. Poly(lactic acid) degrades through aqueous hydrolysis, and in this study, water permeability for films consisting of various amount of NCC was studied in diffusion cells. The storage modulus and its variation with air humidity were characterized by using dynamic mechanical analysis and the crystallinity and transition temperatures of the material were determined using differential scanning calorimetry. Moreover, the microstructure of the composite films were studied with scanning electron microscopy and compared with pure PLA. The water permeability was found to decrease for films consisting of 5% (w/w) NCC compared to pure PLA, while the permeability increased for films with 7.5 and 10% (w/w). All films were almost totally amorphous, and the glass transition was lower in the film with 10% (w/w) NCC. The storage modulus of the material increased with an increased amount of NCC. It was also seen that pure PLA became less elastic at increased air humidity, while the elasticity of the films containing NCC increased.

Keywords: Permeability, poly(lactic acid), diffusion cells, nanocrystalline cellulose, biocomposite, mechanical properties, interface

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List of Abbreviations

CPM	Counts per minute
DMA	Dynamic mechanical analysis
DPM	Disintegrations per minute
DSC	Differential scanning calorimetry
NCC	Nanocrystalline cellulose
PLA	Poly(lactic acid)
SEM	Scanning electron microscopy

1. Introduction

1.1 Background

The interest for materials from renewable feedstock increases as the world's petroleum resources drops further. Also, since waste management is a large problem and many materials are difficult and/or costly to recycle, biodegradability is a desired property in modern and future materials [1]. Cellulose is not only biodegradable and from a renewable feedstock, it is also the most abundant biopolymer in the world. As a consequence new cellulose-based materials are constantly developed and improved.

One new cellulose based material is Södra's DuraPulp. DuraPulp is a composite material that consists of cellulose fibers combined with a biodegradable polymer matrix. The appearance and behavior of this material is similar to paper, but with advantageous properties like high tear strength, creep resistance, bendability and air permeability [2]. Södra Cell in Värö started the production of DuraPulp in December 2011 [3] and the initial sales have been directed towards customers within specialty paper and design materials [2]. It is not fully clear in which areas the material is going to be used and Södra is currently working on finding new application areas and customers [2].

The polymer used as a matrix in DuraPulp can vary, but poly(lactic acid) (PLA) is an example. PLA is one of the first polymers produced from a totally renewable feedstock [4] and the matrix polymer this project will focus on. It is advantageous towards other biodegradable polymers due to its relatively low price, which is expected to drop further [4, 5] to become even more competitive with commodity plastics like polystyrene (PS), poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET). Due to the competitive price and biodegradability, poly(lactic acid) has received extensive attention and making composite materials through reinforcing PLA with different kinds of cellulose is a popular research topic [6-10].

Poly(lactic acid) degrades in contact with water, which means that the water uptake will affect the rate of degradation. Since air humidity varies in different parts of the world, the water uptake has to be considered to enable global marketing of PLA based composite materials. A composite material, where one material is dispersed in a matrix material, contains numerous amounts of interfaces, defined as boundaries where the two components meet. Therefore, it is relevant to ask the question if the water transport in the material is affected by the presence of all the interfaces between cellulose and PLA.

In this thesis, biocomposites consisting of poly(lactic acid) and some kind of cellulose were produced and investigated. Nanocrystalline cellulose was chosen prior to other types of cellulose since composite materials with NCC are a promising class of new materials [11, 12], and it was available within the research group. It is also possible to disperse in dichloromethane, a solvent that dissolves PLA.

1.2 Purpose

The purpose of this project is to investigate the water permeability of composite films consisting of poly(lactic acid) and nanocrystalline cellulose. It is also of interest to evaluate whether the interfaces within the material affect the permeability.

1.3 Outline

The first focus is to develop a method for production of films consisting of PLA and NCC. In order to investigate the effect of the interfaces, films with varying amounts of NCC is produced and water permeability is investigated in diffusion cells using radioactive labelled water. Differential scanning calorimetry experiments are performed to determine the crystallinity of the material and to see if crystallinity depends on the added concentration of NCC. Further, dynamic mechanical analysis is used to study how the mechanical properties are affected by an increased amount of NCC. The microstructure of the composites was compared to pure PLA, by using scanning electron microscopy.

2. Theory

2.1 Poly(Lactic Acid)

Poly(lactic acid) is a polymer with lactic acid as the repeating unit, see figure 1. Lactic acid is a small optically active hydroxy acid that can be produced by fermentation of simple sugars, which are common in agricultural by-products [13]. The sugars are broken down into pyruvate, which during anaerobic conditions is transformed to lactic acid by the enzyme lactic acid dehydrogenase [14]. Lactic acid is an optically active molecule, meaning that two isomers L(+) and D(-) [4] exists. In mammals, only the L(+) isomer is produced while bacterial systems can produce both [13]. The existence of two monomeric enantiomers means that the stereochemistry of the polymer obtained from polymerization of lactic acid can be controlled and thus the crystallinity of the final polymer [13].

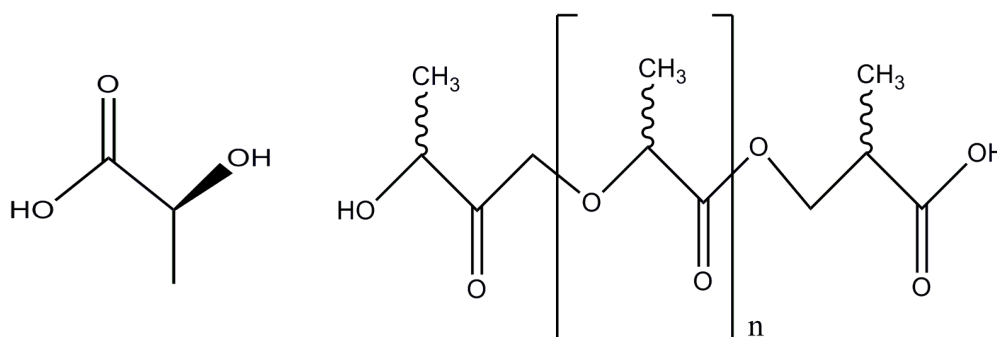


Figure 1. The structure of the monomeric unit lactic acid (left) and a poly(lactic acid) polymer chain (right).

There are different polymerization processes possible for producing poly(lactic acid) but the most common is the ring opening polymerization of lactide dimers [4]. It usually starts with fermentation of dextrose followed by condensation of the lactic acid that is obtained into oligomers. The oligomers are later purified and depolymerized into lactide dimers using a catalyst to obtain a high stereopurity and to speed up the process. The lactide dimers obtained is after purification melt polymerized into the final polymer by a ring opening mechanism [4].

The properties of the final polymer are very dependent on stereochemistry and molecular weight [13], and are often compared to polystyrene and poly(ethylene terephthalate) [15]. The melting point of isotactic PLA is around 180° C [14] and for semicrystalline poly(lactic acid) that is not enantiomerically pure the melting point is in the range of 130-180° C [15]. The glass transition lies around 55° C and is not affected by the stereochemistry of the polymer to the same extent as the melting point [13].

The ester bonds in PLA are sensitive towards hydrolysis. The hydrolysis reaction, which can be seen in figure 2, leads to polymer degradation and the rate depends on water concentration and temperature. The degradation reaction is catalyzed by the

presence of acids and bases, and since the degradation results in carboxylic acid groups at the degraded chain ends, the reaction is considered to be autocatalytic [4]. Higher molecular weight gives a longer degradation time [16] and the degradation rate is also very dependent on the crystallinity since the crystalline regions of poly(lactic acid) are more impermeable towards water [13].

Figure 2. The degradation reaction for PLA in contact with water [4].

2.2 Nanocrystalline Cellulose

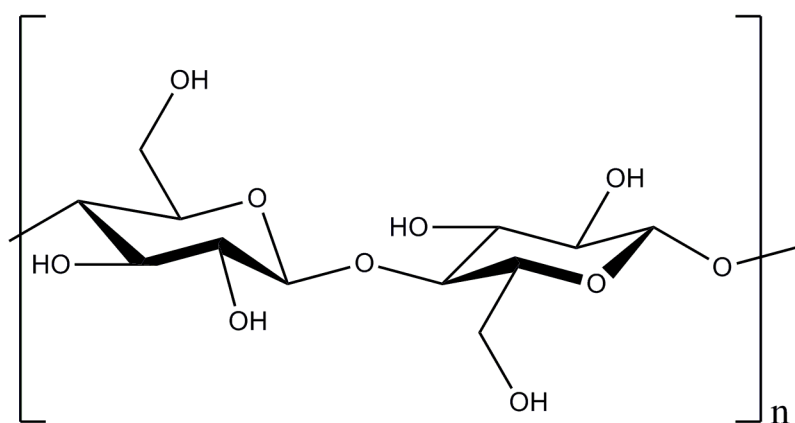


Figure 3. The repeating unit of cellulose.

The starting material for the acid hydrolysis can be any kind of cellulose ranging from pulp to microcrystalline cellulose [18]. The dimensions of the crystals depend on the starting material, but the fibers are generally a few hundred nanometers in length and 10-20 nm in diameter [18]. The properties of the fibers depend on the cellulose source, but also on reaction parameters like time and temperature and which kind of acid that is used for the hydrolysis; the acid can be sulphuric acid [19], hydrochloric acid [20] or nitric acid [21]. Even though it depends on the cellulose source and the above mentioned parameters, the mechanical properties of these fibers are said to be comparable to Kevlar and steel [22].

The nanocrystalline cellulose that is obtained from acid hydrolysis will have negative surface charges, which enables the fibers to disperse in water. If the concentration of NCC is above 1-10% (w/w), the fibers will align to form an anisotropic nematic liquid crystalline phase [23].

2.3 Permeability

According to Van den Mooter et al [24], film permeability can be determined from diffusion cell experiments. Starting from Fick's first law one can express the mass transport rate for a diffusing specie across a membrane, assume linear concentration drop within the film (two-film theory) and that the aqueous boundary layers on the surfaces of the film does not affect the transport at all. By using a partition coefficient K , the bulk concentrations in the diffusion cell chambers can be related to the concentrations at the film surfaces. Another assumption that is made is that the concentration of the diffusing specie present within the film is negligible compared to the total chamber concentrations. The whole derivation can be seen in Van den Mooter et al [24]. The following equation is obtained:

$$\frac{2PS}{V}t = -\ln\left(\frac{C_0 - 2C_a}{C_0}\right) \quad (1)$$

Where P denotes the permeability coefficient, S the film area, V is the chamber volume in each cell and C_0 and C_a represents the zero donor chamber concentration and the concentration in the acceptor chamber at any given time, respectively. Using this equation, P can be calculated from the slope of a plot of $-\ln\left(\frac{C_0 - 2C_a}{C_0}\right)$ against time. It is important to note that the permeability is scaled against the film thickness, resulting in the unit m^2/s .

2.4 Liquid Scintillation Counting

Liquid Scintillation Counting is a method for detecting the presence of low-energy radionuclides. To be able to detect the radiation, the samples are mixed with a scintillation cocktail, which consists of aromatic solvent, a fluorescent molecule (scintillator) and surfactants [25]. The energy released during a radioactive decay is transferred to the aromatic solvent, causing excitation of solvent molecules. The energy is then further transferred from the solvent to the scintillator, which causes a light pulse of a scintillator characteristic wavelength that is detected by a

photomultiplier tube detector [26]. The light pulses measured by the instrument are sorted according to their intensities in a sample spectrum. From this spectrum the instrument software calculates the counts per minute (CPM) using count correction calculations [25]. Some decays are quenched, meaning that all the radiation energy is not transferred to the scintillators. By the use of a quench correction method, the instrument determines the real activity in a sample, expressed as disintegrations per minute (DPM) [25].

2.5 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a way to determine energy changes within a material during constant heating rate. These energy changes corresponds to either chemical reactions occurring in the sample or physical changes such as glass transition, crystallization, melting of crystals or sample decomposition [27]. The instrument has two sample pans, one is for the sample and one is a reference pan, which is left empty. The two pans are heated at a constant rate and the instrument measures the difference in heat flow needed to keep the pans at the same temperature [28].

At melting or crystallization of a polymeric sample, energy is either liberated or needed, which will result in a peak in the heat flow through the sample. The position of the peak gives the temperature at which the melting/crystallization occurred and the area of the peak gives the change in heat flow during the process [27].

The crystallinity of a polymer sample can be calculated through the following formula:

$$\text{Crystallinity (\%)} = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100 \quad (2)$$

Where ΔH_m and ΔH_c represents the measured heat of fusion during melting and heat released during cold crystallization, respectively, and ΔH_m^0 denotes the heat of fusion for a 100% crystalline polymer. For poly(lactic acid), ΔH_m^0 is generally considered to be 93,1 J/g [4]. This formula can be used for pure polymeric samples, but in a composite material where the crystallinity of the matrix polymer is to be calculated, the equation looks as follows [29]:

$$\text{Crystallinity (\%)} = \frac{1}{1 - w_f} \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100 \quad (3)$$

Where the weight fraction of the matrix polymer, w_f is included.

DSC is commonly used to determine the glass transition of polymeric materials. At the glass transition, the thermal energy will be high enough to enable larger chain segments to become mobile. This leads to an increased heat capacity of the material which is observed as a shift in the slope when the heat flow is plotted against the temperature [27]. Figure 4 below shows a typical DSC-curve, where the glass transition T_G , melting point T_M and cold crystallization temperature T_C are shown.

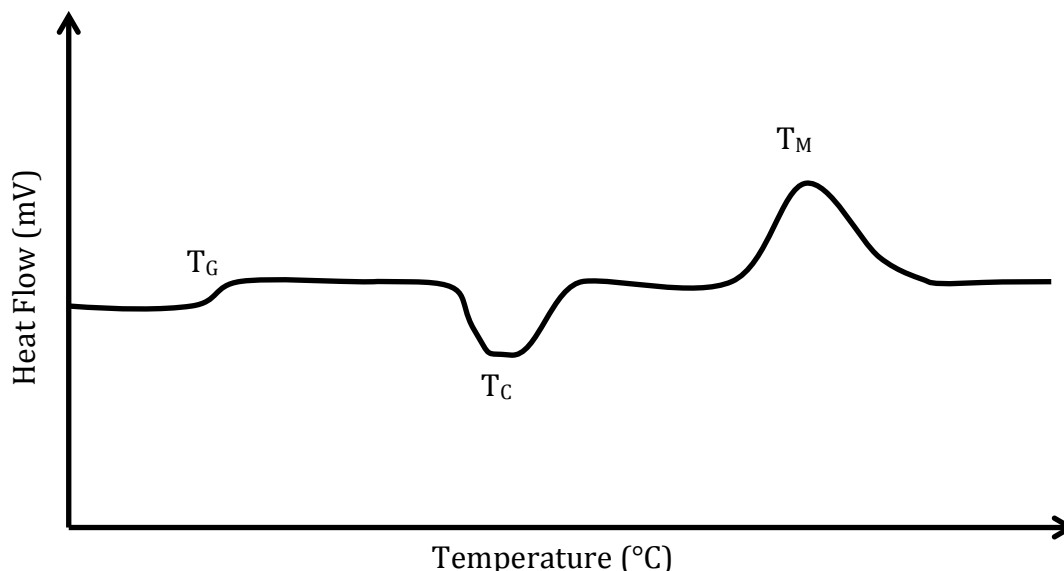


Figure 4. Schematic picture of a DSC thermogram, showing a glass transition as well as peaks corresponding to cold crystallization and melting.

2.6 Dynamic Mechanical Analysis

When a material is subjected to stress, most often denoted σ , it will lead to a deformation known as strain, which is denoted ϵ . Stress is measured in force per unit area; which is equivalent to pressure and the SI-unit is Pa. Strain is defined as the positional change of a reference point, and in practice it is expressed in percentage as the length difference divided by the original sample length [28].

Elastic materials respond to stress by converting the energy to potential energy that can be stored in the material and later used for recovery of its original shape. A viscous material, on the other hand, cannot store energy. When a viscous material is subjected to stress it will respond in the form of flow. Almost no material is purely elastic or purely viscous; most known materials show both these stress response behaviors and are thus viscoelastic [28].

Dynamic mechanical analysis (DMA) is a method to determine short time mechanical behavior of materials. The sample is subjected to a small sinusoidal stress of a certain frequency and the material will respond with a sinusoidal strain of the same frequency. A purely elastic material will respond immediately and will therefore be in phase with the oscillating stress. If the material instead is purely viscous, the responding strain will be out of phase with the sinusoidal applied stress and the phase

angle between these will be 90 degrees. This means that DMA can be used to determine the viscoelasticity of a material [30].

Since every sinusoidal stress that the sample is subjected to gives a modulus value, it is possible to monitor the change in modulus when changing one variable such as temperature, frequency or humidity. These scans are known as sweeps and makes it possible to evaluate at which conditions a material have good enough mechanical properties for a certain application.

Through DMA, it is possible to determine shear storage and shear loss modulus, which represent the shear modulus for the elastic and viscous parts of the material. The shear modulus is not the same as the Young's modulus of a material, which for elastic solid is the proportionality constant that relates stress to strain, when Hooke's law is obeyed, usually at small strains [28].

2.6 Scanning Electron Microscopy

Scanning electron microscopy can be used to determine the morphology and microstructure of samples. A focused electron beam scans across the sample surface resulting in signals that are converted to an image on a computer screen. The most widely used signals for imaging are secondary electrons[31], which is electrons that is excited from the sample molecules by the scanning electron beam. The secondary electrons gives information about surface texture, and dark regions in the obtained image means that the secondary electrons are prevented from reaching the detector [31]. In addition, there are also other signals obtained when the beam strikes the sample; for example backscattered electrons, Auger electrons and X-rays [31].

3. Materials and Methods

3.1 Materials

The poly(lactic acid) used in the project was of the type Ingeo 3051D from NatureWorks® and the nanocrystalline cellulose was made within the research group through acidic treatment of the microcrystalline cellulose Avicel PH101 using sulphuric acid following the process of Bondesson et al.'s (sample number 7 in table 2) [32]. The solvents dichloromethane and acetone were purchased from Sigma-Aldrich and [³H]-water and the scintillation liquid UltimaGold used in the permeability experiments were purchased from Perkin-Elmer.

3.2 Film Production

Composite films with poly(lactic acid) and 5, 7.5 and 10% (w/w) NCC were produced. NCC was initially dispersed in water and the solvent was exchanged to dichloromethane through several steps, using acetone as an intermediate solvent. First, the aqueous NCC dispersion was added to Falcon tubes together with some millilitres of acetone. The tubes were then placed in a centrifuge (Sigma 4K15, Sigma Zentrifuges, Germany) set to 5000 rpm and 20° C for 5 min. The supernatants were poured off and the NCC pellets were washed four times with acetone and once with dichloromethane using the same centrifuge settings. The NCC were resuspended in DCM and PLA was added to the tubes and left to dissolve for a couple of hours. The solutions were then casted onto glass Petri dishes and left in a fume hood for the solvent to evaporate over night. As reference, pure PLA films were made by dissolving PLA pellets in DCM and cast those solutions onto Petri dishes. The films were removed from the Petri dishes by dipping them into a glass bowl with milli-Q water for 10 seconds and then the films were carefully peeled off from the glass and placed between two Kleenex wipes to remove excess water. The films were stored in a desiccator until use.

3.3 Permeability Experiments

The permeability experiments were carried out in diffusion cells. A diffusion cell consist of two compartments, denoted donor and receptor chamber, separated by a hole with a radius of 3.9 mm where the films are placed. A schematic picture of a diffusion cell and the experimental setup can be viewed in figure 5.

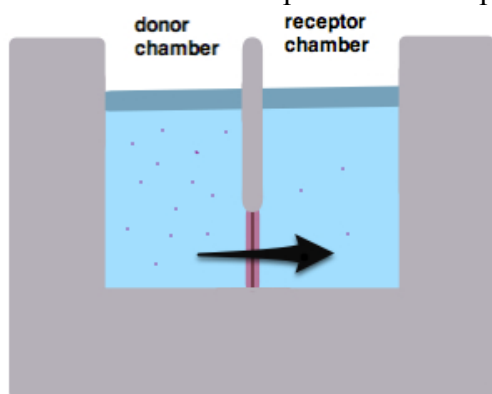


Figure 5. A schematic image of a diffusion cell during an experiment with one donor and one receptor chamber, separated by the film of interest.

Each compartment was filled with 15 ml milli-Q water and 10 μ l of [3 H]-water were added to the donor chambers. 0.5 ml zero samples were taken from each chamber, beginning with the donor sides. This means that the new chamber volumes were 14.5 ml. At certain time intervals, samples were taken out from the receiver chambers and to compensate for the volume losses, 0.5 ml of milli-Q was added after each sample was taken. Since the concentration of [3 H]-water in the zero samples from the donor chambers will be high compared to the concentrations in the receptor chamber samples, they were diluted 100 times before analysis.

The samples were weighed and 3 ml of a scintillation liquid, UltimaGold, were added before the analysis. The samples were analysed in a liquid scintillation analyser (Tri-Carb 2810TR, Perkin-Elmer, USA), which gave CPM and DPM (CPM divided by the efficiency) of each sample. The permeability was determined using equation 2 as described in section 2.3. In addition to this equation, the dilution of the receptor chamber was compensated for in the calculations.

3.4 Dynamic Mechanical Analysis

The storage modulus and its dependence on air humidity were investigated for the films containing pure PLA and PLA with 5 and 10% (w/w) NCC using a dynamic mechanical analyzer (DMA Q-800, TA Instruments, USA). Samples with a width of 85-90 mm were cut out and their thickness and length were measured. They were then analyzed at a constant frequency of 1 Hz, 0.05% strain, 0.01 N preload force and 125% force track, using the following program:

1. Humidity 10%
2. Equilibrate at 25°C
3. Isothermal for 60 min
4. Data storage on
5. Step humidity 1% for 10 min up to 90%

Three samples of each type of film were analyzed.

3.5 Differential Scanning Calorimetry

The crystallinity and transition temperatures of the films with pure PLA, and PLA reinforced with 5 and 10% (w/w) NCC were analysed in a differential scanning calorimeter (Pyris 1 DSC, Perkin-Elmer, USA). Sample pans with 3-7 mg of sample were prepared and analysed with the program below:

1. Hold at 10° C for 1 minute
2. Heat from 10°C to 180°C with 10°C/min
3. Hold at 180°C for 1 minute
4. Cool from 180°C to 10°C with 10° C/min
5. Hold at 10°C for 1 minute
6. Heat from 10°C to 180°C with 5° C/min
7. Go to 30° C

Each kind of film was analysed twice.

3.6 Scanning Electron Microscopy

The microstructures of the films were analysed with a scanning electron microscope (Leo Ultra 55 FEG-SEM, LeoElectron Microscopy Ltd, UK). Films were drawn apart in an Instron 5565A device (Instron, USA) before the analysis to reveal the cross-sections. The cross-sections were surface coated with a thin layer of gold to prevent the material from becoming charged by the electron beam during the analysis.

4. Results

4.1 Film Production

The film production worked well, but in some cases the NCC particles aggregated quite a lot during the process of solvent exchange and some films could therefore not be used. Also, sometimes the dispersion of NCC in the film was not optimal.

Regarding the appearance, the pure PLA films were visually transparent, while the films containing NCC were mainly transparent but with quite well dispersed white fragments.

4.2 Permeability Experiments

The following graph (figure 6) shows the water permeability of pure PLA and PLA with 5, 7.5 and 10% (w/w) NCC.

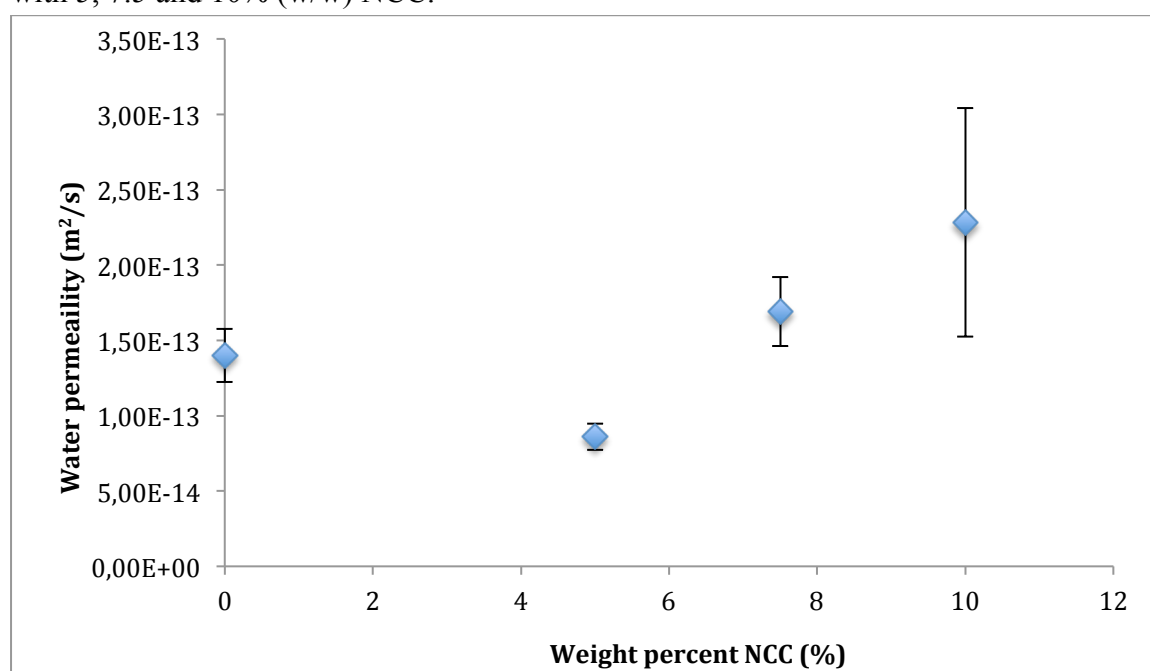


Figure 6. The water permeability for poly(lactic acid) filled with different weight percentage NCC.

As can be seen from the graph, the permeability decreases in the film with 5% (w/w) NCC. For the films with 7.5 and 10% (w/w) NCC the permeability increases compared to the film with pure PLA. Since the values for the water permeability can be difficult to tell from the graph, they are presented together with the standard deviations in table 1 below.

Table 1. Table showing the average water permeability for the different films, as well as standard deviations and number of replicates.

Film	Average water permeability (m^2/s)	Standard deviation	Number of replicates
Pure PLA	1.40E-13	1.77E-14	8
PLA with 5% NCC	8.61E-14	8.78E-15	5
PLA with 7,5% NCC	1.69E-13	2.28E-14	5
PLA with 10% NCC	2.28E-13	7.60E-14	7

The standard deviations, seen both as error bars in figure 6 and listed in table 1, seems to increase with NCC content. But, the error is lower for the film with 5% (w/w) NCC than for pure PLA.

4.3 Dynamic Mechanical Analysis

The variation in storage modulus for the different films can be seen in figure 7 below. From the graph, it can be determined that the storage moduli were higher for the films filled with NCC, and that the modulus increased with an increased amount of NCC in the film. Further, it can be seen that for pure PLA the storage modulus decreased with increased humidity, while it increased for the films containing NCC. The latter is more evident when comparing the tabulated values in table 2.

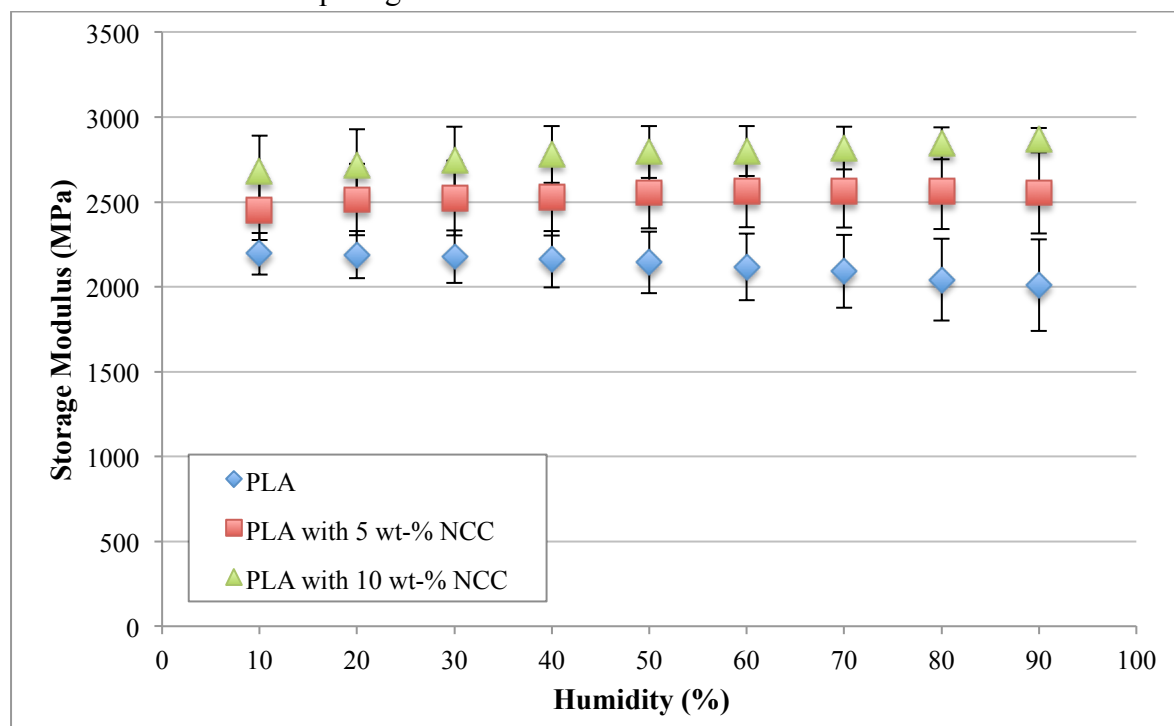


Figure 7. The variation in storage modulus with air humidity is compared for pure PLA and PLA that has been reinforced with 5 and 10% (w/w) NCC. 2.01 ± 0.27

Table 2. The average storage modulus at different humidities together with the standard deviations, obtained from three replicates of each film.

Air humidity	Average storage modulus (GPa)		
	PLA	PLA with 5% NCC	PLA with 10% NCC
10%	2.20 ± 0.12	2.46 ± 0.18	2.68 ± 0.21
20%	2.19 ± 0.14	2.51 ± 0.21	2.72 ± 0.21
30%	2.18 ± 0.15	2.52 ± 0.22	2.75 ± 0.20
40%	2.16 ± 0.17	2.53 ± 0.23	2.78 ± 0.10
50%	2.14 ± 0.18	2.56 ± 0.21	2.80 ± 0.15
60%	2.12 ± 0.20	2.56 ± 0.21	2.80 ± 0.10
70%	2.09 ± 0.21	2.56 ± 0.21	2.82 ± 0.10
80%	2.04 ± 0.24	2.56 ± 0.22	2.85 ± 0.09
90%	2.01 ± 0.27	2.55 ± 0.24	2.87 ± 0.06

4.4 Differential Scanning Calorimetry

In figure 8, cold crystallization and melting peaks from the DSC measurements can be observed, while the information given from two replicates of each kind of films are viewed in table 3. The degree of crystallinity is calculated according to equation 3 and all samples are found to be almost fully amorphous.

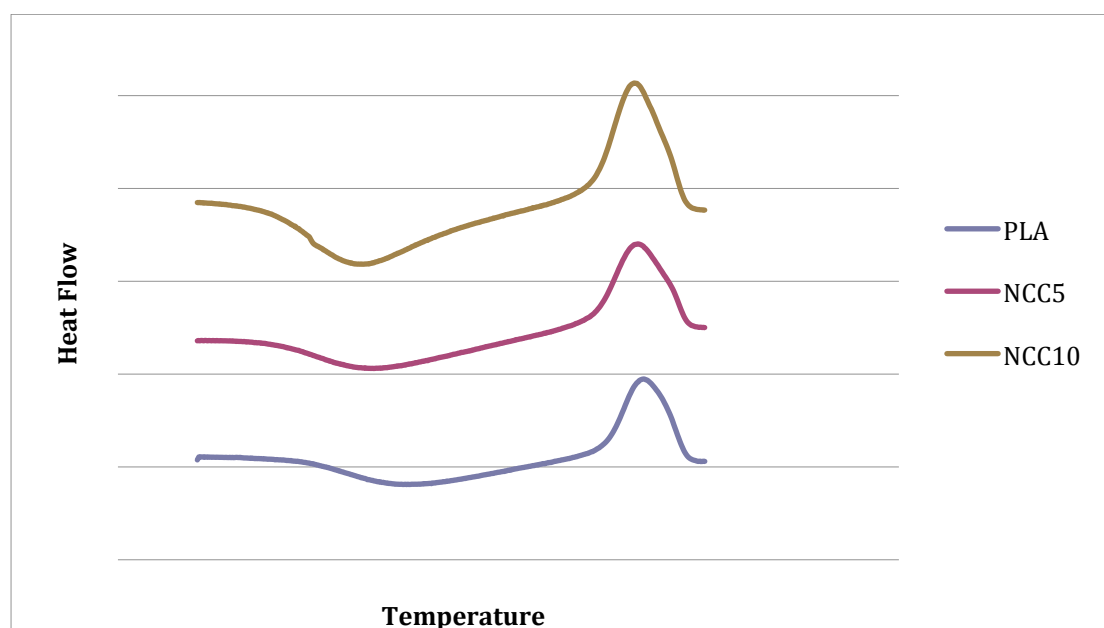


Figure 8. Melting and cold crystallization peaks from the DSC measurements.

Table 3. Comparison of T_G , T_C , T_M , ΔH_c , ΔH_m and degree of crystallinity for PLA filled with different amounts of NCC. The values are averages from two measurements.

	Pure PLA	5% (w/w) NCC	10% (w/w) NCC
T_G (°C)	53.8 ± 0.1	54.6 ± 3.4	49.8 ± 1.1
T_C (°C)	117.7 ± 2.0	114.0 ± 1.2	113.0 ± 1.8
T_M (°C)	147.3 ± 0.3	148.0 ± 1.3	146.7 ± 0.6
ΔH_c (J/g)	-15.0 ± 2.0	-17.8 ± 1.0	-20.3 ± 0.5
ΔH_m (J/g)	15.8 ± 2.2	18.6 ± 1.0	20.6 ± 0.6
Crystallinity (%)	0.9 ± 0.3	0.9 ± 0.1	0.3 ± 0.1

4.5 Scanning Electron Microscopy

SEM images showing the crosssections of pure PLA (figure 9 a-b), PLA with 5 (figure 9 c-d) and 10% (w/w) NCC (figure 9 e-f) taken at different magnifications can be seen below. The small black pattern that looks like cracks comes from the protective gold coating present to protect the samples from the electron beam. The film with pure PLA seems quite smooth, while particles can be seen in the other films. In the film with 5% (w/w) NCC, two different kinds of particles can be observed. Most evident are the larger rounder, but there are also smaller cylindrical that corresponds to single NCC fibers. One of these single fibers is emphasized with a red ring in figure 10.

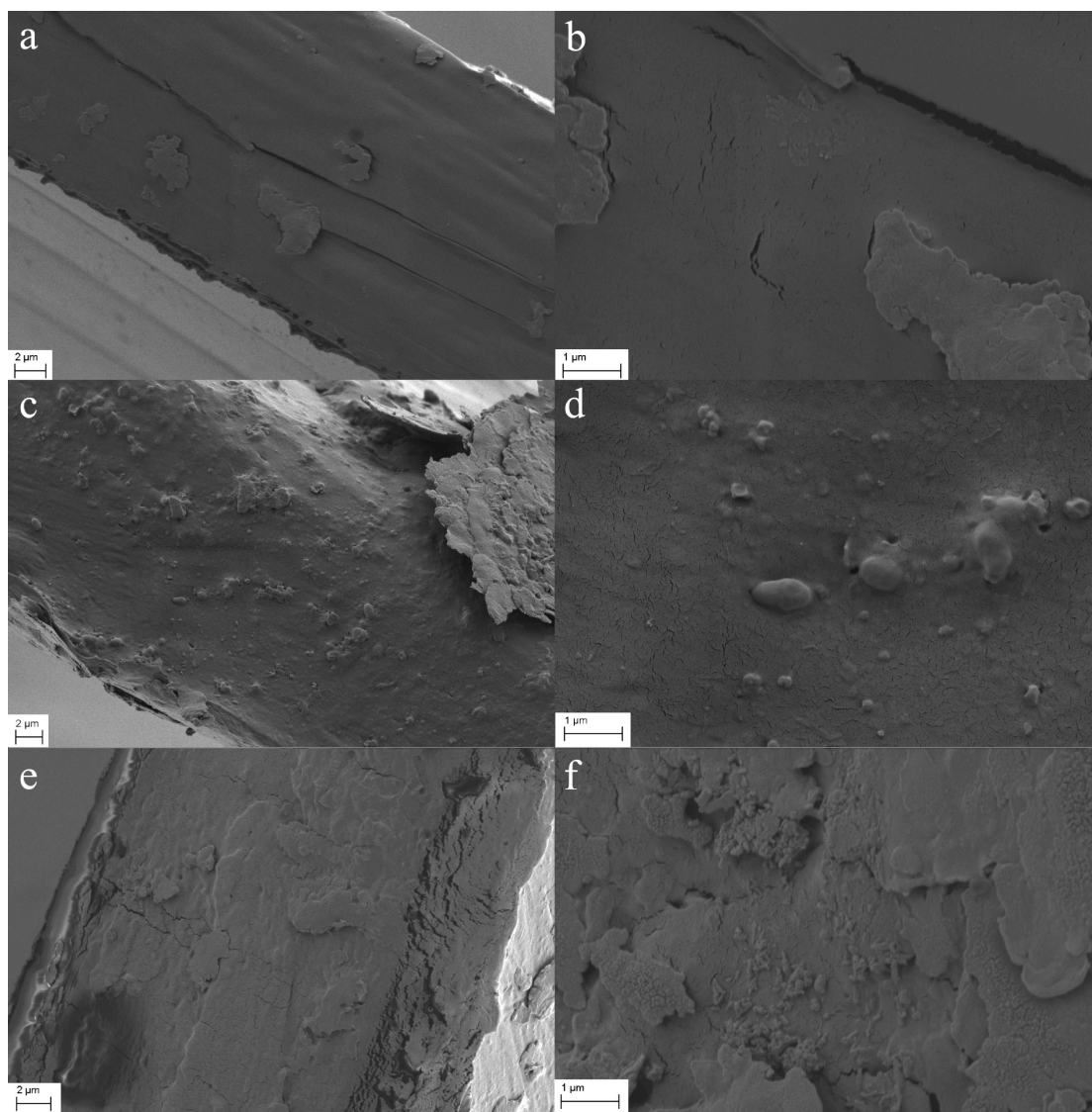


Figure 9. SEM pictures showing: (a) pure PLA at 8 160x magnification, (b) pure PLA at 30 000 x magnification, (c) PLA with 5% (w/w) NCC at 6 910x magnification, (d) PLA with 5% (w/w) NCC at 30 000x magnification, (e) PLA with 10% (w/w) NCC at 8 980x magnification and (f) PLA with 10% (w/w) NCC at 30 000x magnification.

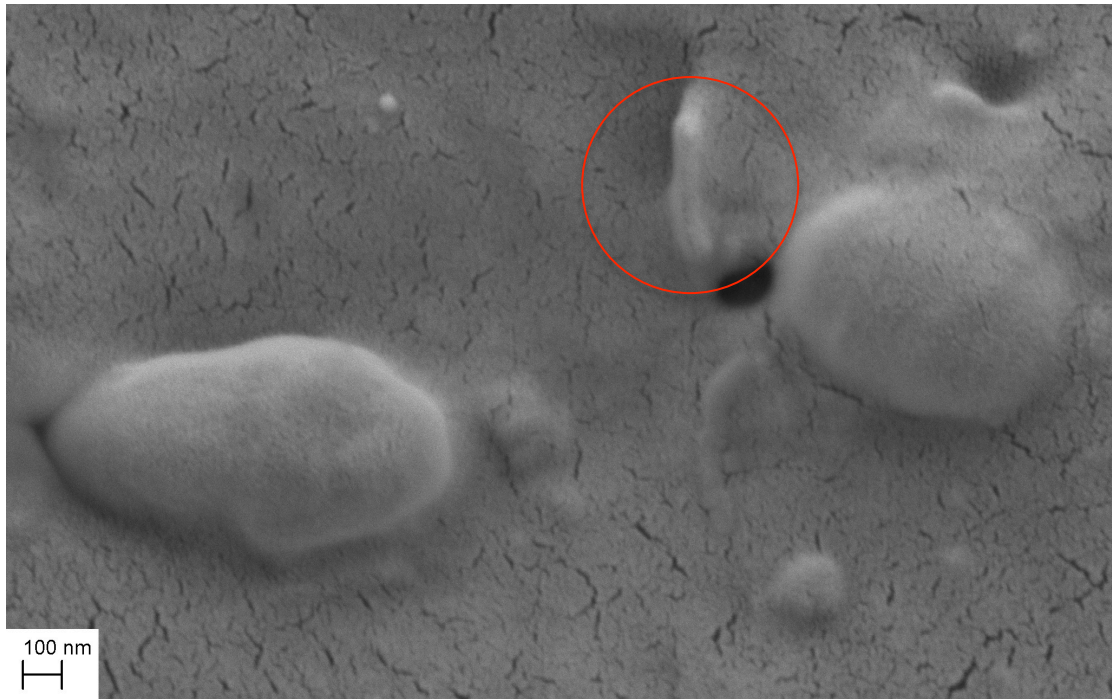


Figure 10. A SEM image of the film with 5% (w/w) NCC at 100 000x magnification, where one single NCC fiber can be seen.

5. Discussion

5.1 Permeability experiments

As seen in figure 6, the water permeability is almost twice as high in pure PLA compared to the film with 5% (w/w) NCC, which implies that small amounts of NCC lower the water permeability of poly(lactic acid). However, in the films with a higher NCC content, the permeability is higher compared to pure poly(lactic acid). This means that a permeability minimum is probably located at a concentration below 7.5 % (w/w) NCC, above which the permeability increases with more NCC.

The variations in water permeability with NCC content means that it is possible to fine-tune the water permeability by changing the amount of NCC in the material. The water permeability in turn influences the degradation time of the material; if it is very permeable towards water it degrades faster than if it is relatively impermeable. This implies that the NCC concentration that gives the lowest water permeability would give the longest degradation time, longer than for pure PLA, and that a high NCC concentration gives shorter degradation time.

Considering the error bars in the permeability results in figure 6, they increase with NCC concentration. This increase is probably due to that variations in amount and distribution of NCC becomes more evident when the relative amount of NCC increases. It has also been observed that more NCC leads to increased NCC aggregation in the film.

5.2 Differential Scanning Calorimetry

From the DSC results, it can be seen that the films are almost totally amorphous upon heating, and the difference between the films are very small compared to the errors. Also, since the crystallinity is calculated from melting and crystallization peak areas in a DSC thermogram, the human factor when drawing the baseline might cause small variations. Therefore, the difference is too small to be significant. The results imply that the crystallinity of PLA is not affected to any larger extent by the presence of NCC. It also indicates that the difference in water permeability is not due to differences in crystallinity between the films. The crystallinity results are confirmed by a literature search, for example: Annur and co-workers [33] have used the same PLA (NatureWorks Ingeo 3051D) for extruding films that also showed to be totally amorphous and Tábi et al [34] has observed significant crystallinity first after annealing the polymer at enhanced temperature. Crystalline regions of poly(lactic acid) degrades slower than amorphous, due to that they are impermeable towards water [13]. Therefore, annealing the material at elevated temperatures could result in a prolonged degradation time.

According to the poly(lactic acid) review by Henton et al [4], T_g is found in the interval 45-65° for PLA that contains a mixture of the two stereoisomers and T_m should be between 130-170° C. This correlates well with the obtained results. Anuar and co-workers [33] have as stated above used the same PLA, they have observed a glass transition at 60° C and a melting point at 150° C. The reason behind the lower values obtained in this project can be several; the glass transition can be difficult to detect properly and also depends on variables such as sample preparation, heating rate and thermal history [35].

5.3 Dynamic Mechanical Analysis

From the DMA results in figure 7 and table 2, it is determined that the modulus increases with NCC content and also that NCC makes the modulus increase with air humidity. Therefore, filling PLA with NCC seems to be a good idea to avoid a decreased modulus when the material is going to be used at high air humidity. The reason why pure poly(lactic acid) becomes less elastic at increased humidity is probably that the material takes up water and becomes plasticized. Many plastics behave in this way in contact with water [28].

Anuar et al. [33] have done a temperature sweep with DMA for the same PLA, although extruded and not casted. They obtained a storage modulus of 2.2 GPa at 50°C, and somewhat higher storage modulus at 25° C, but no value is reported for that temperature. This indicates that our DMA values are relevant and probably accurate.

5.4 Scanning Electron Microscopy

Studying the SEM images in figure 9, and 10, the larger spherical particles observed are probably NCC that has aggregated during the film production. Single nanofibers were also detected, which means there is also non-aggregated NCC present in the films. The aggregation might have been avoided if the resuspended solutions were sonicated after each step in the solvent exchange. Another way to avoid the aggregation could have been to put the NCC solution on stirring after the solvent exchange.

Considering the film with pure PLA, it looks smooth and homogeneous, this means that casting is a viable production method for PLA films. Also, Tábi et al [34] has used the same PLA and have obtained very similar SEM pictures for extruded PLA films.

In summary, the results from the permeability experiments and SEM have led to a theory regarding how water transports through the material. The SEM images taken at the cross-sections of pure PLA shows that the material is homogeneous, meaning that no structural differences inside the material have been discovered. In a water permeable homogeneous material, water can take any diffusion path since no part of the material is preferred. In the composites however, the material also contains NCC and there are several possible paths to diffuse due to the presence of NCC. Based on the SEM images showing the cross-sections of the films containing NCC, it is believed that NCC is present both as aggregates and as single NCC fibers. The surface of nanocellulose fibers, prepared by hydrolysis of microcrystalline cellulose in sulphuric acid, are strongly hydrophilic, and the adhesion between the obtained NCC and PLA is reported to be bad [36]. This leads to the theory that water prefers to be in the interfaces between NCC and PLA. In these interfaces, the water transport is also believed to be faster since water can follow the interfaces instead of diffuse randomly. When the films contain 7.5 or 10% (w/w) NCC, the water can transport larger distances in the interfaces which lead to the higher permeability observed. However, in the film with 5% (w/w) NCC, both the amount and the aggregation of NCC have decreased. The interfaces are still believed to be the most favourable place for the water molecules, and the increased average distance between the particles means that the diffusion path between each interface is longer. Also, the water transport is believed to be delayed since leaving the interfaces is not favourable. This leads to a decreased mass transport rate through the film, which then is observed as a lower permeability.

From the DMA results, the conclusion is drawn that water acts as a plasticizer for PLA. However, when NCC is present in the material the plasticizing effect has not been observed. The reason behind why the material is no longer plasticized is because most of the water that the material has taken up prefers to be in the interfaces instead of in the PLA phase. This is supported by the theory presented above.

6. Conclusion

The main purpose of this thesis work was to investigate whether reinforcement of PLA with NCC affects the water permeability of casted films. It has been determined that the presence of NCC within the material affects the water permeability, to which extent depends on the NCC concentration. Based on the permeability results, it is believed to exist a permeability minimum somewhere below 7.5% (w/w) NCC. Since PLA degrades by water, decreased water permeability should decrease the degradation rate. Therefore, the existence of a permeability minimum means that the lifetime of the material hopefully can be prolonged.

An additional purpose was to investigate how mechanical properties of the material were affected by increased air humidity. The storage modulus of poly(lactic acid) has been seen to increase when it is reinforced with NCC. Further, when the humidity is increased, the storage modulus does not decrease when PLA is reinforced with NCC. Instead, the elasticity of the material is enhanced. Therefore the material seems promising to use in different parts of the world, where humidity can vary.

7. Future Work

Some suggestions on how to further investigate and gain a deeper understanding of the water transport in poly(lactic acid) and nanocrystalline cellulose composites are presented here. Enhancing the dispersion of NCC in the film and avoiding aggregation would probably improve the mechanical strength further. Also, the material would be more homogeneous and the measurement errors from the permeability would probably decrease. Two possible solutions are suggested in this thesis. The first is to sonicate the solution after each centrifugation step during the solvent exchange process. The other would be to after the solvent exchange has been completed, put the NCC solution on stirring for 24 hours.

Considering the diffusion cell experiments, it would be interesting to investigate whether the water transport can still be described by equation 1, which is linear, if the experiments are allowed to continue for a longer time. Also, it would be interesting to determine at which NCC concentration the suspected minimum in water permeability is located. This would be investigated through additional diffusion cell experiments

The effect of crystallinity on the water permeability could also be investigated. To test this, the material can be annealed at enhanced temperatures before the diffusion cell experiments. It is important that the crystallinity has to be controlled by for example differential scanning calorimetry.

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