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Composites with surface modified cellulose nanocrystals

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LINUS WIKELUND

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Composites with surface modified cellulose nanocrystals (CNC)
LINUS WIKELUND

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Abstract

Cellulose is the most abundant polymer in nature and has several benefits like its strength, cost, biodegradability and thermal stability. It could be used in many applications such as packaging, textiles or as reinforcement in a polymer matrix. Today's requests on a renewable biobased material could shift the attention to using cellulose as a reinforcement in polymers to achieve better mechanical properties.

Crystalline nanocellulose (CNC) has a smaller size which makes them easier to mix and increase the contact area between the reinforcement and the matrix due to the large surface to size ratio. The surface of CNC is hydrophilic and most polymers are hydrophobic which makes the interaction between them a challenge for making an useful composite. Surface modification of CNC to increase this interaction has been the focus in this study.

CNC has been produced with a yield of 78,6% and a sulphate content of 360 µmol/g determined by conductometric titration. The proton on the sulphate group was switched for a sodium and a triethanolamine (TEOA). It was modified with synthesized 1,1' -dihexyl-3-hydroxyazetidinium chloride (Az-DHA, both open and closed form), 1,1' -dibenzyl-3-hydroxyazetidinium chloride (Az-DBA) and an alkyl ketene dimer (AKD). These reactions were confirmed with Fourier transform infrared spectroscopy (FTIR) and after freeze-drying and grinding they were investigated with thermogravimetric analysis (TGA). Removal of the proton on the sulphate group was the biggest factor that affected the thermal stability.

Polylactic acid (PLA), polypropylene (PP) and low-density polyethylene (LDPE) was examined as matrices. Mixing the polymer in an extruder with 5 % CNC was challenging due to aggregation of the CNC. Mixing with the CNC manufactured by CelluForce worked better due to the finer particles. When PLA and AKD was mixed with the polymer, the composite turning black as a result of too bad thermal stability.

No tensile testing could be done on a composite with PP due to the brittleness. For both LDPE and PLA a CNC reinforcement made it break at a lower elongation both with modified and unmodified CNC. The bad mixing is a possible main reason for this. For LDPE, the modulus was highest for the one modified with Az-DHA which made it stiffer and reduced its elongation before breakage.

The mixing has to be the focus in the future to achieve better properties. A lower concentration of CNC in the matrix should be evaluated and the best possible extrusion method needs to be explored. Grinding the polymer by hand as in this research won't give small enough particle for this application.

Acknowledgements

I want to thank Gunnar Westman for his guidance during my work and his emphasis on that the project should be both interesting and fun for me to accomplish. Thank you for your talent of explaining complex chemistry in a way I understand.

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1 Introduction

1.1 Background

In a world with a growing demand for materials based on renewable resources, cellulose as a strong and light raw material could be a particularly interesting option. Polymer composites with cellulose-based reinforcements aim for combining the best properties of both materials [1]. There are however challenges with the use of cellulose as reinforcement in a polymer matrix such as poor mixing where the polymer that normally is hydrophobic while cellulose is hydrophilic. One solution is to chemically modify the surface of the fiber to improve interaction with the matrix. During the last years the interest in nanocellulose has increased, as the small size (approximately 10 nm in thickness and a length of a few hundred nanometers) of the cellulose nanocrystal (CNC) make the surface to volume ratio rather high.

The polymer used is requested to be biodegradable and biobased. Polylactic acid (PLA) is one of the most popular polymers produced by renewable resources, normally corn or sugarcane that is fermented to the monomers [2]. The properties of PLA are similar to PET and polystyrene, but PLA is more expensive to produce. CNC as a reinforcement could improve the mechanical properties and thermal stability of the material. Low-density polyethylene (LDPE) as the matrix will be examined as well as polypropylene (PP).

1.2 Aim

The purpose of the project is to produce a composite with good mechanical properties and thermal stability. CNC is produced and characterized with Fourier-Transform Infrared Spectroscopy (FTIR), conductometric titration and thermogravimetric analysis (TGA). It is reinforced in a PLA matrix by being mixed, melted and pushed through an extruder. This formed composite is tensile tested and thermally verified with thermogravimetric analysis (TGA). The process is repeated but with a surface modified version of CNC. Several surface modifications are examined to find the one giving the best mechanical properties. Both LDPE and PP as matrices are evaluated with the goal both to find a composite with better properties and that is cheaper than the quite expensive PLA.

1.3 Demarcations

Cotton is the only source of CNC that is examined in this thesis and only at only 5 weight percent in the polymer. Only PLA, PP and LDPE will be explored. There may be other ways to synthesize CNC that is more environmentally friendly that is not investigated. Only one type of extrusion procedure is used. The batch of CNC is the same throughout the research with the same sulphate content at start.

1.4 Problem description

Does a modification of the CNC as a reinforcement in PLA improve the thermal and mechanical properties of the composite? How does the different kinds of surface modification influence the thermal and mechanical properties? How does the chemical structure of the CNC change with the reinforcement? How is the choice of polymer affecting the mixture and properties of the composite?

2 Theory

2.1 Polymer matrix

Three different polymer matrices will be used in this research with CNC as reinforcement: polylactic acid (PLA), low-density polyethylene (LDPE) and polypropylene (PP).

2.1.1. Polylactic acid (PLA)

PLA is one of the most commonly produced bioplastics in the world and the most used for 3D printing [2]. It could be made by and ring-opening and polymerizing of lactide, (a ring closed dimer of two lactic acid units). The structure of PLA is shown in figure 1. The mechanical properties of PLA are between polystyrene and PET with a glass transition temperature between 60 and 65°C and a melting temperature between 130 and 180°C. The properties could be changed due to the chiral monomer of lactic acid. It exists in poly-L-lactide (PLLA) and poly-D-lactide (PDLA). For example, the melt temperature of PLLA could be increased by 40-50°C by adding PDLA that will act as a nucleating agent and improve the crystallinity rate of the polymer. Different properties could be obtained by different ratios between the two stereo isomers. The properties of the PLA used in this research can be find in appendix A.

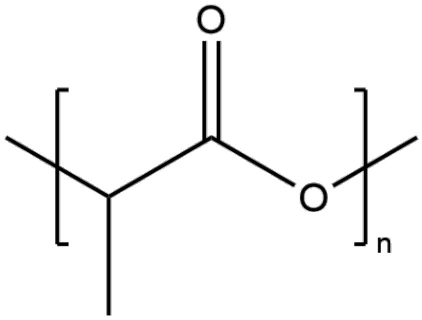


Figure 1. Structure of polylactic acid (PLA).

2.1.2. Low-density polyethylene (LDPE)

Polyethylene is the most common plastic in the world and consists only of carbon and hydrogen [3]. Its basic strcutrure is shown in figure 2. It could be classified into three different main groups: high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). At HDPE the main chain is essentially linear with a few shorter carbon chains on. It's produced with a catalyst at lower temperatures and pressures and melts around 120-135 °C. LDPE is produced by radical polymerization at higher temperatures and pressures. Longer carbon chains are attached to the main chain of LDPE. It melts around 95-115 °C and has a lower crystallinity than HDPE. LLDPE is chemically somewhere between these two types. LDPE has a low cost and is used to produce containers, dispensing bottles, tubing, plastic bags and more. One of the drawbacks is its low stiffness and tensile strength. The properties of the LDPE used in this research can be find in appendix A.

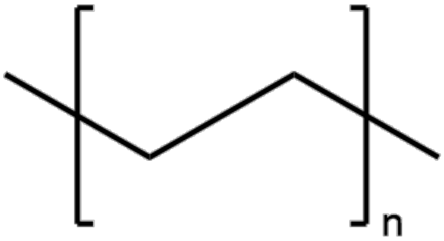


Figure 2. Structure of polyethylene (PE).

2.1.3. Polypropylene

Polypropylene (PP) is the second most produced plastic after polyethylene. It’s made up by a carbon chain where every other carbon atoms is bonded to two hydrogen atoms and every other is bonded to one hydrogen and one methyl group, as shown in figure 3 [3]. It’s produced by chain growth polymerization of propylene monomers [4]. It’s cheap but very brittle if it’s unmodified. The mechanical properties depend on several factors including molecular weight distribution and tacticity and crystallinity. An isotactic polypropylene molecule has all methyl groups on the same side of the carbon chain. This leads to higher crystallinity and a stiffer material. Isotactic polypropylene has a melting point between 160-170 °C.

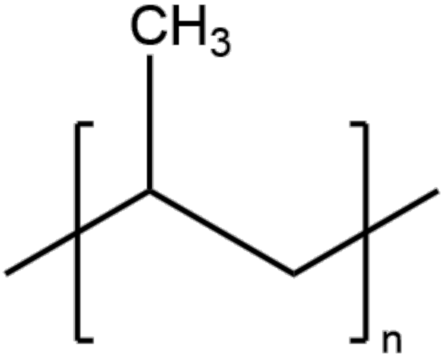


Figure 3. Structure of polypropylene (PP).

2.2 Cellulose

Cellulose is the most common organic compound on earth and is also a bio based raw material like PLA, coming mainly from wood and cotton which consist of cellulose to a large extent [5]. Common products produced by cellulose are paper and paperboard. It’s not soluble in water and has a melting temperature at 260-270°C. Cellulose consists of D-glucose units bound with β-1,4-glycosidic bonds as shown in figure 4. Hydroxyl groups on the chain form hydrogen bonds to oxygen on the same or another chain. The formed fibrils give the cellulose a high tensile strength and is therefore making wood stronger as it is acting as a reinforcement.

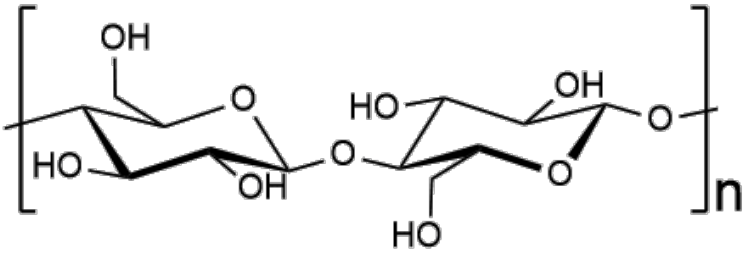


Figure 4. Structure of cellulose.

2.3 Cellulose nanocrystal (CNC)

The fibrils of cellulose contains both amorphous and crystalline regions [5]. A strong acid could be used to hydrolyze the amorphous parts to produce short cellulose nanocrystal (CNC or NCC) that are only a few 100 nm long. This is one of three types of nanocellulose. The other two are bacterial nanocellulose (nanocellulose produced by bacteria) and cellulose nanofibers (CNF or NFC). CNF are unlike CNC a few micrometers long but also a few nanometers wide. In addition to being made from renewable raw materials CNCs are also relatively stiff, strong and inexpensive.

2.4 Azetidinium salts

Azetidium salts consists of a four atom ring with two end groups at the 1,1-nitrogen position and one hydroxyl group at the 3-position [6]. The nitrogen has a positive charge and a negatively charged chloride ion act as a counter ion. Figure 5 is showing the structure with two hexyl groups as end groups. The ring strain and the charge makes the molecule rather reactive and it has been shown in previous researches that it reacts well with carboxylates, amines, phenols, phosphorus nucleophiles and sulfate esters. When prepared, a less thermodynamically favorable open form of the molecule could be formed as well. The end groups could be changed to obtain different properties of the molecule.

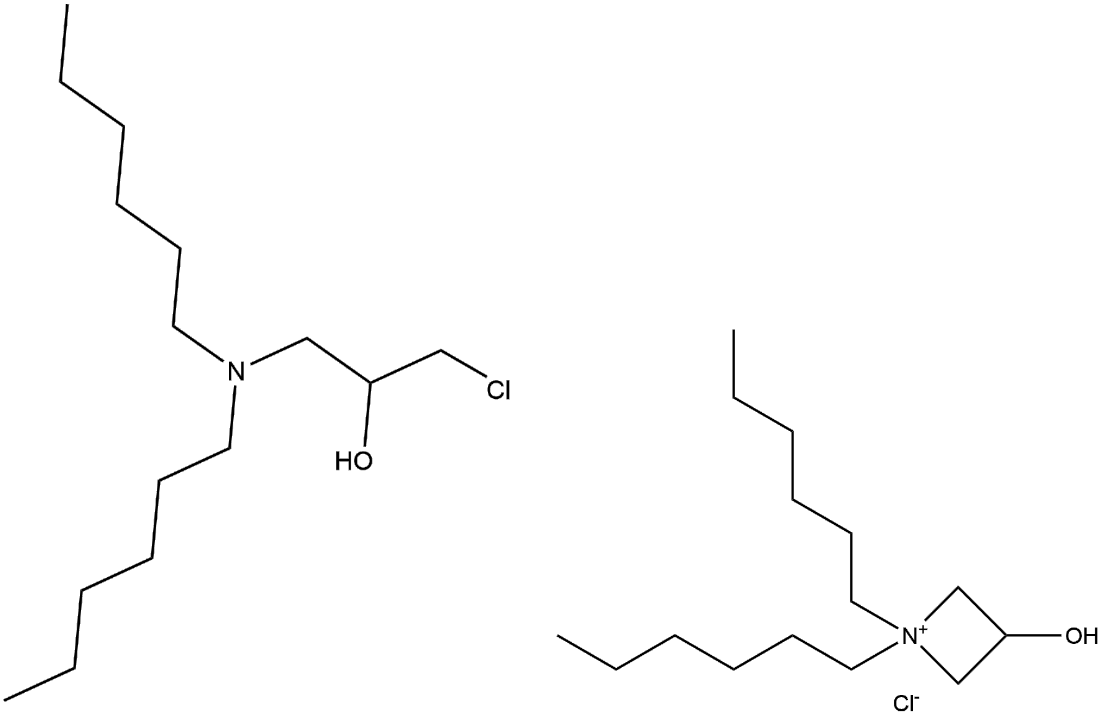


Figure 5. Structure of the open (left) and the closed form (right) of 1,1' -dihexyl-3-hydroxyazetidinium chloride.

2.5 Alkyl ketene dimer (AKD)

Paper is to a great extent made of cellulosic fibers [7]. However, cellulose is hydrophilic and paper does often need to be water-resistant. Chemical additives are introduced to increase the hydrophobicity, known as internal sizing of paper, to avoid spreading and absorption of the liquid. One type of molecules used to make the material hydrophobic is the alkyl ketene dimers (AKDs). The compound is based on the 4-membered ring system of oxetan-2-one with two attached alkyl chains, where one of the chains is double bonded to the ring. It reacts with the hydroxyl group on the cellulose via an esterification reaction. The AKD used in this research will have two butyl groups, as shown in figure 6.

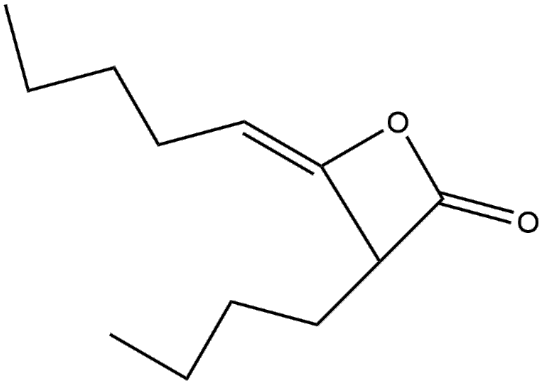


Figure 6. Structure of AKD with two butyl groups.

2.6 Surface modification

When treating cellulose with sulphuric acid to obtain CNC some hydroxyl groups are converted to negatively charged sulphate ester groups as seen in figure 7 [8]. These will improve the stability of the water dispersion of cellulose but on the other hand decrease the thermal stability. One way to remove these groups is to sonicate the suspension. Another way to increase the temperature of degradation was reported by Sahlin et al. where the surface of CNC was modified by reacting azetidinium salts to the sulphate groups [9]. By doing this, according to Sahlin et al, the CNC is hydrofobized and the compatibility between the reinforced CNC and the polymer matrix is improved when azetidinium salts with alkyl chains are grafted on the CNC. This would result in a better dispersion the CNC in the polymer. AKDs could also be used to hydrophobize by forming a ketone ester structure on the CNC surface and it may increase the compatibility with the polymer matrix. These react with the hydroxyl and a CNC with fewer sulphates and more hydroxyl groups is therefore requested. Researches from Li et al. found that AKD-modified CNC as a reinforcement would decrease the thermal stability a little bit but improve the mechanical properties [10].

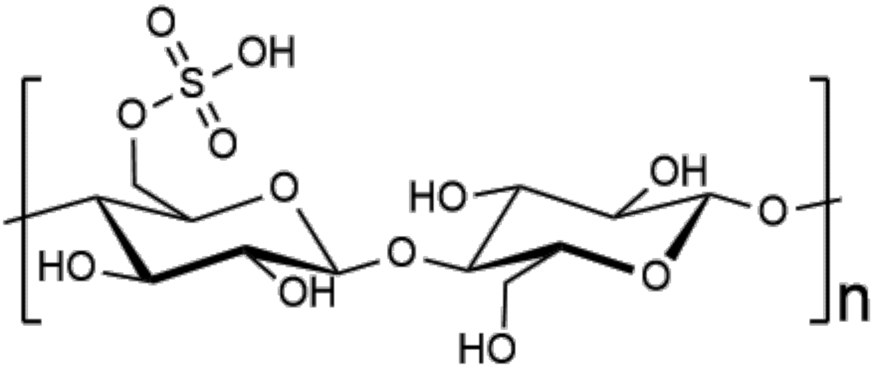


Figure 7. Structure of sulphated CNC.

When modifying a CNC surface with an azetidinium salt, it should be the same number of moles of additive as sulphates present on the surface (determined in conductometric titration). An excess would lead to impurities and should be avoided. AKDs probably react with the hydroxyl groups, and the amount of AKD should therefore be the same as the amount of hydroxyl groups. This is estimated by Eyley et al. to be 0,51-0,59 mmol/g CNC [11].

2.7 Composites

Several researchers have during the recent years found that CNC and CNF as a reinforcement in a polymer matrix could improve the stiffness, strength and toughness [12]. In this study CNC will be used to decrease the probability of aggregates due to the entanglements of the longer CNF. The small size of CNC will lead to a high contact area between the reinforcement and the matrix.

2.8 Analyzing methods

Several analyzing methods have been used in this study. FTIR has been used continuously both for analyzing CNC and the composites. TGA and conductometric titration is used to investigate the CNC and tensile testing to determine the mechanical properties of the composites. NMR is used during the project to confirm hypothesis with model reactions.

2.8.1. Fourier-transform infrared spectroscopy (FTIR)

The idea behind spectroscopy in general is to measure at what wavelengths a certain sample absorbs light [13]. For FTIR the vibrational part of the infrared region is of interest. This range from 2.5 µm and 25 µm, corresponding to the wavenumber 4000-400 cm^{-1} which is the inverse of the wavelength in centimeters. The absorption process is quantized, meaning that only radiation at certain wavenumbers (energies) will be absorbed. Only molecules that change their dipole moment over time are capable of absorbing infrared radiation. The given spectrum could be viewed as a fingerprint of the investigated molecule. More importantly, it's used to recognize functional groups in a molecule, since the functional groups have a corresponding absorption range.

2.8.2. Conductometric titration

Conductometric titration is used to determine the amount of sulfate groups on the CNC surface [14]. The protons functioning as a counterion to the sulphate will be consumed when adding NaOH until all of them consumed and the suspension is neutralized. Keep adding NaOH will lead to an excess of NaOH and increased pH. The amount of NaOH added when neutralized corresponds to the amount of surface sulphate groups, where the pH rises rapidly. At the same time the conductivity will be measured, which will reach its lowest value when the least number of free ions are occurring. This will also be the point where the suspension is neutralized and the amount of sulphate could be calculated as shown in equation 1.

$$\frac{V_{NaOH} * c_{NaOH}}{V_{tot} * drymass} \tag{1}$$

where V_{NaOH} is the added volume of NaOH with the concentration c_{NaOH}. V_{tot} is the total volume of the sample, where the volume of the added base is viewed as negligible. The calculated amount of sulphate will be given in mol/gram of CNC. A lower dry content will improve the mixing due to a lower viscosity.

2.8.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a method where changes in weight is measured as a function of increased temperature [15]. The technique provides information about phase transitions, adsorptions, decomposition, oxidation and more phenomenons that are affecting the weight of the material. A material that is thermally stable in a certain temperature range will show no change in mass. The toughness of a material is calculated as the area under the weight-temperature graph.

2.8.4. Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) gives information of the number of distinct atoms of the studied atom type, normally hydrogen or carbon [13]. 1H and 13C could have two different spins, either clockwise (+1/2) or counterclockwise (-1/2), both with the same energy. In a magnetic field, the nuclear magnetic moment, generated by the charge and spin of the nucleus, could be aligned with the field or opposed to the field. Since the nucleus is charged, this creates an energy difference between the two spin states that is larger in a larger magnetic field. The nuclear magnetic resonance phenomenon occurs when a nucleus aligned with the field absorbs energy and change spin orientation. Nuclei don't have resonance at the same frequency due to that the surrounding of electrons differ and create different electronic environments. The nucleus is shielded by the electrons. This information is used to determine the structure of a molecule.

2.8.5. Tensile testing

In tensile testing, elongation as a function of force is measured in a stress-strain diagram [16]. Young’s modulus, stress and strain before break and toughness is determined. All dimensions will be measured to control for differences and the speed will be the same for all samples. A sample usually has two shoulders and a gauge. The shoulders are normally larger to make sure that the grip will be good enough and that the break will be in the gauge section. In this research however the shape will be rectangular. This shape is easier to create without utilities and all samples are more likely to be uniform.

3 Methods

3.1 Production of 64% sulphuric acid

0,94 l of sulphuric acid is measured in a graduated cylinder and poured into a dropping funnel. The funnel is checked and did not leak. 0,97 l distillated water is measured in the graduated cylinder and is poured into a round-bottomed flask. The funnel is adjusted to 90 droplets/minute in order to avoid sudden heat generation due to the exothermic reaction between sulphuric acid and water. A stirring rod is used to mix the solution every 30 minutes. Although no thermometer is used, the solution was kept at a low temperature according to how it felt to the hand.

3.2 Production of CNC

The CNC is prepared as described by Hasani et al [17]. The produced 64% sulfuric acid is held at 46°C with the help of the water bath set to 48°C. 200 g of Avicel is added slowly to the solution to avoid lump formation. The reaction occurred for 2 hours before terminated by pouring into 11 l of water. A temperature control is carried out every 30 minutes to keep the suspension at 46°C. The samples are then centrifuged for 10 minutes where the content in all four beakers weigh 600+/-2 g. After 10 minutes the solution is decanted, and new suspension is poured into the beakers to again reach 600+/-2 g. This is repeated until all the suspension is centrifuged, and the samples are weighed. To remove any sulfuric acid that might be left between the particles, water is added to reach 600+/-2 g of content, and a spatula is used to mix it and resuspend all particles in the water. These beakers are centrifuged once again, and the washing step is repeated with one additional centrifugation. The samples are weighed.

A dialysis step of the product is needed to remove any sulfuric acid left in the samples. The produced CNC is put into membranes which only let smaller molecules through. The membranes are knotted and placed in a bucket of water. Due to the concentration difference of sulfuric acid, the acid will diffuse out through the membrane to the water until equal concentration is reached. The water is then switched for new about three times per day until low conductivity (5 µm) is reached. Conductivity is measured with a conductometer halfway down in the bucket for 15 seconds before a stabilized value is noted before every water switch.

3.3 Measuring dry content

The measurement of dry content is made both in an oven and by a moisture analyzer. A few grams of the sample are put on three petri dishes that then is put into an oven at 55°C for 24 hours. The sample was weighed before and after and the dry content is calculated as

$$dry\ content = \frac{m_{dry}}{m_{wet} + m_{dry}}$$

where m_{wet} + m_{dry} is the weight before drying and m_{dry} is the weight after drying. As a way to increase the accuracy a moisture analyzer is used as well to calculate the same thing. A sample lighter than a gram is put onto a metallic plate in the instrument that dried the sample for 15 minutes and then measured the weight difference and thereby the dry content. This is repeated three times to give an as accurate result as possible.

3.4 Conductometric titration

A volume of 20 ml of the sample is requested with the mass percentage, or dry content, of 0.5% CNC in order to improve the mixing [14]. A higher dry content wouldn't make the mixing good enough and the added base wouldn't reach all of the surface. With an assumed density of 1 g/ml for the suspension and water, the volume of suspension could be calculated as

$$V_1 = \frac{w_2 V_2}{w_1}$$

where V_1 and V_2 are the volume of suspension before and after dilution respectively, and w_1 and w_2 are the dry contents of CNC in the suspension before and after respectively. The calculated volume V_1 is then diluted to 20 ml with 40 µl of NaCl to make the suspension conductive.

The suspension is poured into a beaker with a magnetic stirrer. A conductometer and a potentiometer is put in the suspension as well as a tube adding NaOH controlled by a computer that also monitored how the pH and conductivity is changing with time and with added volume of NaOH. The calculation of sulphate content is described in the theory section.

3.5 Surface modification

The CNC suspension is mixed with the amount of AKD or azetidinium salt as was given in the theory section during four hours at 70 °C. The suspension is poured into 10 ml plastic vials sitting in dry ice and acetone for 15 minutes. After that the vials are freeze dried for 72 hours and then grinded to a fine powder for 15 minutes per vial. The powder together with the polymer matrix is used in the extrusion step.

3.6 Extrusion

Two screws are mounted in the barrel and are driven by the motor. The extruder is closed and the bolts are screwed, and screwed again when the extrusion temperature is reached. 180 °C is used for LDPE and PLA while 170 °C is enough for PP to melt. Start by press ”feed up” and pour 2,5-3 ml of mixture into the feeder and then press ”feed down”. When the arm is all the way down, then press ”feed up” and pour in additionally 2,5-3 ml, which in total is the maximum volume that could be held in the extruder at the same time. Then press ”feed down”. Let it go for five minutes and change from ”cycle” to ”flush” to get the product out. Wait a few minutes, then switch to “cycle” and “feed up” and repeat by adding 2,5-3 ml of the mixture. Clean the extruder by adding 30 g of a cleaning polymer in batches of 3 g at 200 °C. Decrease to 110 °C, increase to 180 °C and the decrease again to 120 °C while switching between flush and cycle once per temperature. The different mixtures tried (all with 5% modified CNC in the matrix) are

- LDPE

- LDPE+ CF
- LDPE + CNC-H
- LDPE + CNC-Na
- LDPE + CNC-Az-DHA
- LDPE + CNC-Az-DBA
- PLA
- PLA + CF
- PLA + CNC-H
- PLA + CNC-Na
- PLA + CNC-Na + LA
- PLA + CNC-TEOA
- PLA + CNC-TEOA + LA
- PLA + CNC-Az-DHA
- PP
- PP + CF
- PP + CNC-Na
- PP + CNC-Az-DHA
- PP + CNC-Az-DBA

TEOA = triethanolamine
LA = lactic acid
Az-DHA = 1,1’ -dihexyl-3-hydroxyazetidinium chloride
Az-DBA = 1,1’ -dibenzyl-3-hydroxyazetidinium chloride
CF = CNC with sodium as counter ion manufactured at the company CelluForce.

Lactic acid is used in 4 weight percent to counteract the aggregation. Triethanolamine is an ion exchanger that has been proving to give easily handled films. After the extrusion, the produced pellets will be made into films with compression molding for 5 minutes at the same temperature as in the extruder.

3.7 Preparation of AKD

6,3 g (30 mmol) butyryl chloride is dissolved in 30 ml diethyl ether. The solution is magnetically stirred and cooled down to 0°C in a bucket with ice and water. A total of 6 g (60 mmol) triethylamine is added dropwise to the solution during a period of 20 minutes. A precipitation is formed and additionally 10 ml diethyl ether was added when the solvent evaporated. The sample is filtered after 24 hours and the filtrate is evaporated under reduced pressure to remove the solvent. The product is again dissolved with 3 ml diethyl ether and 3 ml hexane and put in a vial in the fridge over night in order to precipitate ammonium chloride. This is filtered once again and the solvent is evaporated using a rotary evaporator. NMR is used to determine the product using $CDCl_3$ as the solvent.

3.8 Preparation of azetidinium salts

5 mmol of dihexylamine (185,35 g/mol, 0,795 g/cm3) is dissolved in 20 g isopropanol according to the literature [18]. The solution is kept below 5 °C with storing the beaker in a bucket with ice. 5 mmol epichlorohydrin (92,52 g/mol, 1,18 g/cm3) is added dropwise for 20 minutes. The reaction runs at 70°C for four hours, is washed with diethyl ether and then the solvent is evaporated under reduced pressure. The obtained product is confirmed as 1,1’ -dihexyl-3-hydroxyazetidinium chloride (Az-DHA) with NMR analysis 1,1’ -dibenzyl-3-hydroxyazetidinium

chloride (Az-DBA) is also produced by using dibenzylamine (197,28 g/mol, 1,026 g/cm3) instead of dihexylamine. [19]

3.9 Tensile test

The composite samples are cut into 6 cm long and 1 cm wide pieces. Six pieces of each material are tested. The grip was 1 cm^2 on each end. A rate of 5 mm/min is used on an Instron 5565A. All composites with polypropylene were considered too brittle to measure.

3.10 Fourier transform infrared spectroscopy

The samples were analyzed with a Perkin Elmer Spectrum One FT-IR Spectrometer. 32 scans were made between 4000-400 cm^{-1} with a resolution of 1 cm^{-1}.

3.11 Thermal gravimetric analysis

The temperature started at 25 °C and was increased to 550 °C with a rate of 10 °C/min on TGA/DSC 3+ STARe System. Both modified and unmodified CNC is analyzed.

4 Results and discussion

4.1 Production of crystalline nanocellulose (CNC)

The production of crystalline nanocellulose gave a yield of 78,6% and it had a dry content of 4,74%. Calculations are shown in appendix B. The sulphur content is determined to 360 µmol/g.

4.2 AKD synthesis

The synthesis of AKD with two butyl groups is verified with NMR seen in figure 8.

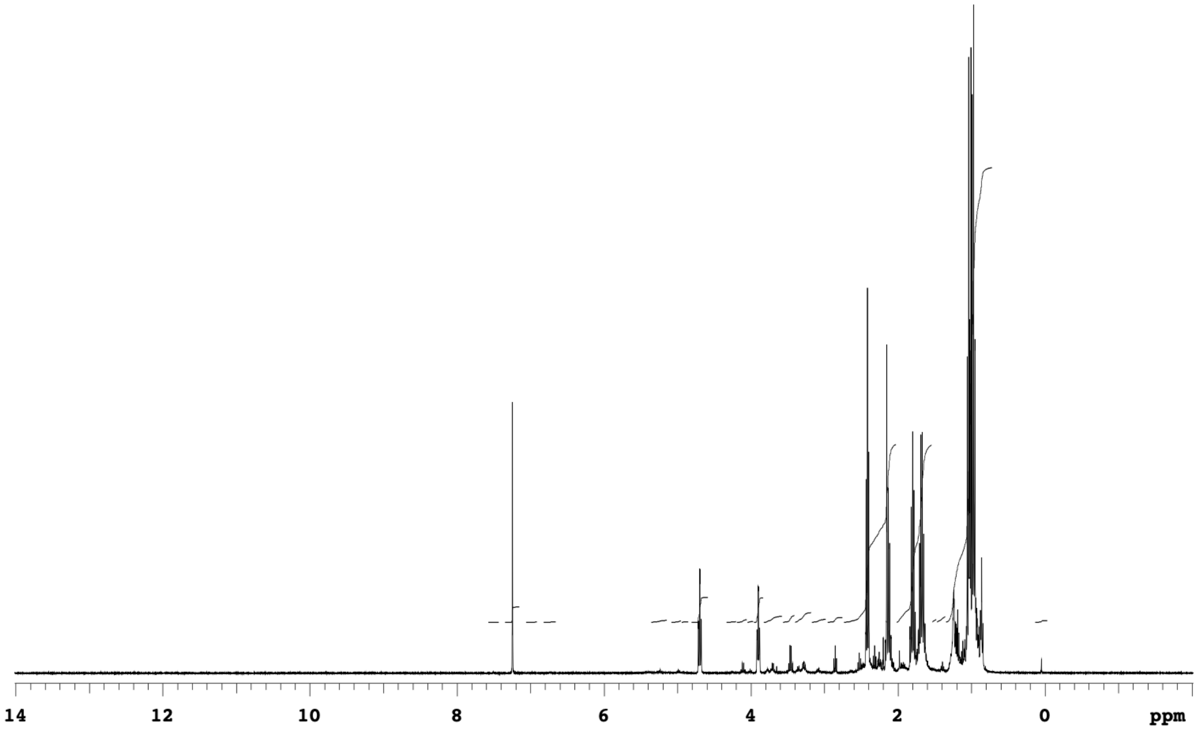


Figure 8. ^{1}HNMR spectrum of AKD.

A similar spectrum is modelled in a software and does not match completely. However other studies have shown spectra like this one and the software is regarded as not good enough at modeling [20]. The synthesis is therefore considered to be working.

4.3 Azetidinium-modified CNC

Unmodified CNC and samples of CNC modified with the open-form and closed-form of 1,1' -dihexyl-3-hydroxyazetidinium chloride (Az-DHA) is analyzed with FTIR in figure 9 together with microcrystalline cellulose. The broad band to the left with a wavelength of 3600-3000 cm^{-1} corresponds to O-H stretching while the peak at 2900 cm^{-1} corresponds to the C-H bonds [18]. The vibrations and stretching vibrations of C-OH leads to a peak at 1050 cm^{-1} and the detected peak at 1160 cm^{-1} is a C-O-C bond. At about 810 cm-1 the peak is expected to be shifted due to a surface modification at the C-O-S stretching. A shift to a lower wavenumber means that the mass of the atoms bonded has increased, here from a hydrogen atom to an azetidinium salt. MCC has no peak there since no sulphates are present. It's also expected that an ion exchange where the hydrogen is switched for a sodium ion or a tetraethyl ammonium (NEt_4) ion will lead to a shift. FTIR for CNC with different counter ions and with Az-DHA is shown in figure 10.

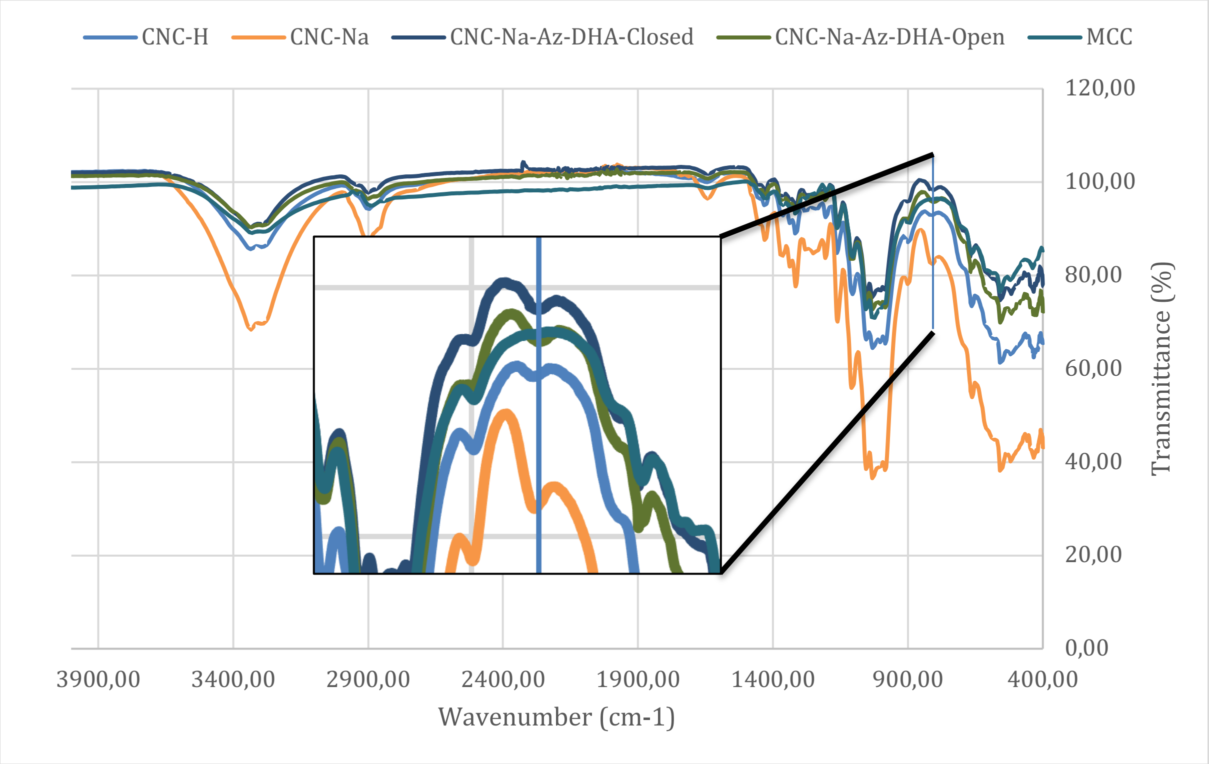


Figure 9. FTIR measurements on MCC, unmodified and modified CNC with sulphur peak marked at 810 cm^{-1}.

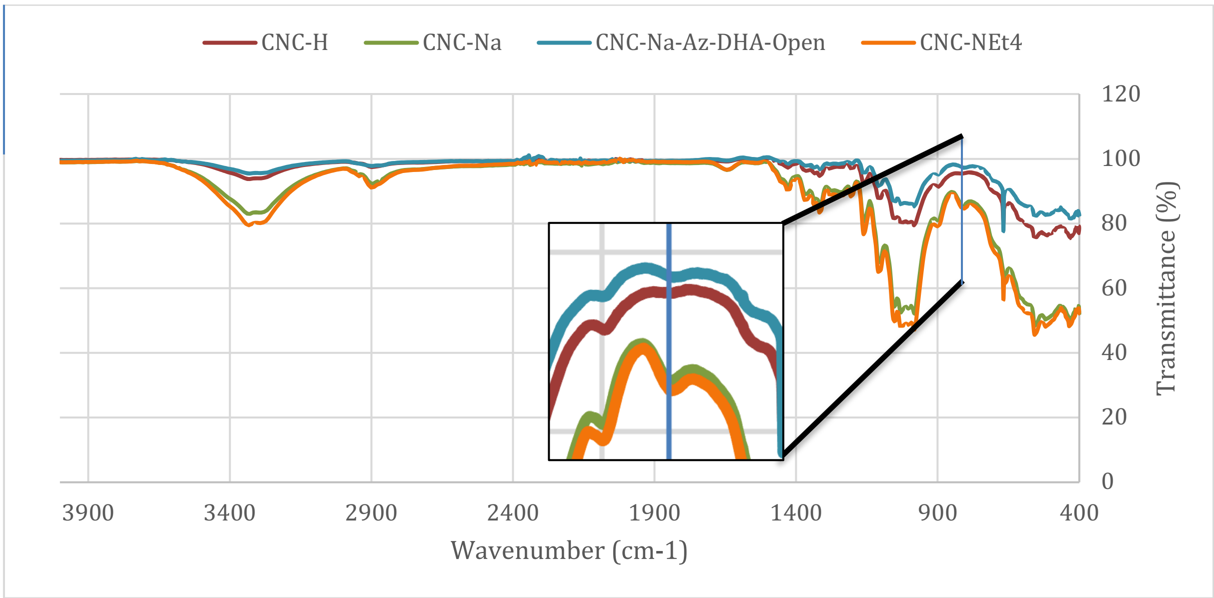


Figure 10. FTIR measurements on modified with open form of 1,1' -dihexyl-3-hydroxyazetidinium chloride (Az-DHA) and unmodified CNC with Na, NEt_4 and proton as a counterion. Sulphur peak is marked at 810 cm^{-1}.

Even though the difference in mass is large the shift is smaller than expected, or not noticeable at all.

The thermal stability of modified CNC is evaluated using TGA and is shown in figure 11.

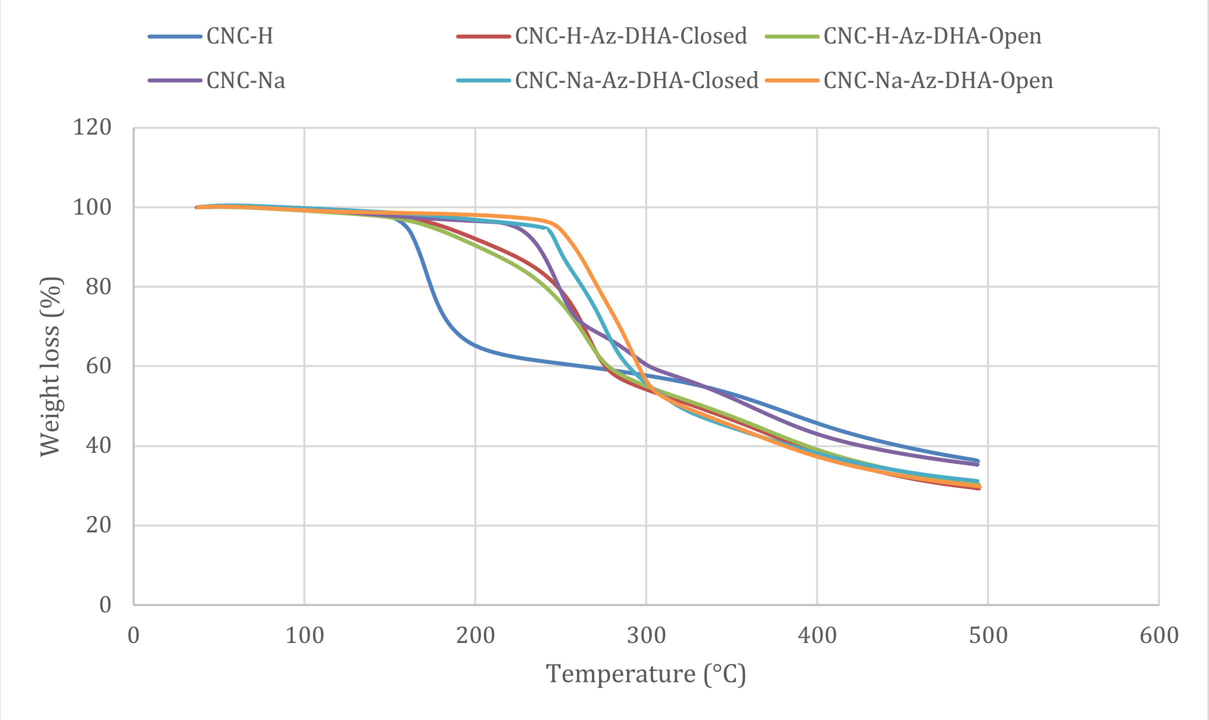


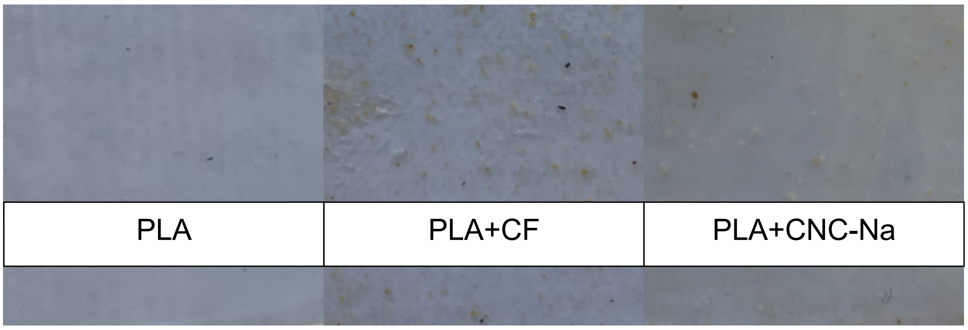
Figure 11. TGA measurements with modified and modified CNC both with Na and proton form of CNC. It's modified with both the open form and closed form of 1,1' -dihexyl-3-hydroxyazetidinium chloride (Az-DHA).

From the graph it's clear that the protonated CNC doesn't resist heat as good as the ones with sodium as a counter ion, and that the open form of Az-DHA resists heat better than the closed form. Wang et al. have described the degradation as the pyrolysis of CNC catalyzed by the acid sulphate groups [19]. An ion switch or through grafting of the Az-DHA will remove the acidic proton and therefore increasing the degradation temperature. The decrement at lower temperatures is considered to be the evaporation of water.

4.4 Composites

4.4.1. Visual inspection

Pictures taken of all composite films are shown in figure 12.



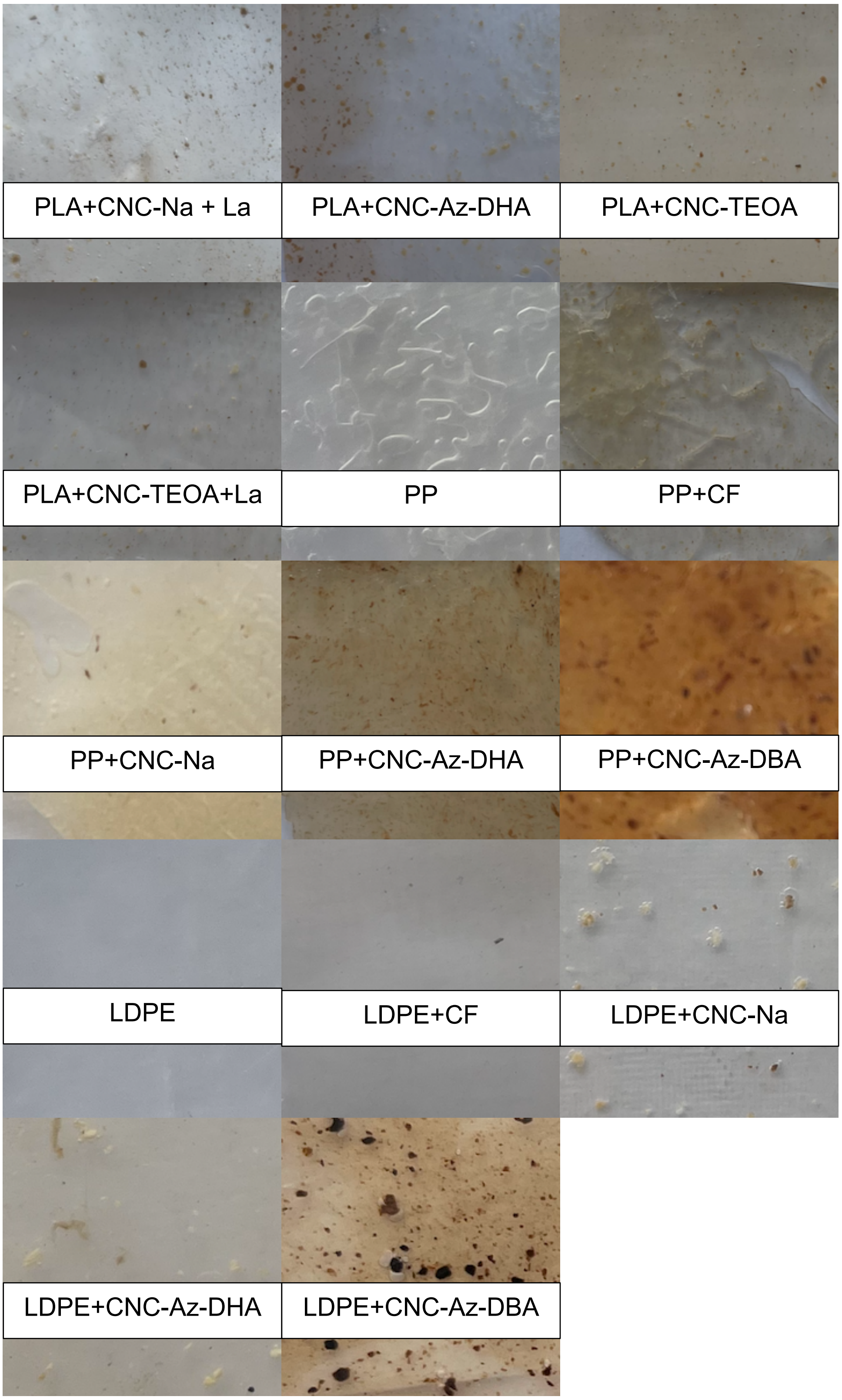


Figure 12. All films produced by extrusion and compression molding.

It’s clear that aggregation is a huge problem for all films except for LDPE+CF. The CNC produced by CelluForce is a finer powder than the one in produced for this study which makes the dispersion better. The modification doesn’t seem to improve the dispersion as expected. Other factors affecting the tensile test is bubbles in the sample and jacks due to cutting.

The sample with CNC modified by AKD in a PLA matrix turned black during the extrusion. It was not possible to run TGA on the AKD during this research to determine the thermal stability, but the previously cited article from Li et al. succeeded to make a composite with an almost nine times higher tensile strength with the same weight percent as used in this research [10]. They did not however extrude the composite, but dissolve PLA in DMSO at 70 °C and added AKD-CNF during magnetic stirring. Another important difference is that they used CNF that is a lot longer than CNC. According to their own TGA data the composite should be stable enough to handle the high temperatures of the extruder.

Polypropylene is not further investigated due to its brittleness. The idea was to see how different modifications would improve the thermal stability and the oxidation induction time (OIT) as suggested by Ye et al, but that hasn't been possible during the research [21].

4.4.2. Tensile test

For the LDPE samples it's clear in figure 13 that the dispersion has an impact on strain at yield when the lumps act as starting points for the break. The modified CNC though leads to a higher strain at break compared to the unmodified, and it gives the highest modulus. This could be seen in table 1. The material has become stiffer and it doesn't deform that much before breaking, probably because of a stronger interaction between the modified CNC and LDPE.

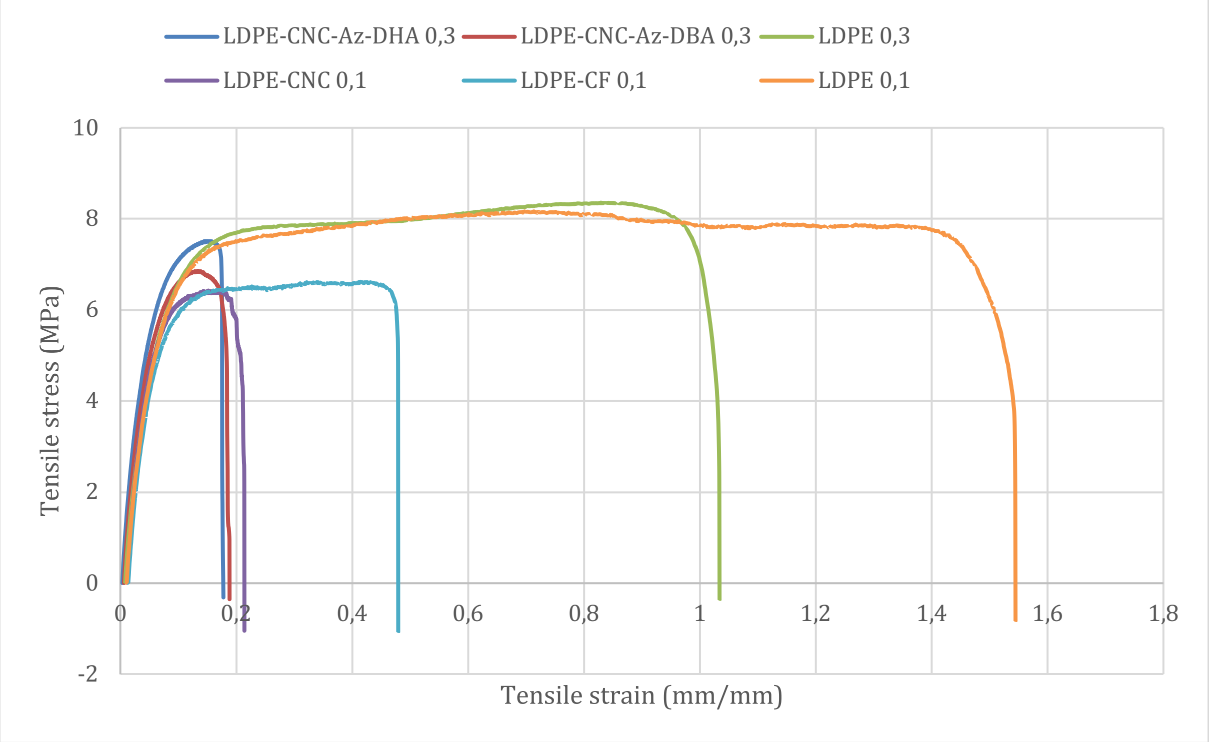


Figure 13. LDPE composites tensile test with modified and unmodified CNC with 0,1 mm and 0,3 mm in thickness.

Table 1. Key values from tensile test with LDPE composites including standard deviation between all six samples.

	Modulus (Automatic Young's) (MPa)	STDEV	Tensile strain at Yield (Zero Slope) (%)	STDEV	Tensile stress at Yield (Zero Slope) (MPa)	STDEV	Toughness (MPa)
LDPE 0,1	152,06	8,97	69,75	21,74	7,99	0,47	11,55
LDPE-CF 0,1	162,78	11,34	23,20	9,25	6,33	0,67	2,80
LDPE-CNC 0,1	178,75	9,68	17,38	6,34	6,26	0,25	1,08
LDPE 0,3	151,31	7,33	90,90	13,15	8,30	0,39	7,76
LDPE-Az-DHB 0,3	181,02	4,43	14,78	2,48	6,90	0,17	0,99
LDPE-Az-DHA 0,3	194,76	10,31	15,08	2,09	7,40	0,53	1,03

For PLA the lactic acid doesn't seem to make the film more resistant by improving dispersion as shown in figure 14 and table 2. TEOA as a counter ion doesn't seem to improve it either. There are still problems with the mixing. As a future improvement, a lower amount than 5 % of CNC in the matrix should be examined to avoid aggregation. All curves are shifted to control for the slippiness, where some elongation is seen without an increasement in tensile stress. Sandpaper was used as well to avoid slippiness.

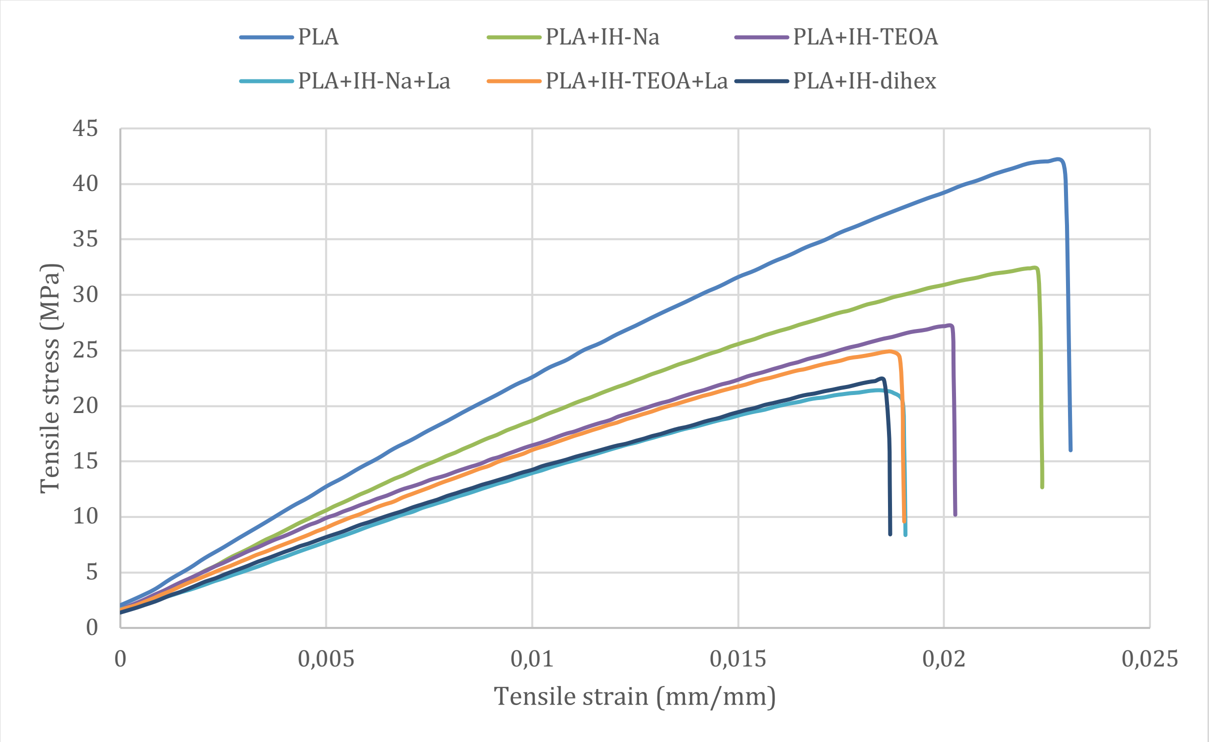


Figure 14. PLA composites tensile test with modified and unmodified CNC with different counter ions and with or without lactic acid (La).

Table 2. Key values from tensile test with PLA composites including standard deviation (STEV) between all six samples of each material.

	Modulus (Automatic Young's) (MPa)	STDEV	Tensile strain at Yield (Zero Slope) (%)	STDEV	Tensile stress at Yield (Zero Slope) (MPa)	STDEV	Toughness (MPa)
PLA	2050,91	153,74	3,405	0,54	43,14	5,00	0,56
PLA-CNC-Na	1777,92	78,55	2,81	0,55	30,67	8,40	0,43
PLA-CNC-TEOA	1652,61	139,56	2,81	0,23	28,86	1,63	0,32
PLA-CNC-Na+La	1286,78	271,66	2,95	0,53	19,77	4,85	0,24
PLA-CNC-TEOA+La	1504,98	203,14	2,50	0,21	25,03	4,67	0,28
PLA-CNC-Na-Az-DHA	1602,80	129,98	1,70	0,58	16,75	4,59	0,16

The extrusion has been accomplished in the same way for all samples. A longer time of mixing in the extruder could improve the mixture with the risk of burning the sample. The extruder is designed in such a way that not all material is coming out when flushing. A substantial amount of 3 ml is left in the chamber and will be mixed with the new added material. This makes it difficult to control the residence time in the extruder. Extruding once again with the obtain composite might improve the mixing as well.

After freeze drying CNC the samples were grinded for about 15 minutes per 10 ml by hand. Smaller particles would improve the mixture, so if the griding step could be done for a longer time or by an instrument it might improve the mixture.

5 Conclusion

Synthesis of both Az-DHA, Az-DBA and the AKD worked well and also the CNC modification according to the FTIR.

Mixing CNC with PLA, PP or LDPE turns out to be difficult, regardless of whether the CNC is surface modified or not. The manufactured CNC (CF) is well-mixed with the LDPE. Lactic acid or switching counter ion doesn’t decrease the aggregation either. More effort should be put on finding a way to improve mixing and decrease aggregation in the films. The composite with CNC-Az-DHA and LDPE was stiffer compared to pure LDPE, which is an improvement depending on what type of material you are looking for. It doesn’t deform as much as LDPE before break. New ways of extruding, freeze-drying and grinding should be examined to improve mixture. A composite with PLA and CNC modified with AKD is not resistant enough to heat, and other methods should be tried than extrusion. It’s also too viscous for the extruder and would cause leakage problems in the extruder.

A modification of CNC will though make it more heat resistant due to the loss of protons. Protons are catalyzing the degradation.

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Appendix A

Table A.1. Properties of PLA, NatureWorks Ingeo 3051D

Physical Properties	
Specific Gravity	1.25 g/cc
Viscosity Measurement	3.0 - 3.5
Linear Mold Shrinkage	0.003 - 0.005 cm/cm
Melt Flow	10 - 25 g/10 min @Load 2.16 kg, Temperature 210 °C
Mechanical Properties	
Tensile Strength, Yield	48.0 MPa
Elongation at Break	2.5 %
Flexural Strength	83.0 MPa
Flexural Modulus	3.83 GPa
Izod Impact, Notched	0.160 J/cm
Thermal Properties	
Melting Point	150 - 165 °C
Glass Transition Temp, Tg	55.0 - 65.0 °C
Optical Properties	
Transmission, Visible	90 %
Processing Properties	
Feed Temperature	165 °C
Nozzle Temperature	205 °C
Melt Temperature	200 °C
Mold Temperature	25.0 °C
Back Pressure	0.345 - 0.689 MPa
Screw Speed	100 - 175 rpm

Table A.2. Properties of LDPE, Borealis CA8200

Property	**Typical value**	**Test method**
Density	920 kg/m^3	ISO 1183
Melt flow rate (190 °C/2,16 kg)	7,5 g/10min	ISO 1133
Melting temperature (DSC)	108 °C	ISO 11357-3
Maximum coating speed	850 m/min	BTM 14921
Minimum coating weight	5 g/m^2	BTM 14922
Total Neck-in	64 mm	BTM 14920

Appendix B

Table B.1. Weights of CNC suspension before and after oven.

Sample	**Weight slurry (g) (before washing)**	**Weight slurry (g) (after washing)**		**Empty beaker**	**Beaker with CNC**	**Beaker with dried CNC**	**Wet CNC**	**Dry CNC**
1	231,31	264,49		18,21	21,76	18,82	3,55	0,61
2	232,22	266,52		18,17	21,31	18,72	3,14	0,55
3	231,17	244,24		17,9	20,65	18,26	2,75	0,36
4	232,44	268,21		18,25	19,25	18,5	1	0,25
Total	**927,14**	**1043,46**					**10,44**	**1,77**

Table B.2. Results from data above with calculations from the method section.

Start material (g)	200
Dry content (%)	16,95%
Total product (g)	157,19
Yield (%)	78,59%

Table B.3. After dialysis with several washing steps before the calculated dry content was 4,74%.

Sample	**Empty beaker**	**Beaker with wet CNC**	**Beaker with dried CNC**	**Wet CNC**	**Dry CNC**	**Dry content**
1	3,6	5,59	3,69	1,99	0,09	4,52%
2	3,6	6,17	3,72	2,57	0,12	4,67%
3	3,6	6,42	3,74	2,82	0,14	4,96%
Total				**7,38**	**0,35**	4,74%

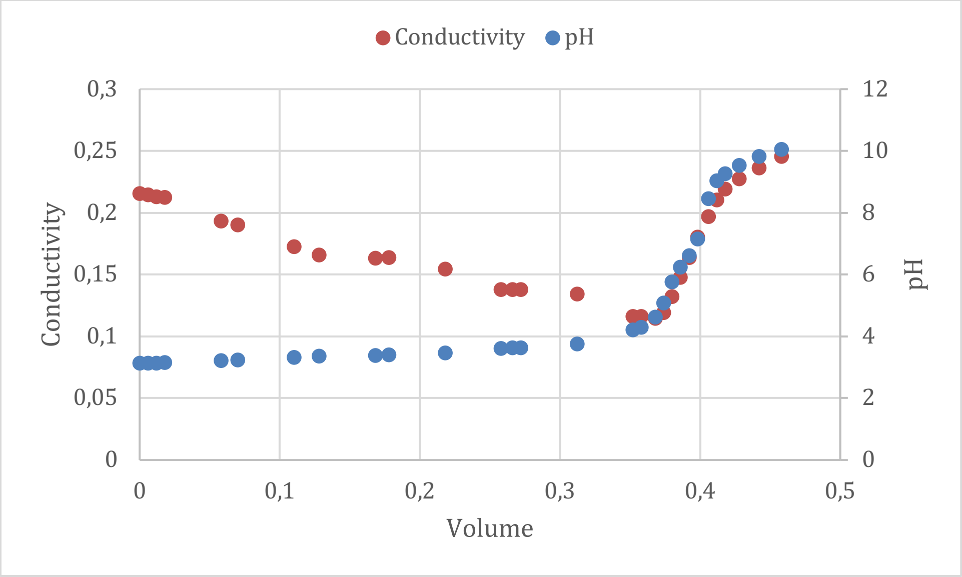

Figure B.1. Results from conductometric titrations.

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