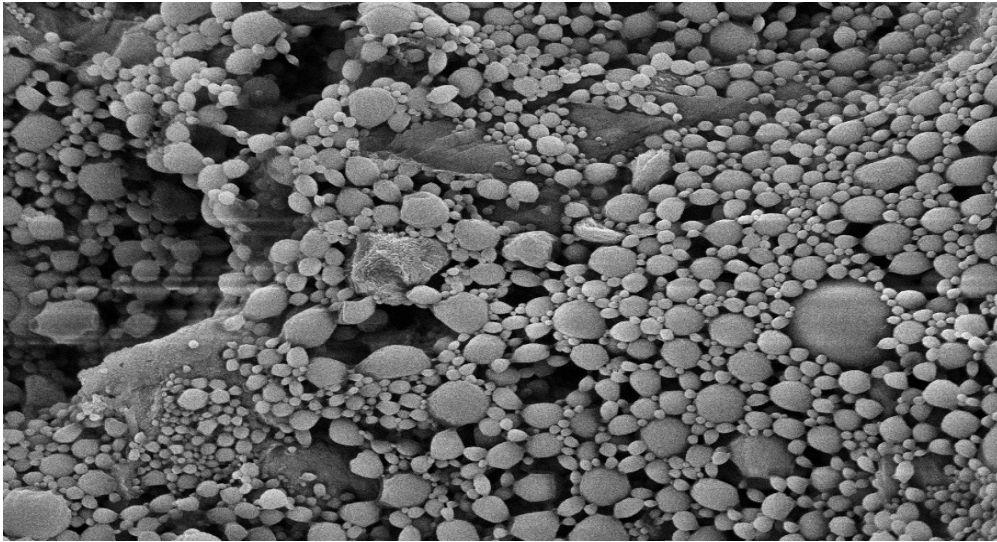




CHALMERS
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Study of cellulose nanocrystal modification and PLA cellulose nanocrystal composites

An investigation of cellulose nanocrystal modification methods and analysis of PLA cellulose nanocrystal composites

Master's thesis in Materials Chemistry

ROBIN NILSSON

MASTER'S THESIS 2017:06

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Investigation of methods to modify cellulose nanocrystals with azetidinium salts, produce and analysing composites consisting of polylactic acid and different ratios of unmodified and modified cellulose nanocrystals

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Gothenburg, Sweden 2017

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Master's Thesis 2017:06

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Cover: Scanning electron image of polylactic acid dispersed in water and dried.

Typeset in L^AT_EX

Gothenburg, Sweden 2017

Functional study of PLA nanocellulosecomposites
Analysis of PLA cellulose nanocrystals composites and an investigationof cellulose
nanocrystals modification methods
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Abstract

Cellulose nanocrystals was modified with dihexylamine and dioctylamine azetidinium salt and mixed with polylactic acid in order to investigate the mechanical properties compared to composites with unmodified cellulose nanocrystals mixed with a dry method and a wet method. Additionally a more practical modification route than the conventional involving DMSO was investigated. The composites were characterized with tensile testing and the unmodified and modified cellulose nanocrystals were inspected with infrared spectroscopy, Attenuated total reflection fourier transform infrared spectroscopy, X-ray diffraction, Zeta potential, thermal gravimetric analysis, atomic force microscopy and conductometric titration. Scanning electron microscopy and differential scanning calorimetry were used on pure polylactic acid. Water showed to be a good candidate for replacing DMSO as solvent in the modification of cellulose nanocrystals due to it being relatively similar to DMSO in most of the analysing methods. The tensile tests of the composites showed that dry mixed composites showed lower stress at maximum load and higher Young's modulus when unmodified and modified cellulose nanocrystals were introduced. The wet mixed composites gave somewhat insufficient data due to a poor PLA matrix were pure PLA couldn't give any tensile data due to being too brittle. Despite that, an introduction of unmodified and modified CNC made the composites tough enough to be measured. The unmodified CNC in the wet mixed composites had higher Young's modulus than dry mixed for the same compositions but for the dihexylamine modified CNC the wet mixed method resulted in insufficient data due to too few specimens.

To be able to use water instead of DMSO would be a huge difference due to DMSO being difficult to work with on a larger scale. The wet mixed method needs further improvement in order to get a better polymer matrix.

Keywords: Cellulose, CNC, modification, Azetidinium salt, PLA, composite, mechanical properties.

Acknowledgements

I want to thank Gunnar Westman, Karin Sahlin and Filip Nylander for their guidance and assistance throughout this project. I also want to thank Johannes Thunberg and Patrik Rosendahl who cooperated with me in my work. Others I want to thank are Mikeala Börjesson, Sheikh Mohammad Habibur Rahman, Anders Mårtensson, Massimiliano Mauri, David Kiefer and Jonna Hynynen.

Robin Nilsson, Gothenburg, June 2017

Contents

List of Figures	xi
List of Tables	xiii
1 Introduction	1
1.1 Aim	1
1.2 Limitation	2
1.3 Problem Description	2
2 Background	3
3 Theory	5
3.1 Polylactic acid	5
3.2 Cellulose	5
3.2.1 cellulose nanocrystals (CNC)	6
3.2.2 Modification of cellulose nanocrystals	6
3.3 Composites	7
3.4 Analysing methods	7
3.4.1 Fourier transform infrared spectroscopy (FTIR)	7
3.4.2 Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR)	8
3.4.3 X-ray diffraction (XRD)	8
3.4.4 Zeta Potential	8
3.4.5 Thermal Gravimetric Analysis (TGA)	8
3.4.6 Atomic force microscopy (AFM)	9
3.4.7 Conductometric titration	9
3.4.8 Scanning electron microscopy (SEM)	9
3.4.9 Differential scanning calorimetry (DSC)	9
3.4.10 Tensile testing	9
4 Method	11
4.1 Modification of CNC	11
4.1.1 DMSO method	11
4.1.2 Isopropanol method	12
4.1.3 Water method	12
4.1.4 Solvent references	12
4.2 Analysis of the unmodified and modified cellulose nanocrystals	13

4.2.1	Fourier transform infrared spectroscopy	13
4.2.2	Attenuated total reflection Fourier transform infrared spec- troscopy	13
4.2.3	X-ray diffraction	14
4.2.4	Zeta potential	14
4.2.5	Thermal gravimetric analysis	15
4.3	Atomic force microscopy	15
4.3.1	Conductometric titration	15
4.4	Composite mixing	15
4.5	Analysis of the composites	16
4.5.1	Scanning electron microscopy	16
4.5.2	Differential scanning calorimetry	16
4.6	Mechanical analysis	16
5	Results and Discussion	17
5.1	CNC modification	17
5.2	Composites	24
6	Conclusion	31
	Bibliography	33
	Bibliography	33
A	Appendix 1	I
A.1	CNC preparation	I
A.2	Azetidinium salt synthesis	I
A.3	Modification methods	I
A.3.1	Solvent exchange for CNC to toluene, Batch 1	II
A.3.2	Dihexyl modification of CNC trial with DMSO as solvent . . .	II
A.3.3	Dihexyl modification of CNC trial with water as solvent . . .	II
A.3.4	Dihexyl modification of CNC with DMSO as solvent	II
A.3.5	Solvent exchange for CNC to toluene, Batch 2	III
A.3.6	Diocetyl modification of CNC with DMSO as solvent	III
A.3.7	Dihexyl modification of CNC with water as solvent 2	III
A.3.8	Dihexyl modification of CNC with isopropanol as solvent 2 . .	IV
A.4	DSC	IV
B	Materials used	V
B.1	PLA	V

List of Figures

3.1	Structure of polylactic acid.	5
3.2	Structure of cellulose chain.	6
3.3	Structure of sulfated cellulose nanocrystals.	7
4.1	Scheme of sulfated CNC and azetidinium modified CNC. The two different R-structures are also illustrated where R_1 is a hexyl group and R_2 is a octyl group. Observe that if the sulfate group binds to a secondary or primary alcohol is not investigated.	12
4.2	XRD graph where the 002 lattice diffraction peak and the amorphous region are displayed.	14
5.1	FTIR measurements of unmodified and modified CNC with the sulfur peak marked at 815.	17
5.2	FTIR measurements of the solvent references, which means CNC treated as in the modification methods but without any azetidinium salt to react with. The unmod-CNC means here untreated CNC . . .	18
5.3	ATR-FTIR measurements of unmodified and modified CNC.	19
5.4	TGA measurements of unmodified and modified CNC.	20
5.5	TGA measurement data of the reference CNC with displayed temperatures at which they were no longer thermal stable.	21
5.6	AFM image of unmodified CNC dispersed in water and dried. The length and width of some selected particles were 39-275 nm and 4.8-6.2 nm	22
5.7	AFM image of dihexylamine azetidinium modified CNC dispersed in isopropanol and dried. The length and width of some selected particles were 220-655 nm and 4.7-5 nm	23
5.8	AFM image of dioctylamine azetidinium modified CNC dispersed in isopropanol and dried. The length and width of some selected particles were 273-447 nm and 2.8-7.6 nm	23
5.9	SEM image of the PLA dispersion used in the wet mixing method. . .	25
5.10	Photos of the dry mixed PLA composites with displayed CNC, DHA-CNC and DO-CNCA content. Where DHA-CNC and DOA-CNC stands for the dihexylamine azetidinium modified CNC and dioctylamine azetidinium modified CNC.	26
5.11	Photos of the wet mixed PLA composites with displayed CNC, DHA and DOA content	27

List of Figures

- A.1 Scheme of azetidinium formation from epichlorohydrin and secondary amine where R is the design choice I
- A.2 DSC measurement of PLA where the first peak is the glass transition temperature, around 59 °C, and the second is the melt temperature, around 144 °C. IV

List of Tables

1.1	Collocation of the different composites with polylactic acid as matrix mixed with dihexylamine azetidinium modified cellulose nanocellulose (PLA-DHA-Az-CNC), dioctylamine azetidinium modified cellulose nanocrystals (PLA-DOA-Az-CNC) and unmodified cellulose nanocrystals (unmodCNC) and a reference of pure PLA	2
4.1	Shows all the different modification methods and the solvent references and their abbreviations. 'az' stands for azetidinium salt.	13
5.1	Crystallinity index of the unmodified and modified CNC. Calculated from XRD measurements as explained in the XRD method.	19
5.2	Zeta potential of 0.05 % solutions of unmodified CNC, modified CNC and the CNC solution references.	20
5.3	Thermal degradation temperature of the unmodified and modified CNC obtained from the TGA measurement and can also be observed in Figure 5.4. The solution references from 5.5 are also shown	21
5.4	Dimensions of the unmodified and modified CNC particles displayed in Figure 5.6 to 5.8. The measurements were spot-checked and are therefore not a full representation of the dimensions	24
5.5	Sulfur content of unmodified and modified CNC	24
5.6	Tensile testing data for dry mixed PLA and PLA integrated with unmodified and modified CNC. The values are the average of the written specimens.	28
5.7	Tensile testing data for wet mixed PLA and PLA integrated with unmodified and modified CNC. The values are the average of the written specimens.	29
B.1	Processing temperature profile where the starting points may be optimized.	V
B.2	Typical physical and mechanical properties of the PLA Resin and what ASTM methods used.	V

1

Introduction

When a polymer is mixed with a matrix consisting of a different polymer the composite tend to have different properties than what the matrix exhibit on its own. The changed properties are often generalised and related to the inherent characteristics of the polymer. In this study the matrix was chosen to be polylactic acid (PLA) due to the fact that it's produced from renewable resources and is biodegradable. The mechanical properties are in comparison poor and that's why cellulose nanocrystals (CNC) are introduced into the matrix. In addition also CNC modified with azetidinium salt is used in the matrix in order to compare the change in mechanical properties between PLA composite with unmodified and modified CNC. These composites will be mixed by two different methods. The conventional modification method of attaching azetidinium salt to CNC involve solvents which are difficult to work with and therefore a investigation is made where other solvents are tried.

1.1 Aim

The purpose of the project was to produce composites of PLA and modified cellulose nanocrystals (CNC) and analyse them by tensile testing. PLA is the matrix material and the amount of modified cellulose nanocrystals was 1, 10, 20 wt%. These composites were compared to PLA mixed with unmodified nanocellulose with the same percentages to observe the impact of the modification with azetidinium salts. The composites were mixed with two method, dry and wet mixing, which will be compared to each other. Two salts were tested in order to compare the impact of their structure, dihexylamine azetidinium (DHA-Az) and dioctylamine azetidinium (DOA-Az). By introducing these azetidinium salt the CNC will get more hydrophobic due to the introduced carbon chains which should increase interaction with polylactic acid. The different composites are summarised in Table 1.1.

A conventional way of modify cellulose nanocrystals in DMSO was used in the composites but also alternative modification routes with greener solvent were investigated such as isopropanol and water.

Table 1.1: Collocation of the different composites with polylactic acid as matrix mixed with dihexylamine azetidinium modified cellulose nanocellulose (PLA-DHA-Az-CNC), dioctylamine azetidinium modified cellulose nanocrystals (PLA-DOA-Az-CNC) and unmodified cellulose nanocrystals (unmodCNC) and a reference of pure PLA

Composite	% CNC		
PLA-DHA-Az-CNC	1	10	20
PLA-DOA-Az-CNC	1	10	20
PLA-unmodCNC	1	10	20
PLA	0	0	0

1.2 Limitation

The composites were not compared to pure CNC and the ratio of CNC in the matrix is limited to the given ones in Table 1.1. Only one type of PLA was used, in question of D-lactic and L-lactic ratio and the microstructure of PLA. The impact of the choice of cellulose source will also not be investigated. The methods used to modify the CNC and the mixing of the composites were not optimised in any way.

1.3 Problem Description

The main area of investigation was whether composites consisting of PLA and modified nanocellulose have any change in properties compared to unmodified CNC-PLA composite. How the structure of the polymers change when made into a composite and how it could relate to the bulk properties. Can an optimal concentration of modified CNC be located. How significant is the choice of azetidinium salt on the composite properties. Alternative methods of CNC modification, compared to the conventional method, were also investigated in order to get a greener method. How does the method of mixing the CNC and PLA affect the composite.

2

Background

The world population is expected to be around the size of 9.3 billion by 2050 and with that growth there will probably be a stronger utilisation of our resources.[1]. This together with the strain humanity puts on the environment creates a demand on durability, reusable and recyclable materials which aren't made from fossil fuels and have less impact on the nature.

Composites made by using natural fibres to reinforce biodegradable polymers have risen in interest in fields like packaging and medicine due to newly developed polymers with increased thermal stability, mechanical and barrier properties. One of those bio-degradable polymers is polylactic acid (PLA), which is made from of wheat, corn, potatoes and other renewable resources. It's a thermoplastic biopolymer and similar to polystyrene in mechanical and optical properties. The range of applications is limited due to low thermal stability, inherent brittleness and low impact strength. [2]

2. Background

3

Theory

3.1 Polylactic acid

Du Pont patented the method to synthesise Poly-lactic acid (PLA) by polymerization lactate in 1954. In the beginning it was produced as a biomedical material such as drug delivery systems due to its bio-compatible and bio-absorbable nature. The field of use have later expanded to tissue engineering, biocompatible materials for prosthesis and sutures. PLA has also been used as bio-degradable plastic for cold drink cups, bottles and other utensils for short time of use. [2]

Lactic acid is a 2-hydroxy carboxylic acid, see Figure 3.1, with the two stereoisomers D and L enantiomers. A high rate of enantiomeric pure lactide is expected to be used as high performance materials. There is a wide variety of PLA microstructures where L-lactic and/or D-lactic acid are combined in different ways and results in different properties. [2]

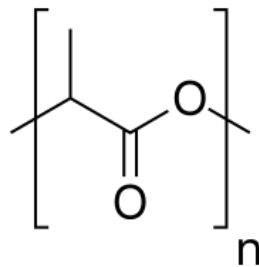


Figure 3.1: Structure of polylactic acid.

3.2 Cellulose

Similar to PLA, cellulose is an interesting material due to being the most abundant polymer in nature. Cellulose can be modified and structured in many ways and therefore be used in a variety of applications like textiles, optical films and advanced functional materials. Cellulose can be produced by many sources like plants, algae and animals but the major source of production is from plant fibre where it occupies about 40% of the mass. [3] Cellulose consists of D-glucopyranose rings unit in 4C1-chair configuration which are linked by β -1,4-glycosidic bonds and therefore there's an alternating 180° turn of the chain axis. The structure of cellulose is shown in Figure 3.2. [3]

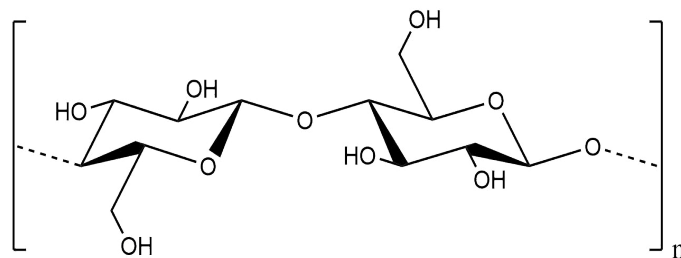


Figure 3.2: Structure of cellulose chain.

3.2.1 cellulose nanocrystals (CNC)

cellulose nanocrystals (CNC), also known as nanocrystalline cellulose or cellulose nanowhiskers is one of the types of nanocellulose, the other two being cellulose nanofibrils (CNF) and bacterial cellulose (BC). The characteristics of CNC are conifer-shaped or rod-like particles where both dimensions are in nanoscale. The width of these is 5-20 nm depending on the starting material which also affects the length. Typical length for CNC from cotton is 100-300 nm and can be in micrometer for sources like algae and tunicate. [2]

Nano-scale cellulose is attractive in research and commercially due to properties such as biodegradable, low weight and high stiffness and strength. Extracting nanocellulose can be done by sulfuric acid hydrolysis of lignocellulosic biomass. [3]

3.2.2 Modification of cellulose nanocrystals

Polysaccharides functionalized with sulfate groups have been an area of investigation for a long time and they can be found in nature or be synthesised by chemical methodologies. They are of interest due to their potential in applications in among others biomedical and bio-active applications. The production of cellulose sulfates could be done by reacting cellulose with sulfamic acid. When cellulose is hydrolyzed with sulfuric acid some of the hydroxyl groups on the surface will be exchanged with $-OSO_3^-$ and the result is sulfated cellulose nanocrystals (CNC) which form stable aqueous suspension. Structure of the sulfated CNC is shown in Figure 3.3. How much substitution of charged sulfate groups there will be can be adjusted during or after the hydrolysis. Desulfation, acylation and oversulfation are used to chemically modify polysaccharides to affect its properties. Sulfated CNC is highly hydrophilic and due to that hard to form homogeneous composites with plastics. Therefore CNC could be hydrophobized by introducing hydrophobic groups to the sulfate groups. [4]

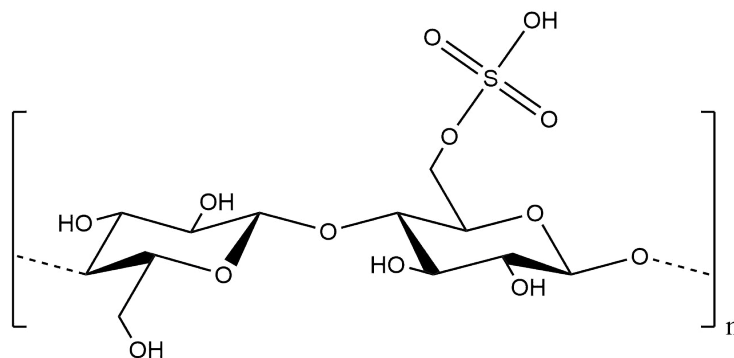


Figure 3.3: Structure of sulfated cellulose nanocrystals.

An less explored area is surface modification with molecules that can react with the sulfate groups on the cellulose. From earlier research azetidinium salts are known to react with carboxylates and phosphorus nucleophiles. The azetidinium salts are positively charged and in combination with its ring of four atoms makes them reactive under moderate conditions. Sulfate esters are suitable for ring opening reactions with azetidinium salt due to large and available orbitals. In comparison to traditional etherification and ester reactions the azetidinium salts can give additional hydrophobization methodology due to its Y-shaped carbon branching. In addition these salts can be design in many ways which opens possibilities for modification. Azetidinium salts are produced from dialkyl amines and epichlorohydrin. [4]

3.3 Composites

Biocomposites of PLA and nanocellulose have been studied before and results where that an increase in nanocellulose content improves strength and tensile modulus. Decreased gas permeability and higher storage modulus above T_g in temperature are also observed. [2]

3.4 Analysing methods

In this project, a number of instruments have been used for analysing the CNC and the composites. The modified and unmodified CNC are investigated with Fourier transform infrared spectroscopy, Attenuated total reflection Fourier transform infrared spectroscopy, X-ray spectroscopy, zeta potential, thermal gravimetric analysis, atomic force microscopy and conductometric titration. Mechanical analysis was used for the analysis of the composites and pure PLA was characterized by differential scanning calorimetry and the PLA dispersion analysed with scanning electron microscopy.

3.4.1 Fourier transform infrared spectroscopy (FTIR)

Covalent bonds in molecules tend to absorb electromagnetic radiation in the infrared electromagnetic spectrum called the vibrational spectrum which is when the

wavelength (λ) between $2.5 \mu\text{m}$ and $25 \mu\text{m}$. The corresponding wavenumber ($\bar{\nu}$) is 400 to 4000 cm^{-1} . Molecules absorb quantized frequencies which depending on the bonds between atoms. All type of bonds have their specific vibrational frequency and therefore infrared spectroscopy can be used to identify the fingerprint of specific bonds. It can also be used to get a molecule's structural information. [5]

3.4.2 Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR)

A method of determining the IR spectra of solids are with ATR-FTIR which is a accessory to the FTIR machine. The method doesn't need any preparation of solid or liquid samples which give fast analysis. Light is reflected on the sample multiple times, instead of transmittance as FTIR often uses. [5]

3.4.3 X-ray diffraction (XRD)

When a atom get exposed to a x-ray beam it could either be scattered or absorbed with electron ejection. In crystals the beams are scattered according to Bragg's law which describes when constructive interference occur. The intensity of the scattered X-rays in crystalline particles depends on the symmetry of the lattice. [6]

3.4.4 Zeta Potential

If two phases like a polar liquid and dipolar molecules are mixed the molecules have a tendency to generate a potential difference due to specific orientations. If ions are present they tend to scatter at the interface in a nonuniform manner. The region between two phases is normally a barrier of electrical charges with one positively and one negatively charged phase. If there is one liquid phase with negative ions a second phase with positive charged surfaces will move into the first phase in order to decrease the potential energy. Electrokinetic effects are observed when one of these two phases move into the other. Depending on which motion is generated there are four electrokinetic effects and the one used in this project was electrophoresis. In this method a second solid or liquid phase is suspended in another liquid or gas phase and movement of the particles are induced by an applied electric field. The velocity of the particles give information about the surface potential or the net electric charge of the particles. [7]

3.4.5 Thermal Gravimetric Analysis (TGA)

In thermal methods of investigation the physico-chemical properties of samples are investigated as function of temperature. In TGA the change in weight when increasing the temperature is investigated which give information for instance about decomposition and vaporisation. [8]

3.4.6 Atomic force microscopy (AFM)

Different from other microscopes which use light or electrons, AFM uses a sharp probe which physically interacts with the surface of the sample. The sample doesn't need much preparation if any at all because it doesn't need to be coated, transparent, electrically grounded or stained. AFM has poor depth of field but compensate with a resolution down to 0.1 nm and doesn't need a special environment for the sample when measuring. [9]

3.4.7 Conductometric titration

Conductometry is a method to measure electrolytic conductivity to monitor progress of a chemical reaction. A solutions conductivity depends directly on concentration of ions present if the area and distance of the electrodes are unchanged. If an reagent is added the conductivity doesn't have to vary linearly as the solution is diluted due to the water in the added reagent and therefore the volume is corrected to account for it. Conductometric titration is a method used for finding the end point in a titration of an acid with a base. [10]

3.4.8 Scanning electron microscopy (SEM)

SEM is an imaging tool were the sample is scanned by an focused electron beam. This beam cause electrons in the sample to excite and by detecting these secondary electrons an image of the surface could be obtained. The sample needs to be conducting or have been coated with a thin film of gold in order to be measured. The resolution is 5 nm and the maximum field of view is 1 mm. [11][9]

3.4.9 Differential scanning calorimetry (DSC)

DSC i a method where the degree and rate of change in heat is measured over temperature or time. It's the primary technique for thermal analysis of organic and inorganic materials and it can measure heat and temperature of reactions or transitions. It gives quantitative information of this heat change and also the heat transfer rate. In addition to the sample there's also a reference sample and when a transition is occurring, heat is added to either reference or sample to get the same temperature in each. This results in a calorimetric measurement of the energy transition at the transition temperature. [12]

3.4.10 Tensile testing

Tensile testing applies a static load on the sample and uses it to determine Young's modulus and Poisson's ratio. A tensile test is usually done according to standard procedures like ASTM D 638 which is standard method for determining tensile properties of plastics. Plastics specimens are often shaped into dumbbell-shapes or tubes which are anchored at the ends in a universal testing machine. When measuring, the test conditions and the testing speed are specified. The tensile

3. Theory

specimens are measured in regard to length, width and thickness for each sample in order to compensate for variation in dimensions. [13]

4

Method

The cellulose nanocrystals (CNC) used was produced previous to this project and so was the dihexylamine and dioctylamine azetidinium salt. How to produce CNC and azetidinium salt are explained in Appendix A1 and Appendix A2. The modification of CNC by grafting either of the azetidinium salts on the surface were done with an conventional method explained later. For the dihexylamine azetidinium salt additional modification methods were tested. The unmodified and modified CNC were analysed with several methods to determine the success of the modifications. The modified CNC and unmodified CNC were mixed with two methods with PLA, dry and wet mixed, and then made into tensile specimens and tensile tested. Pure PLA were also tested as a reference. All chemicals used in this project were received from Sigma-Aldrich except PLA which was received from Natur Works with product specification in Appendix B1.

4.1 Modification of CNC

cellulose nanocrystals (CNC) was modified with dihexylamine and dioctylamine azetidinium salt which were synthesised previously at the department. The tested method for modifying CNC is a reaction in DMSO at 90 °C, which was the method used for the modified CNC that were integrated in the composites. As an additional study the dihexylamine azetidinium modification was studied for reaction in water and isopropanol. All the modification procedures are explained thorough in Appendix A3.

4.1.1 DMSO method

CNC dispersed in water was prepared and the water was exchanged to DMSO by an azeotrope with toluene, resulting in CNC dispersed in DMSO-toluene mixture with ratio 4:1. An excess of the azetidinium salt, dihexylamine azetidinium respectively dioctylamine azetidinium, was added to the mixture and reacted at 90 °C for 1 day. This was followed by cooling down to room temperature and washed in several centrifuging sessions with ethanol. Figure 4.1 show a schematic picture of the modified CNC. A modification with a smaller amount of DMSO was also tried and it will be referred to as DMSO-test [4]

4. Method

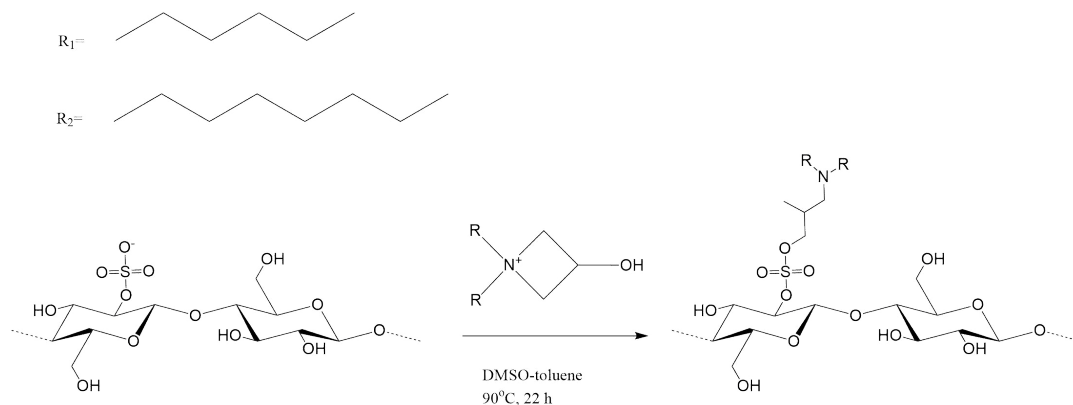


Figure 4.1: Scheme of sulfated CNC and azetidinium modified CNC. The two different R-structures are also illustrated where R_1 is a hexyl group and R_2 is a octyl group. Observe that if the sulfate group binds to a secondary or primary alcohol is not investigated.

4.1.2 Isopropanol method

Two different kinds of varieties of the DMSO-method were tested with isopropanol instead of DMSO. One where the CNC in water was exchanged to isopropanol with azeotrope with toluene and will be referred to as "isoprop1". The other method was an exchange to isopropanol directly and this will be referred to as "isoprop2". Except for the choice of solvent during the reaction the methods are exactly alike.

4.1.3 Water method

Two kinds of modifications were also tried in water where a CNC dispersion in water was used. This was then modified by adding the azetidinium salt and then for one of the methods putting it in an oven and the other method being the same as in the DMSO-method.

4.1.4 Solvent references

References to the methods were also done where CNC was dispersed in the solvents DMSO, isopropanol and water and stirred at 90°C for a day in order to analyse what happens without the azetidinium salt. These will be referred to as the solvent references.

All the different modifications are displayed in Table 4.1 along with abbreviations that will be used to later in the report.

Table 4.1: Shows all the different modification methods and the solvent references and their abbreviations. 'az' stands for azetidinium salt.

CNC sample	Method/solvent	$T_{reaction}$	Abbreviation
Unmodified			Unmod-CNC
Dihexylamine az	DMSO	90 °C	DHA-Az-CNC-DMS
Diocetylamine az	DMSO	90 °C	DOA-Az-CNC-DMSO
Dihexylamine az	small amount of DMSO	90 °C	DHA-Az-CNC-DMSO-test
Dihexylamine az	toluen \rightarrow <i>isopropanol</i>	90 °C	DHA-Az-CNC-isoprop-1
Dihexylamine az	isopropanol	90 °C	DHA-Az-CNC-isoprop-2
Dihexylamine az	water in oven	110 °C	DHA-Az-CNC-water-1
Dihexylamine az	water	90 °C	DHA-Az-CNC-water-2
Unmodified	DMSO	90 °C	CNC-DMSO-ref
Unmodified	toluen \rightarrow <i>isopropanol</i>	90 °C	CNC-toluene-isoprop-ref
Unmodified	isopropanol	90 °C	CNC-isoprop-ref
Unmodified	water	90 °C	CNC-water-ref

4.2 Analysis of the unmodified and modified cellulose nanocrystals

The unmodified and modified CNC samples were analysed with Fourier transform infrared spectroscopy, Attenuated total reflection Fourier transform infrared spectroscopy, X-ray spectroscopy, zeta potential, thermal gravimetric analysis, atomic force microscopy and conductometric titration.

4.2.1 Fourier transform infrared spectroscopy

All the samples were analysed with an Perkin Elmer Spectrum One FT-IR Spectrometer, 20 scans, 1 cm^{-1} resolution and wavelength $400\text{-}4000\text{ cm}^{-1}$. The measurements were done on pressed pellets consisting of 2 mg of each sample and 300 mg potassium bromide.

4.2.2 Attenuated total reflection Fourier transform infrared spectroscopy

The modification of CNC is on the surface of the particles and therefore the sampling technique attenuated total reflection was used in order to get a more specific measurement of the surface. The ATR mount used was a Pike GladiATRTM on a PerkinElmer FT-IR Spectrometer Frontier. The settings were 20 scans, 1 cm^{-1} resolution and wavelength $400\text{-}4000\text{ cm}^{-1}$. The measurements were done on powder of unmodified and modified CNC.

4.2.3 X-ray diffraction

The X-ray diffraction measurements were performed on an Bruker D8-Advance, X-ray source monochromatic CuK α 1 with $\lambda=1.5406 \text{ \AA}$ 2θ from 10°C to 60°C based on area of interest[14], step size of $0.024^\circ/\text{step}$, $1.5 \text{ s}/\text{step}$ and 1 hour measuring time. The generator current was 40 kV and the generator voltage was 40 mA.

X-ray diffraction was used to get a value for the crystallinity of the cellulose nanocrystals and that it is unchanged after the modifications. In order to roughly estimate the crystallinity of the samples a peak deconvolution method was used where Equation (4.1) was used where CrI stands for Crystallinity Index. I_{002} is the intensity peak for the 002 lattice diffraction and I_{am} is the intensity at the amorphous region. These peaks are marked in Figure 4.2 along with other lattice diffractions which aren't taken into account in the calculations. [15][14][16]

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (4.1)$$

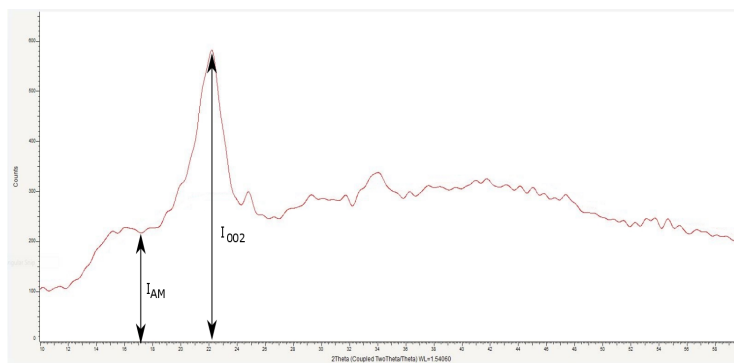


Figure 4.2: XRD graph where the 002 lattice diffraction peak and the amorphous region are displayed.

This method is not recommended when analysing crystallinity compared to other methods but should be sufficient in this work where it was used for comparison between samples.[14]

4.2.4 Zeta potential

A 0.05 wt% CNC dispersion was prepared of each sample and stirred for 15 h with an small amount of ion exchanger, Dowex[®] Marathon TM MR-3 hydrogen and hydroxide form from Sigma-Aldrich. Then the ion exchangers were extracted and the dispersions were measured on an MALVERN instruments Zetasizer Nano-ZS at 25°C in TTS1070 folded capillary cells. The zeta potential gives information about surface charge which corresponds to sulfate groups due to its negative charge. In modified CNC the sulfate is bonded to azetidinium salt and therefore doesn't add any surface charge.

4.2.5 Thermal gravimetric analysis

The unmodified and modified CNC were analysed with TGA to get the thermal stability. The measurements were done in air and the temperature was changed from 25 to 550 °C by 10 °C/min on an TGA/DSC 3+ STAR^e System.

4.3 Atomic force microscopy

AFM was used to see if the particle size of CNC was the same for unmodified and modified, in this case DHA-CNC and DOA-CNC. The samples were prepared by making a 0.0046% dispersion and dry a droplet of each on M054 mica sheets 3×1×0.006mm thick. The measurements were done on a Digital Instrument Dimension 3000 Scanning Probe Microscope and the software used to get the images and the dimensions is called NanoScope version 4.22ce.

4.3.1 Conductometric titration

The conductivity and pH were measured on the unmodified and modified cellulose nanocrystals with a method written by Qi Zhou and Nuria Butchosa with some modifications [17]. A 0.1 M solution in milli-Q water was prepared of each sample and to these 0.1 M HCl were added until the pH reached 3.5. After that 0.01 M NaOH was added in portions of 400 μl while measuring both pH and conductivity. A value for the amount of NaOH at the equivalent point was received by using tangents in Excel. This amount of NaOH is then, after compensating for the HCl, equivalent to the amount of sulfate groups on the CNC.

4.4 Composite mixing

The PLA and CNC were mixed in two ways, dry mixing where PLA powder was mixed with modified and unmodified CNC powder. The CNC powder was achieved by drying and grinding by hand to a powder. The other way was dispersion mixing where a PLA-water dispersion was mixed with a water dispersion of CNC. The water dispersion of PLA was achieved by a method written by Vähä-Nissi et. al. with some modifications, it contains dissolving PLA in tetrahydrofuran (THF) and then precipitation in water [18]. In the dry mixing method PLA pellets were grinded in a Retsch polymer grinder and mixed with dry CNC that was grinded by hand into a powder. The mixtures, according to Table 1.1, were all stirred for 5 min and then put in a mixing chamber, Brabender AEV 330, at 160 °C for 5 min at 30 rpm.

For the wet mixing method PLA was dissolved in THF at 50 °C and stirred for 6 h. Then NaOH and mQ-water were added to the PLA solution while stirring with an IKA T25 digital Ultra Turrax at 9000 rpm. The amount of NaOH and water in order to get a good dispersion were 0.83 ml/gPLA and 8.3 ml/gPLA, the amounts weren't optimised. The THF was removed with a rotary evaporator and a milky PLA dispersion in water was obtained. This PLA dispersion was mixed with modified and unmodified CNC water dispersion with the same Ultra Turrax at 6000 rpm for 10 min. The mixture was then dried on a plate in room temperature for three days.

The samples from the dry mixing and the wet mixing method were then pressed into 0.5 mm plates at 160 °C and 5 ton for 5 min. From the plates tensile specimens were pressed. The press used was a Fontune Holland table press and the tensile specimens punch was of the type EP 04/ISO 527-5A. The specimens were 4 mm width and 0.5 mm thickness.

4.5 Analysis of the composites

Mechanical analysis was used for the analysis of the composites and pure PLA was characterized by differential scanning calorimetry and the PLA dispersion analysed with scanning electron microscopy.

4.5.1 Scanning electron microscopy

A droplet of the PLA dispersed in water was dried on a SEM-test plate and sputtered with gold. Then the surface was imaged with an Ultra 55 FEG SEM with EHT at 5 kV and 15000 magnification.

4.5.2 Differential scanning calorimetry

PLA was analysed with DSC in order to get glass transition and melt temperature. The measurement was done on a METTLER TOLEDO DSC 2 STAR^e from -50 to 200 °C two times with 10 K/min. The temperature was held 1 min at 200 °C before going down and a nitrogen flow of 30 ml/min during the whole session. The data from this measurement was the starting point for the temperatures chosen in the mixing chamber and the press discussed in next section. The data from this analysis is displayed in Appendix A4.

4.6 Mechanical analysis

All the composite tensile specimens were analysed with tensile testing on an Instron 5565 with an extension rate of 3.6 mm/min.

5

Results and Discussion

This chapter has two main parts, the first one about the modification of CNC and the second about composites consisting of PLA with CNC, DHA-CNC and DOA-CNC as additive.

5.1 CNC modification

FTIR on unmodified and modified CNC are illustrated in Figure 5.1 and the solvent references are shown in Figure 5.2.

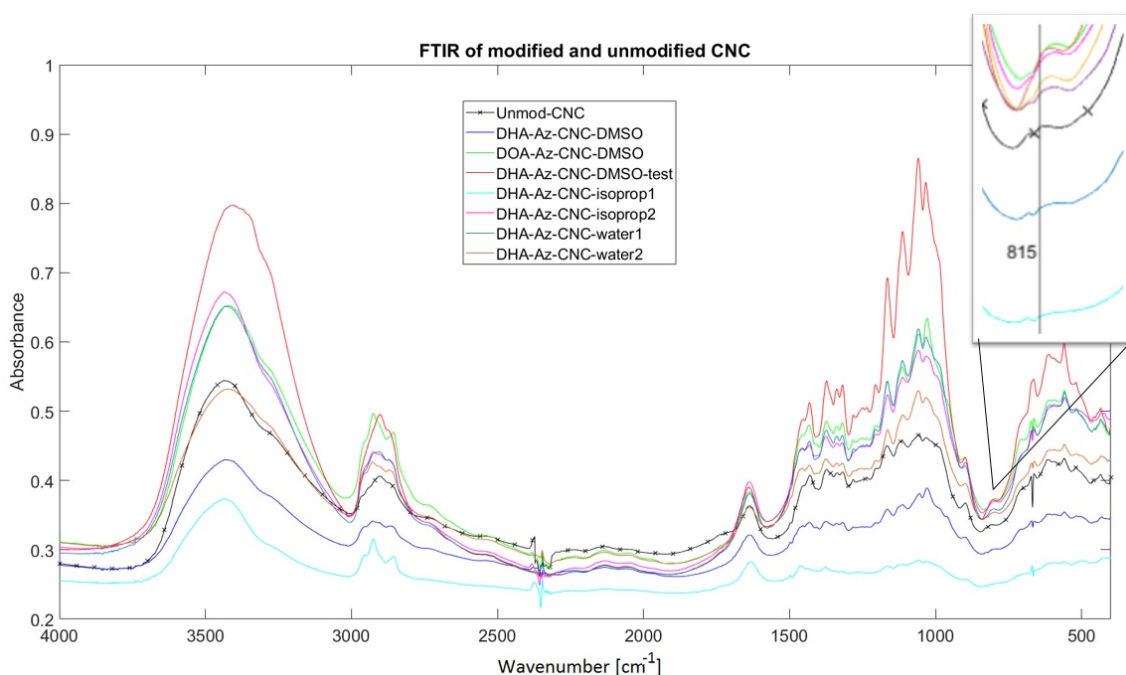


Figure 5.1: FTIR measurements of unmodified and modified CNC with the sulfur peak marked at 815.

The absorption peak of the carbon-oxygen-sulfur bond is at 815 which is marked in Figure 5.1. A small shift can be observed for all the modified CNC to the right in comparison to unmodified CNC. This mean something has happened to that bond and could indicate a coupling with the azetidinium salt.

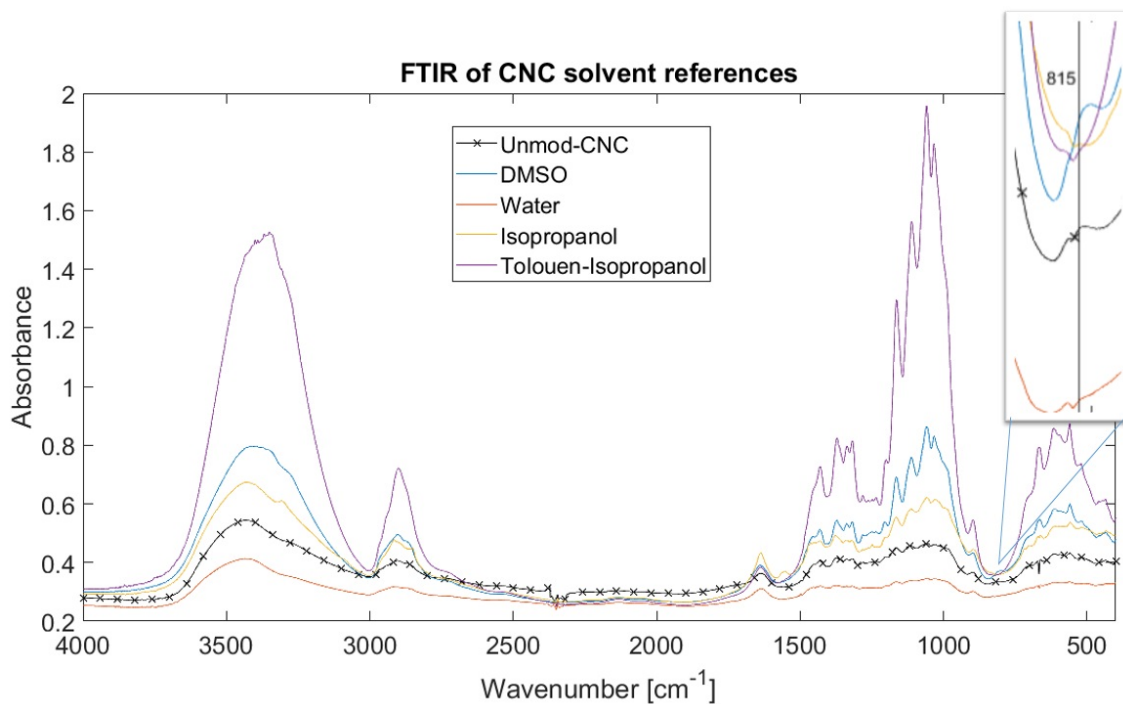


Figure 5.2: FTIR measurements of the solvent references, which means CNC treated as in the modification methods but without any azetidinium salt to react with. The unmod-CNC means here untreated CNC

For the solvent references there is a peak visible at 815 cm^{-1} for the untreated CNC (unmod-CNC) and DMSO but nothing for the other curves. This could indicate that the sulfate groups have detached from the CNC for reaction in isopropanol and water. Both have a peak or variation slightly left to that of DMSO which untreated CNC also have.

ATR-FT-IR on the unmodified and modified CNC are shown in Figure 5.3. Due to much noise in the data it's difficult analyse.

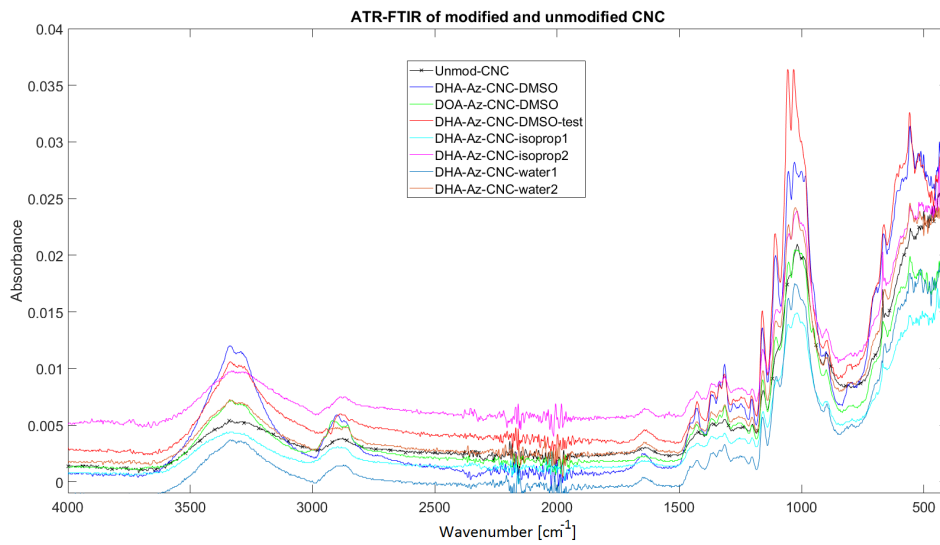


Figure 5.3: ATR-FTIR measurements of unmodified and modified CNC.

The crystallinity index (CrI), calculated from the XRD-results as explained in methods, for unmodified and modified CNC are shown in Figure 5.1.

Table 5.1: Crystallinity index of the unmodified and modified CNC. Calculated from XRD measurements as explained in the XRD method.

CNC sample	Crystallinity index[%]
Unmod-CNC	62.0
OH-Az-DHA-CNC-DMSO	74.4
OH-Az-DOA-CNC-DMSO	76.1
OH-Az-DHA-CNC-DMSO-test	75.5
OH-Az-DHA-CNC-isopropanol-1	69.7
OH-Az-DHA-CNC-isopropanol-2	71.4
OH-Az-DHA-CNC-water-1	67.9
OH-Az-DHA-CNC-water-2	75.6

All the different modifications of CNC have similar crystallinity index, Figure 5.1 as the unmodified which could mean that the modification routes don't lower the crystallinity of the starting material.

The values from the zeta potential measurement of the samples are shown in Table 5.2.

Table 5.2: Zeta potential of 0.05 % solutions of unmodified CNC, modified CNC and the CNC solution references.

CNC sample	Zeta potential mean value [mV]	standard deviation
Unmod-CNC	-70.78	1.26
OH-Az-DHA-CNC-DMSO	-30.8	2.19
OH-Az-DOA-CNC-DMSO	-35.22	0.98
OH-Az-DHA-CNC-DMSO-test	-36.1	2.11
OH-Az-DHA-CNC-isopropanol-1	-33.94	1.04
OH-Az-DHA-CNC-isopropanol-2	-67.88	2.01
OH-Az-DHA-CNC-water-1	-29.8	0.45
OH-Az-DHA-CNC-water-2	-42.96	0.83
CNC-water-ref	-54.18	2.51
CNC-DMSO-ref	-30.32	3.93
CNC-isoprop-ref	-32.72	0.82
CNC-toluene-isoprop-ref	-29.04	0.79

The zeta potential in Figure 5.2 show that for the modifications in DMSO the zeta potential is around -30 mV which is much closer to zero than unmodified CNC which is -70,78 mV. This lowering in surface charge indicates that the modifications with azetidinium salt were in an extent achieved. By looking at the other modification methods the reaction in pure isopropanol look relatively unchanged compared to unmodified CNC which indicates that it's not the best route. CNC in azeotrope from toluene to isopropanol show a number closer to zero and could therefore have a successful modification. The reactions in water also have values closer to zero and to those of DMSO which makes water a good solvent candidate for modification. This is also strengthened by the reference solvent samples which show that water has the value closest to unmodified CNC.

The TGA measuerments of the unmodified and modified CNC are displayed in Figure 5.4 and for the method references in Figure 5.5

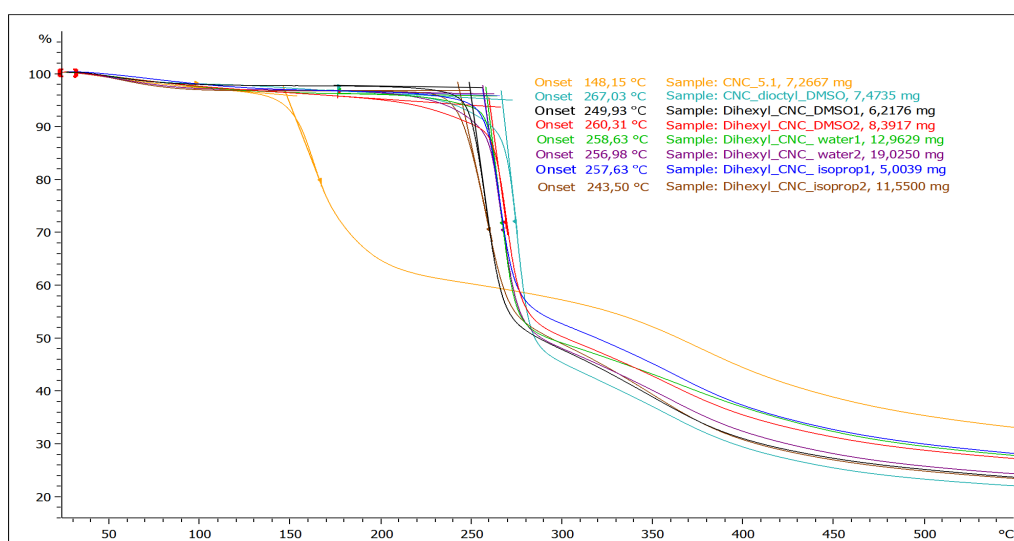
**Figure 5.4:** TGA measurements of unmodified and modified CNC.

Table 5.3: Thermal degradation temperature of the unmodified and modified CNC obtained from the TGA measurement and can also be observed in Figure 5.4. The solution references from 5.5 are also shown

CNC sample	Thermal degradation temperature [°C]
Unmod-CNC	148,15
OH-Az-DHA-CNC-DMSO	260,31
OH-Az-DOA-CNC-DMSO	267,03
OH-Az-DHA-CNC-DMSO-test	249,93
OH-Az-DHA-CNC-isopropanol-1	257,63
OH-Az-DHA-CNC-isopropanol-2	243,50
OH-Az-DHA-CNC-water-1	258,63
OH-Az-DHA-CNC-water-2	256,98
CNC-water-ref	160,54
CNC-DMSO-ref	210,53
CNC-isoprop-ref	266,64
CNC-toluene-isoprop-ref	289,97

The TGA curves in Figure 5.4 and Table 5.3 show that all the modified CNC have higher thermal stability, around 250 °C, than unmodified CNC which is stable up to around 146 °C.

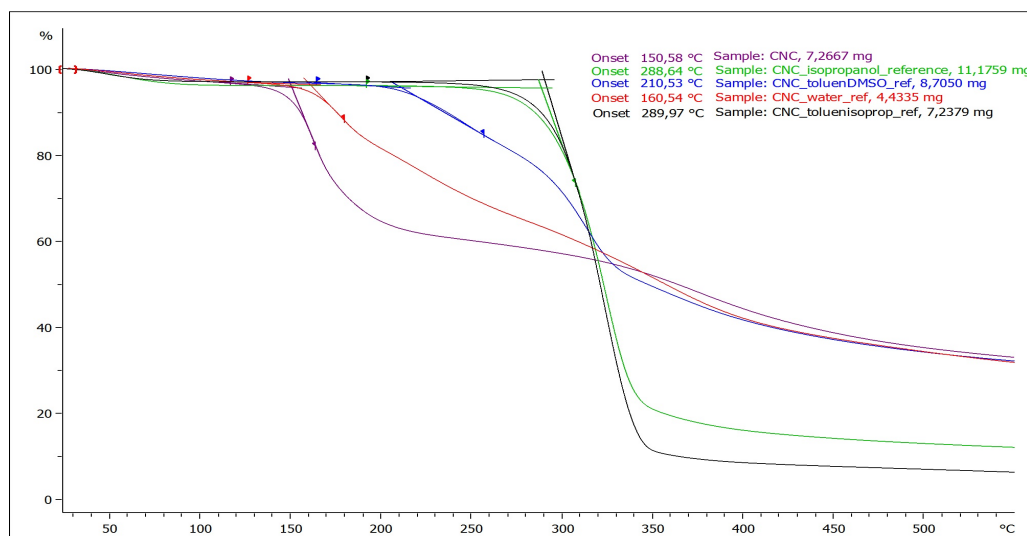


Figure 5.5: TGA measurement data of the reference CNC with displayed temperatures at which they were no longer thermal stable.

In Figure 5.5 there's a wide variation between the CNC solution references were the two CNC isopropanol references are thermally stable up to 290 °C. This is much higher than the other and there's around 20 % of the initial weight left which non of the other are even close to. This could indicate that the sulfate groups no longer are present. The isopropanol references also miss the curvature that the other references have. The curve for CNC treated in water is more similar to the unmodified and untreated CNC than what the CNC treated in DMSO is. CNC is thus less affected

5. Results and Discussion

by water than DMSO at 90°C and should based on this be a better candidate for the modification of CNC.

AFM images of CNC, dihexylamine and dioctylamine modified CNC are displayed in Figure 5.6, Figure 5.7 and Figure 5.8 respectively. The dimensions were received from analysing the particles with the AFM software.

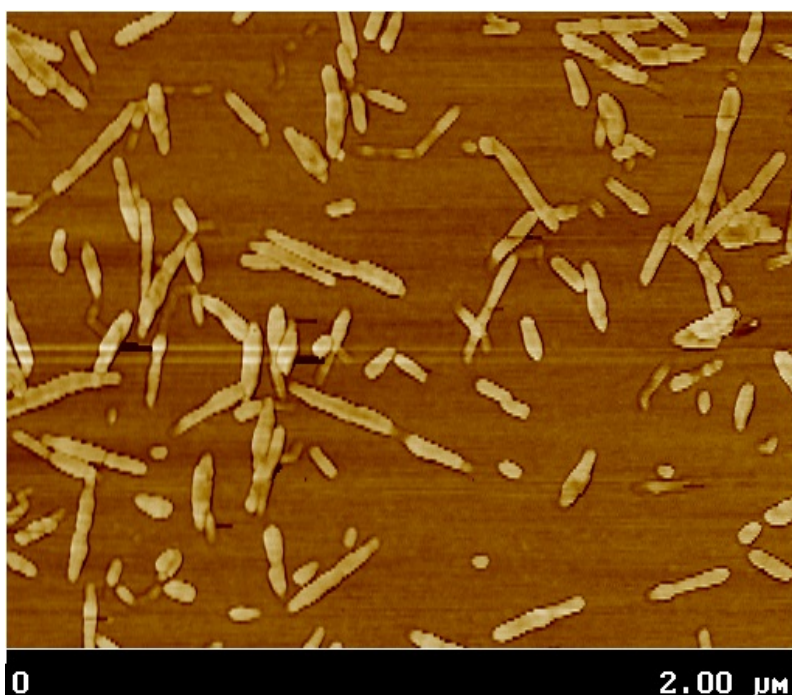


Figure 5.6: AFM image of unmodified CNC dispersed in water and dried. The length and width of some selected particles were 39-275 nm and 4.8-6.2 nm

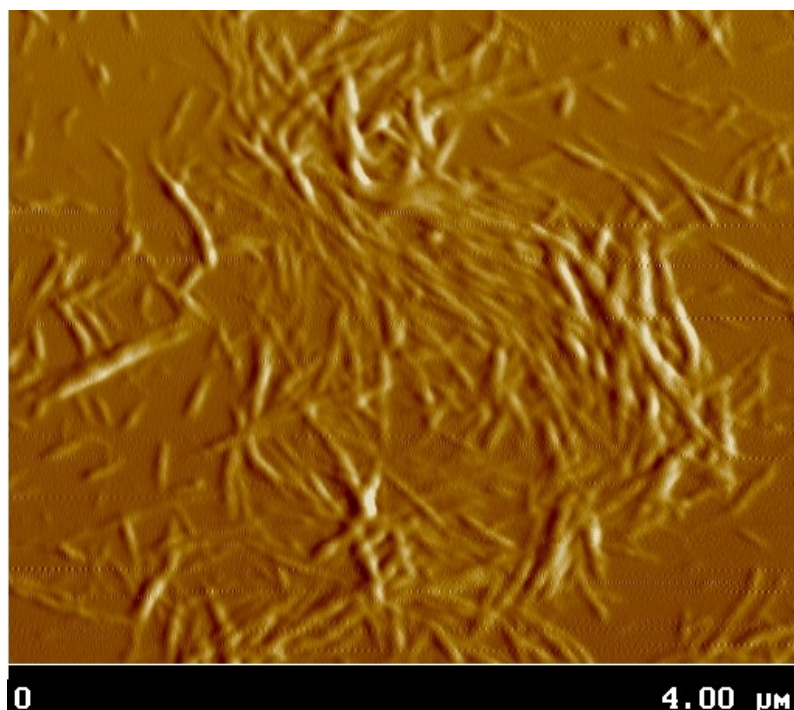


Figure 5.7: AFM image of dihexylamine azetidinium modified CNC dispersed in isopropanol and dried. The length and width of some selected particles were 220-655 nm and 4.7-5 nm

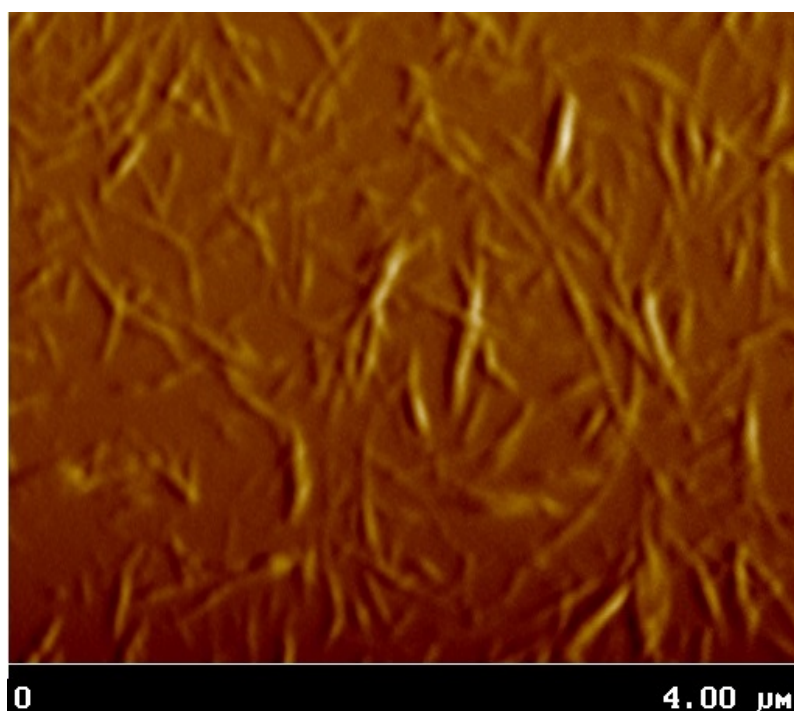


Figure 5.8: AFM image of dioctylamine azetidinium modified CNC dispersed in isopropanol and dried. The length and width of some selected particles were 273-447 nm and 2.8-7.6 nm

Table 5.4: Dimensions of the unmodified and modified CNC particles displayed in Figure 5.6 to 5.8. The measurements were spot-checked and are therefore not a full representation of the dimensions

CNC sample	Length[nm]	Width[nm]
Unmod-CNC	39-275	4,8-6,2
OH-Az-DHA-CNC-DMSO	220-655	4,7-5
OH-Az-DOA-CNC-DMSO	273-447	2,8-7,6

By analysing the AFM images, Figure 5.6 to 5.8, it could be observed that the DHA-CNC and DOA-CNC have almost the same dimensions as unmodified CNC. The modified CNC seems to be slightly longer according to the values in Table 5.4 but they are still on nano scale and both dimensions overlap with the unmodified. They look more clustered and more in number which makes it harder to get an good image and harder to measure more exact dimensions. This agglomeration could be because of the introduced DHA and DOA which increase the intermolecular attractions.

The amount of sulfate groups of the unmodified and modified CNC were supposed to be obtained from conductometric titration but the method was unsuccessful and doesn't give any arguable data. A negative value for the surface charge density, as can be seen in Table 5.5, is not representative. The method needs further adjustments and probably in the data analysis rather than the actual measurement.

Table 5.5: Sulfur content of unmodified and modified CNC

CNC sample	Surface charge density [mol/g]
Unmod-CNC	385,71
OH-Az-DHA-CNC-DMSO	-87,57
OH-Az-DOA-CNC-DMSO	5,23

5.2 Composites

Figure 5.9 show an SEM image of the PLA dispersion prepared for the composites.

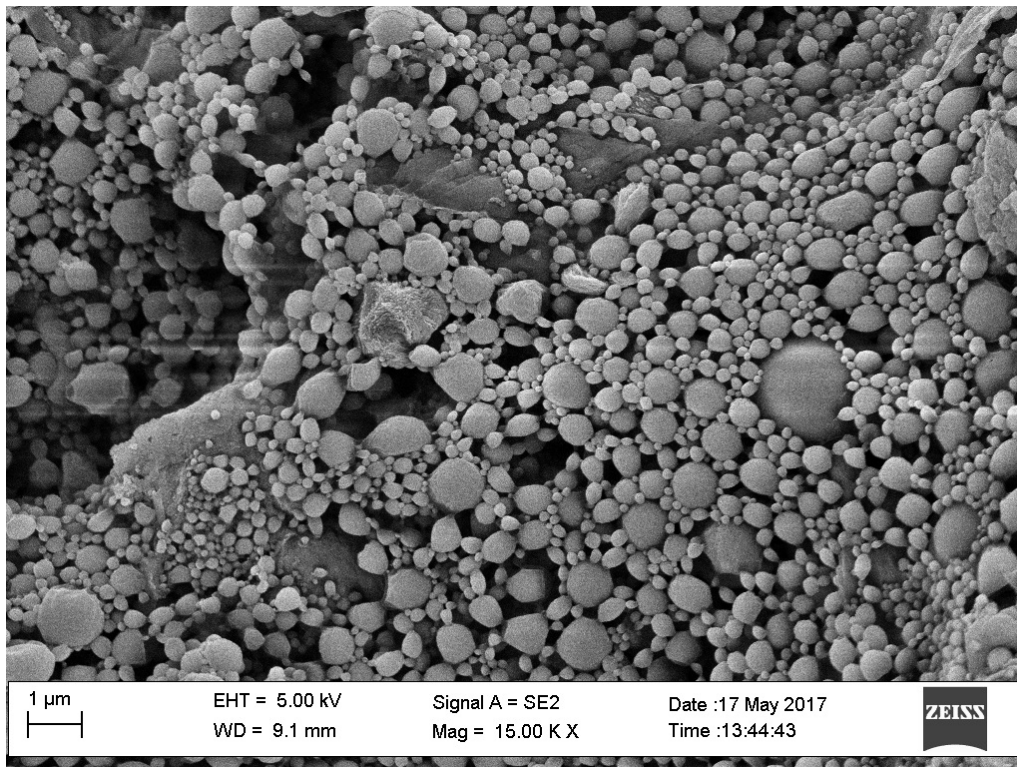


Figure 5.9: SEM image of the PLA dispersion used in the wet mixing method.

The particle size of the PLA dispersion in water is according to the SEM image, Figure 5.9, around $1\ \mu\text{m}$ with many smaller and some larger particles. Small particles are favourable for the mixing process because it gives larger surface area for the unmodified and modified CNC to attach on.

Images of the dry mixed and wet mixed composites are displayed in Figure 5.10 and Figure 5.11.

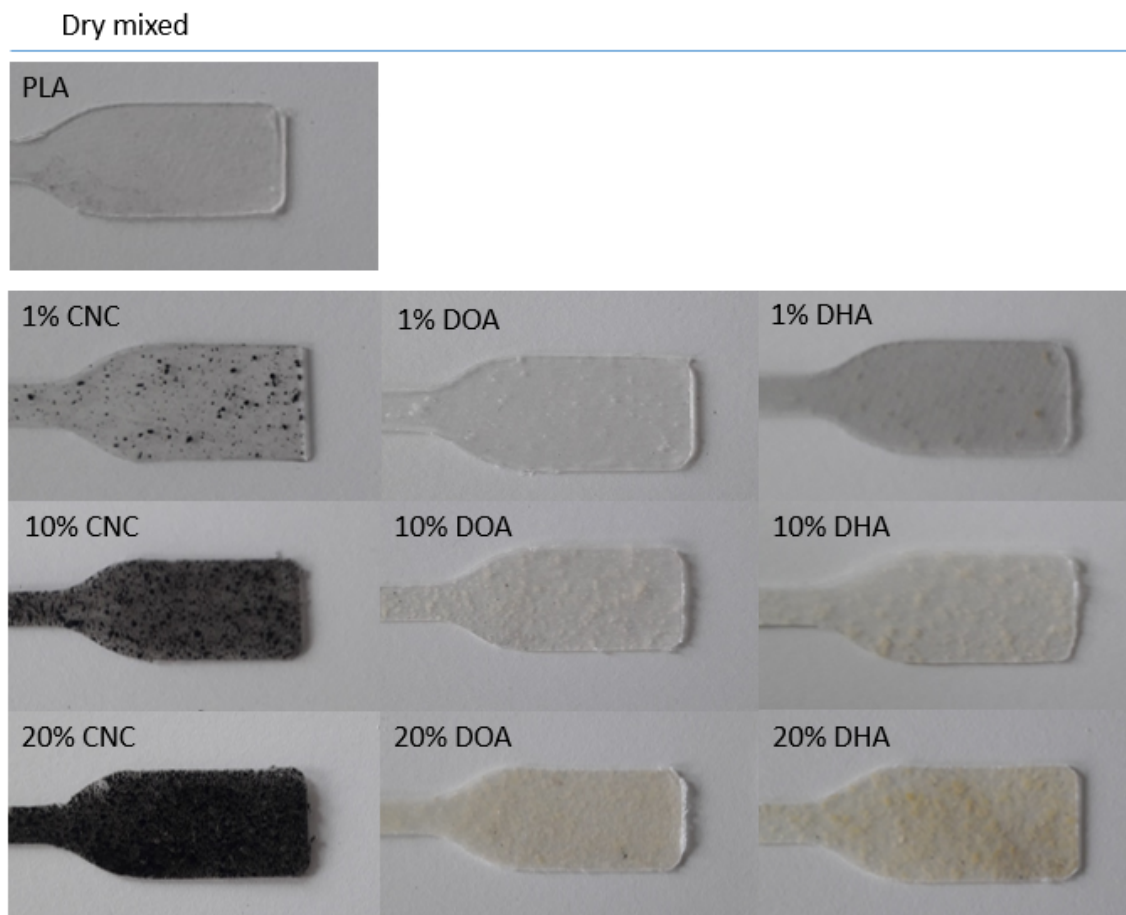


Figure 5.10: Photos of the dry mixed PLA composites with displayed CNC, DHA-CNC and DO-CNCA content. Where DHA-CNC and DOA-CNC stands for the dihexylamine azetidinium modified CNC and dioctylamine azetidinium modified CNC.

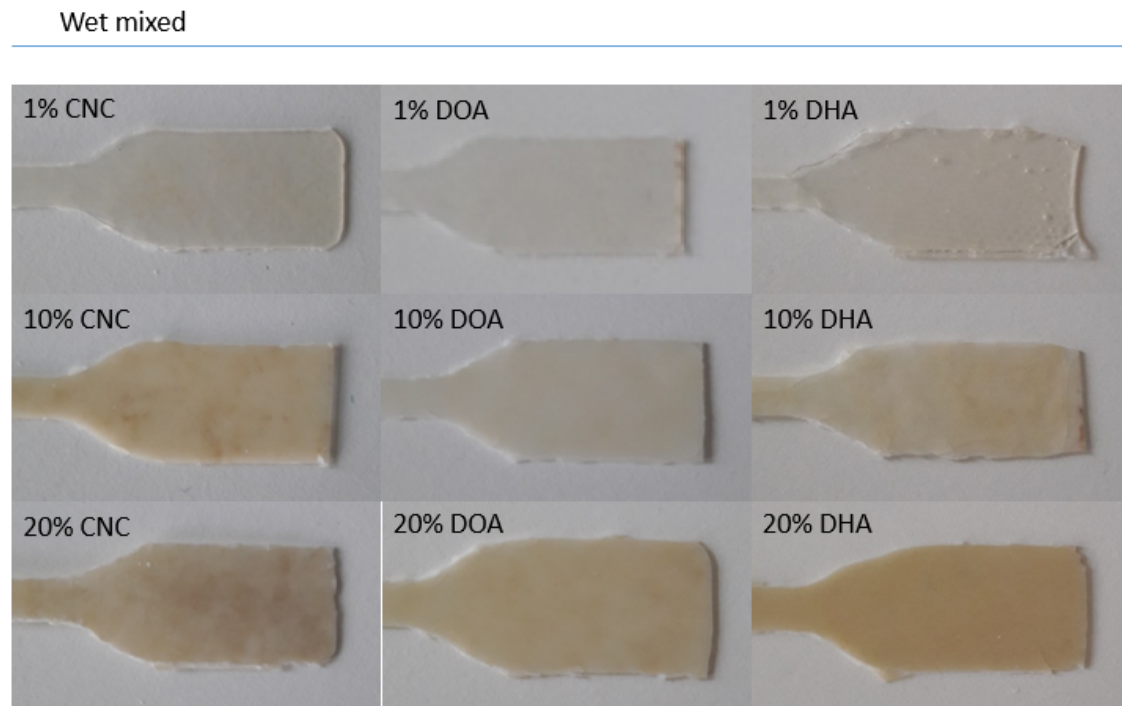


Figure 5.11: Photos of the wet mixed PLA composites with displayed CNC, DHA and DOA content

By analysing the appearance of the dry mixed PLA composites in Figure 5.10 particles of CNC, DHA-CNC and DOA-CNC can be observed in all specimens. The CNC particles got burnt due to the 160 °C mixing chamber which is expected due to the TGA result provided earlier. A colour change in the higher percentages for DOA and DHA modified composites can be observed and could imply smaller particles than the ones visible. The wet mixed composites, Figure 5.11, show in comparison to the dry mixed no visible particles. Some inhomogeneous patterns are noted in the unmodified CNC composites which could indicate less integration with the PLA than in the modified counterparts. Over all the wet mixed method appears, based on visual observation, to be the better mixing method in order to get a homogeneous composites.

The tensile test results of the composite tensile specimens are displayed as Young's modulus and stress at maximum load in Figure 5.6 for the dry mixed and in Figure 5.7 for the wet mixed. The variation of tensile specimens is due to how many that was able to be punched depending on amount and brittleness of the samples after pressing. The dry mixed specimens were punched without concern compared to the wet mixed which were more brittle and more difficult to punch into whole tensile specimens.

Table 5.6: Tensile testing data for dry mixed PLA and PLA integrated with unmodified and modified CNC. The values are the average of the written specimens.

Dry mixed composites			
Composite	Young's Modulus [MPa]	stress at maximum load [MPa]	Specimens
PLA	2206.41	58.56	6
PLA/CNC			
1 %	2446.54	54.52	5
10 %	2406.57	33.28	5
20 %	2367.77	23.71	7
PLA/DHA-CNC			
1 %	2231.19	55.80	6
10 %	2469.26	39.41	6
20 %	2627.26	32.72	6
PLA/DOA-CNC			
1 %	2327.01	51.78	5
10 %	2520.72	40.85	6
20 %	2518.48	32.93	5

The stress at maximum load of the dry mixed composites, Figure 5.6, follow the same trend for increasing content of unmodified and modified CNC which is that it decreases. The samples with 1 % do not affect the load by much while the 10 % and 20 % lowers it significantly. The samples with modified CNC do not decrease the load as much with increased amount as the unmodified CNC which could mean better interaction with the PLA matrix. The variation between the composites could also be because of difference in particle size distribution from the grinding of the unmodified and modified CNC. The modulus is related to the stiffness and the dry mixed composites do all have a higher stiffness than pure PLA. The unmodified CNC increase the stiffness but it's close to unchanged between different concentrations. For the modified CNC on the other hand the stiffness increases with concentration which could imply stronger interaction between matrix and the additive.

Table 5.7: Tensile testing data for wet mixed PLA and PLA integrated with unmodified and modified CNC. The values are the average of the written specimens.

Wet mixed composites			
Composite	Young's Modulus [MPa]	stress at maximum load [MPa]	Specimens
PLA	-	-	-
PLA/CNC			
1 %	2252.68	31.11	6
10 %	2605.16	28.13	5
20 %	3275.33	29.09	4
PLA/DHA-CNC			
1 %	-	-	-
10 %	2297.65	9.39	2
20 %	1523.62	7.62	1
PLA/DOA-CNC			
1 %	2258.58	23.75	6
10 %	2554.64	29.96	6
20 %	2337.12	9.51	3

In comparison to the dry mixed samples the wet mixed, Figure 5.7, were harder to handle and get tensile specimen due to brittleness. This could be because of an overall poor PLA matrix. The pure PLA sample, dried from the water dispersion, was too delicate to make any specimens at all which is a big difference from all dry mixed ones. With that in mind the CNC, DHA-CNC and DOA-CNC integrated composites were punchable indicating that something might have happened to the mechanical properties. The amount of CNC integrated in the composites doesn't seem to affect the stress at maximum load among themselves. The modulus increases with concentration for the unmodified CNC composite which means that the stiffness increases. For the DHA-CNC composite there's a decrease in stiffness in the 10 % composite to 20 % while the DOA-CNC first increases and then decreases. Not many specimens were achieved for the DHA-CNC and the measurable ones show poor stress at maximum load which doesn't show any increased interaction between matrix and additive. This could also be because of the PLA matrix itself. DOA modified CNC were more punchable and has values similar to unmodified CNC in regard of modulus while the stress at maximum load is lower for 1 % and 20 %. The 20 % is similar in value. DOA-CNC gave more stable composites than DHA-CNC in the wet mixed method and it could be because of higher interaction with the PLA matrix.

It seems that the PLA matrix in the wet mixed method is poor in comparison to the dry mixed one which indicates that the wet mixing method used doesn't give a stable matrix from which proper analysis could be done. The instability is probably due to that the spherical PLA particles observed in SEM didn't get mixed enough to form a more stable matrix. Although adding unmodified and modified CNC changed the overall properties of the composite making it sturdy enough to be measured on. The significance of the additive would probably have been clearer if the PLA matrix itself were more stable. The wet mixing method needs further adjustments, for instance add a mixing step where the temperature is above the melt temperature of

the PLA. The results from the dry mixed method could also be deceptive because of the relatively big particles of unmodified and modified CNC. Thus the results could be the same if other particles with the same size distribution were introduced instead. This because the particles would then only introduce defects in the matrix.

6

Conclusion

Modifying CNC with dihexylamine azetidinium salt in water seems to be an alternative route to reaction in DMSO. TGA results indicate that the modification could be more effective in water. The unmodified and modified CNC did affect the composites by increasing the stiffness for both dry and wet mixed method. The modified CNC introduced more stiffness than unmodified in the dry mixed method at higher at 10 % and 20 %. The opposite could be observed in the wet mixed method where stiffness increased with amount of unmodified CNC in the composite and in general decreased with amount modified CNC. The wet mixing method give more homogeneous composites than the dry mixed method but in terms of mechanical properties it is in need of improvement due to a weak PLA matrix. Due to this the data from the wet mixed method is not as complete as the dry mixed one and analysing it is thus more difficult.

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A

Appendix 1

A.1 CNC preparation

The crystalline nanocellulose was made by hydrolysis using sulfuric acid, 64 wt%, for 2 h steering at 45 °C. The reaction was stopped by 3-time dilution in deionized water and directly succeeded by centrifuging for 15 min at 4300 rpm. This in order to get rid of the acid. After removal of the supernatant the precipitate was dispersed again in deionized water and centrifuged. This process was repeated two times and removal of remaining sulfuric acid was removed by dialysis with deionized water until the effluents conductivity stays below 5 μ S. The CNC particles were made into a colloidal suspension by sonication at 40 % output. [4]

A.2 Azetidinium salt synthesis

Azetidinium salt is made from secondary amines and epichlorohydrin. The general reaction is illustrated in Figure A.1. The salt is generally produced by making a solution with 0.1 mol secondary amine and dropwise add 0.1 mol epichlorohydrin with the temperature below 5 °C. Then the mixture is put in an ice bath and stirred for 1 h and further stirred for 2 days at room temperature. The mixture is be purified with diethylether. Solvent and water are removed by using vacuum. [4]

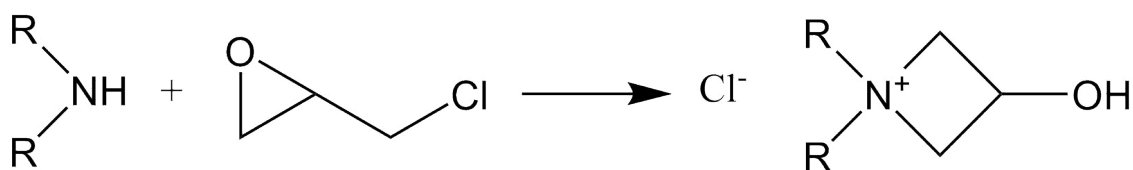


Figure A.1: Scheme of azetidinium formation from epichlorohydrin and secondary amine where R is the design choice

A.3 Modification methods

In all the reactions an equimolar amount of azetidinium salt was added. The CNC was assumed to have the molar mas of glukos, 180.156 *g/mol* and the molar mass of dihexylamin and dioctylamin are 242 *g/mol* and 298 *g/mol*.

A.3.1 Solvent exchange for CNC to toluene, Batch 1

An amount of CNC was dialysed in deionized water and then centrifuged at 4300 rpm and 15 min, the resulting water layer was decanted. Thereafter centrifugation was repeated with 100 ml of 95 % ethanol which was poured of after the centrifugation. The mass fraction of the CNC was measured to 12.4 %. The remaining water in the CNC was removed by evaporating it twice together with 200 ml toluene in an rotary evaporator.

A.3.2 Dihexyl modification of CNC trial with DMSO as solvent

From CNC in toluene Batch 1 was 1 g dry CNC (7.9 g wet CNC) taken to a plastic cup and 7 ml DMSO was added. The solution was sonicated 3 * 15 sekunds with amplitude at 40 % before put in a round bottom flask and submerged in a water bath together with an excess of dihexylamine salt, 1.34 g (0.0056 mol and 242 *g/mol*), at 90 °C for 1 day. After a day the round bottom flask was taken out of the bath and cooled to room temperature. 5 ml of ethanol was added and the CNC moved to an glass beaker. After 20 min the ethanol was decanted of and some deionized water was added. The pieces of CNC was mashed before the solution was poured into a dialysis membrane tube and submerged in deionized water for three days.

A.3.3 Dihexyl modification of CNC trial with water as solvent

100 g wet (2.98 g dry) CNC was measured up in an glass beaker from CNC batch 5.1 with mass fraction 2.98 %. The solution was sonicated 3*15 seconds with amplitude at 40 %. 3.99 g dihexylamine azetidinium salt (0.0056 mol and 242 *g/mol*) was added to the CNC while stirring. The Solution was poured onto a aluminium foil form in an oven at 110 °C during the night. The CNC was assumed to have the molar mas of glukos, 180.156 *g/mol*. After a day the round bottom flask was taken out of the bath and cooled to room temperature. 5 ml of ethanol was added and the CNC moved to an glass beaker. After 20 min the ethanol was decanted of and some deionized water was added. The pieces of CNC was mashed before the solution was poured into a dialysis membrane tube and submerged in deionized water for three days.

A.3.4 Dihexyl modification of CNC with DMSO as solvent

73.08 g 12.4 % solution of CNC in toluene (Batch 1) was measured and DMSO was added in a 4:1 relationship to the existing toluene, 300 ml. The mixture was sonicated for 3x2 min, until the CNC was well dispersed. 12.14 g dihexylamine-azetidinium salt was weighed in a round bottom flask and then the CNC was added slowly during stirring. The mixture was stirred and heated at 90 °C during 1 day for the reaction to take place. After a day the round bottom flask was taken out of the bath and cooled to room temperature. The Solution was poured into a dialysis membrane tube together with 5 ml of water and submerged in deionized water for three days. After

the three days the solution was poured into a glass beaker and 1 L water was added and then membrane filtration was tried and abandoned due to CNC being able to go through the membrane. The solution was then centrifuged at 4300 rpm for 15 min 2 times with decanting the water-DMSO-toluene liquid after each session. Then it was washed with ethanol by centrifuging for 10 min 4 times with 50 ml ethanol and decanting each session. The first two decantings had particles floating and was therefore saved for investigation. The endproduct had a mass fraction of 10 % and weighed 114.8 g wet and the weight of only CNC was 11.48 g. 2.7 g of the wet CNC was dried for analysis with XRD and IR.

A.3.5 Solvent exchange for CNC to toluene, Batch 2

An amount of CNC was dialysed in deionized water and then centrifuged at 4300 rpm and 15 min, the resulting water layer was decanted. Thereafter centrifugation was repeated with 100 ml of 95 % ethanol which was poured of after the centrifugation. The mass fraction of the CNC was measured to 13.62 %. The remaining water in the CNC was removed by evaporating it twice together with 200 ml toluene in an rotary evaporator.

A.3.6 Dioctyl modification of CNC with DMSO as solvent

73.13 g 16.62 % solution of CNC in toluene (Batch 2) was measured and DMSO was added in a 4:1 relationship to the existing toluene, 300 ml. The mixture was sonicated for 3x2 min, until the CNC was well dispersed. 16.12 g dihexylamine-azetidinium salt was weighed in a round bottom flask and then the CNC was added slowly while stirring. The mixture was stirred and heated at 90 °C during 1 day for the reaction to take place. After a day the round bottom flask was taken out of the bath and cooled to room temperature. 200 ml of water was added followed by stirring and then centrifuging at 4300 rpm for 15 min. what didn't precipitate was decanted into a separating funnel due to floating particles. The CNC was then washed by centrifuging with 100 ml ethanol 4 times followed by decanting. The mass fraction of the finished product was 17.72 % and the amount wet sample was 66.35 g and 2.37 g was dried for XRD and IR.

A.3.7 Dihexyl modification of CNC with water as solvent 2

112.8 g 2.69 % dialysed CNC was sonicated for 3x15 seconds with amplitude at 40 %. An equimolar amount of dihexylamine-azetidinium salt, 4 g, was weighed in a round bottom flask and then the CNC was added slowly while stirring. The mixture was stirred and heated at 90 °C during 1 day for the reaction to take place. Thereafter the mixture was cooled in room temperature and then centrifuged for 15 min at 4300 rpm. The supernate was poured of and the precipitate was washed by centrifuging with 50 ml ethanol 4 times for 10 min at 4300 rpm. The mass fraction of the finished product was 10.94 %.

A.3.8 Dihexyl modification of CNC with isopropanol as solvent 2

36.9 g 7.23 % centrifuged CNC was centrifuged with 50 ml isopropanol 4 times 10 min at 4300 rpm with decanting after each time. The last precipitate was sonicated in 100 ml isopropanol for 3x1 min at 40 % amplitude. To this an equimolar amount of dihexylamine-azetidinium salt, 3.58 g, was weighed in a round bottom flask and then the CNC was added slowly while stirring. The mixture was stirred and heated at 90 °C during 1 day for the reaction to take place. Thereafter the mixture was cooled in room temperature and then centrifuged for 15 min at 4300 rpm. The supernate was poured of and the precipitate was washed by centrifuging with 50 ml ethanol 4 times for 10 min at 4300 rpm. The mass fraction of the finished product was 20.28 %.

A.4 DSC

A DSC measurement on PLA powder from the grinding process is shown in Figure A.2.

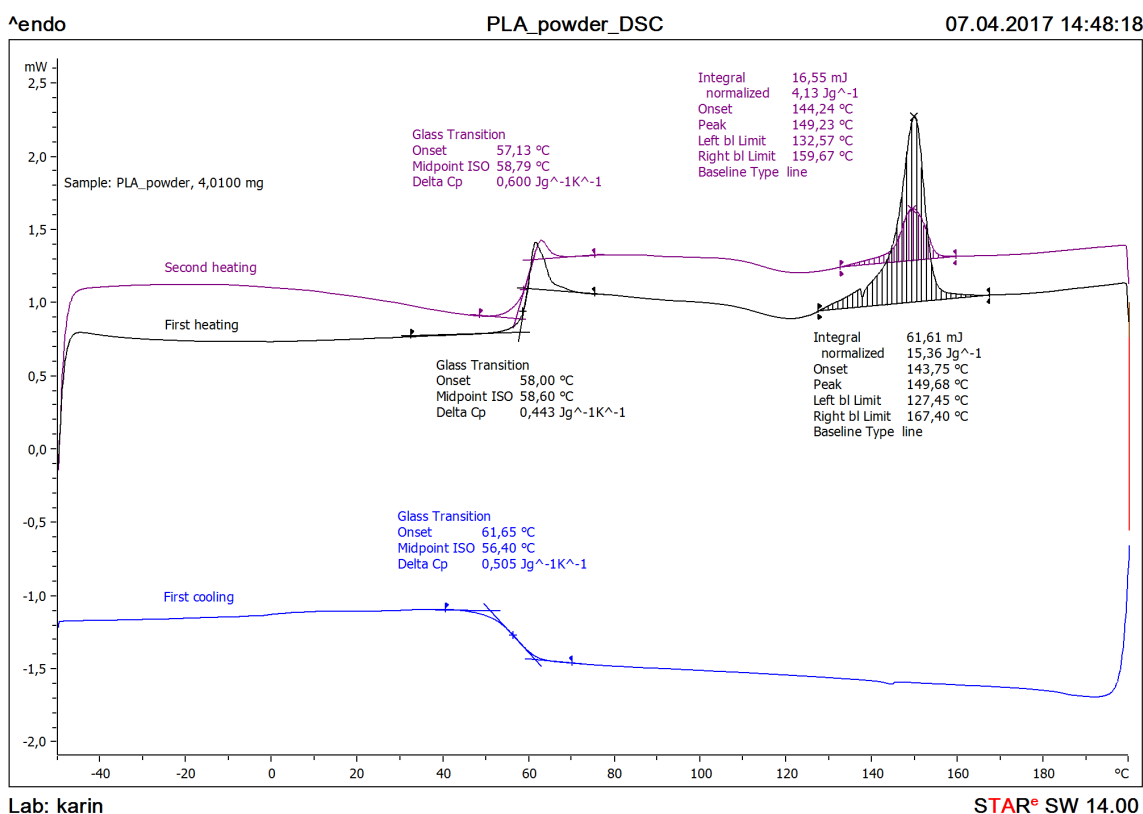


Figure A.2: DSC measurement of PLA where the first peak is the glass transition temperature, around 59 °C, and the second is the melt temperature, around 144 °C.

B

Materials used

B.1 PLA

The PLA (polylactic acid) polymer was required from Nature works with the product name Ingeo 3051d. The specifics of this polymer are described in Table B.1 and B.2.

Melt Temperature	200 °C
Feed Throat	20 °C
Feed Temperature	165 °C
Compression Section	195 °C
Metering Section	205 °C
Nozzle	205 °C
Mold	25 °C
Screw Speed	100-175 rpm
Back Pressure	3.5-6.9 bar
Mold Shrinkage	.004 in/in+/-0.001

Table B.1: Processing temperature profile where the starting points may be optimized.

Physical properties	Value	ASTM
Specific Gravity	1.25	D792
Melt Index, g/10 min (210°C/2.16Kg)	10-25	D1238
Relative Viscosity	3.0-3.5	
Crystalline Melt Temperature (°C)	150 – 165	D3418
Glass Transition Temperature (°C)	55-65	D3417
Clarity	Transparent	
Mechanical Properties	Value	ASTM
Tensile Yield Strength, psi (MPa)	7,000 (48)	D638
Tensile Elongation, (%)	2.5	D638
Notched Izod Impact, ft-lb/in (J/m)	0.3 (0.16)	D256
Flexural Strength (MPa)	12,000 (83)	D790
Flexural Modulus (MPa)	555,000 (3828)	D790

Table B.2: Typical physical and mechanical properties of the PLA Resin and what ASTM methods used.