THESIS FOR THE DEGREE OF LICENTIATE ENGINEERING

Physical properties of dispersions and composites containing surface-grafted cellulose nanocrystals

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Department of Industrial and Materials Science
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2018

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Cover:

Composite material with an EAA matrix containing 10 weight-% cellulose nanocrystals (CNC), with unmodified CNC in the upper row and surface-modified CNC in the lower row. The specimens were exposed to a heat gradient ranging from right to left between 120 and 160 °C for 8 min.

(More information presented on page 11 in paper II)

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Abstract

The needs and requests from the society for non-fossil-based materials as well as more lightweight products are constantly increasing. The increasing awareness of the sustainability of the resources available paralleled by a growing population, point to a need for changes, if the population also aim for constantly higher standard of living. Cellulose is a renewable material, produced by all plants on earth through photosynthesis using solar energy. It has promising properties, being the supportive and stiff structure in plants and trees, and has been widely used throughout history as a construction material and in everyday life.

The smallest entity of the cellulose fibre, the cellulose nanocrystals (CNC), exhibit even greater promising properties with their low weight, high aspect ratio and high specific stiffness in combination with biodegradability and renewability. Using CNC as reinforcements in a polymer matrix reduces in principle the need for fossil-based materials and reduces also the weight of the component. There are however some challenges, the hydrophilic nature of cellulose and the hydrophobic nature of most polymers causing low adhesion and poor dispersion. The temperatures needed for most thermoplastic processes also exceed the onset temperature for thermal degradation of cellulose, about 150-200 °C.

Here, azetidinium salts have been used to graft three different functional groups onto the CNC surface, aiming at improving the thermal stability of the CNC but also the compatibility between a polymer matrix and CNC in a composite material. The focus in the first part of the study was to evaluate the properties of and interactions between the grafted groups in aqueous dispersions of surface-treated CNC. This was followed by manufacturing of composites using dispersion mixing of CNC and an ethylene-acrylic acid copolymer and compression moulding of plaques. The composites were then evaluated in terms of mechanical properties and thermal stability.

The surface-grafting resulted in a large increase in thermal stability of the CNC; the onset temperature for thermal degradation increased from 150 °C to 250 °C. The addition of CNC also had a strong influence on the mechanical properties of the composites, e. g. resulting in an up to three times higher elastic modulus when adding 10 weight-% CNC. Several experimental methods indicated enhanced interactions either between the grafted groups and/or between the polymer matrix and the grafted groups.

Keywords: *Cellulose, Cellulose nanocrystals, Composite, Thermal stability, Rheology, Tensile properties*

Preface

This Licentiate thesis is based on the work performed at the Department of Industrial and Materials Science at Chalmers University of Technology between April 2016 and August 2018 under the supervision of Mikael Rigdahl and Antal Boldizar.

List of appended papers:

I. Surface treatment of cellulose nanocrystals (CNC): effects on dispersion rheology
K. Sahlin, L. Forsgren, T. Moberg, D. Bernin, M. Rigdahl & G. Westman
Cellulose, Volume 25, Issue 1, Pages 331-345, January 2018

II. Composites with surface-grafted cellulose nanocrystals (CNC)
L. Forsgren, K. Sahlin, A. Venkatesh, J. Thunberg, R. Kádár, A. Boldizar, G. Westman & M. Rigdahl
Manuscript, submitted for publication.

Abbreviations

AA – Acrylic acid

CNC – Cellulose nanocrystals

CNC-dihexyl-OMe – CNC surface grafted with dihexyl group using methoxyazetidinium

CNC-diallyl-OMe – CNC surface grafted with diallyl group using methoxyazetidinium

CNC-morph-OMe – CNC surface grafted with morpholine group using methoxyazetidinium

CNC-diAllyl-OH – CNC surface grafted with diallyl group using hydroxyazetidinium

CNC-diHexyl-OH – CNC surface grafted with dihexyl group using hydroxyazetidinium

CNC-Morph-OH – CNC surface grafted with morpholine group using hydroxyazetidinium

CNC-unmod – Unmodified/untreated CNC

DMA – Dynamic mechanical analysis

DSC – Differential scanning calorimetry

E – Ethylene

EAA – Ethylene acrylic acid

FTIR – Fourier transform infrared spectroscopy

MCC – Microcrystalline cellulose

NMR – Nuclear magnetic resonance

TGA – Thermal gravimetric analysis

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1 Introduction

Since the concern of the environment is increasing in the world, the need for new, more environmentally friendly materials is rapidly growing. Researchers, scientists and the overall society are simultaneously trying to find substitution for fossil-based products. Making products lighter and being able to reduce the amount of material needed to fulfil the same purpose is one way to go, but reducing the usage of fossil-based materials is vital. Looking into "new" materials, a commonly used group, that has been somewhat forgotten the last years, but widely used throughout history is the cellulose-based materials, e. g. from wood and other types of plants. This is a huge material resource of renewable matter, produced by the plants using sunlight during the photosynthesis.

The forest industry is for obvious reasons large in Sweden, with 2/3 of the country is covered by forest. (Forest statistics, 2018) National regulations impose replanting of the forest, resulting in an increase of the growing stock of about 100 % over the last century. But, the need for printing paper has been reduced as printed resources are more and more converted into online versions and the forest and paper industry are searching for new applications for the wood material. At the same time, there is a growing interest from companies and society to use more environmentally friendly or "green" materials, being able to market a more sustainable choice to the customer and also to fulfil the more demanding regulations and restrictions from governments and EU regarding both additives, plastics and emissions.

Cellulose from wood could be used to reinforce polymeric materials, creating a strong and more environmentally friendly alternative to for example glass fibres since cellulose is lighter, non-fossil-based and even more interesting, there are large amounts available at a relatively low cost.

However, processing of polymers and polymer composites (of the thermoplastic type) requires normally high temperatures and pressures and when mixing cellulose into the thermoplastic, new challenges occur. Cellulose has a rather low thermal stability and is expected to degrade at elevated temperatures and extended residence times. Depending on the polymer matrix used, the required processing temperatures can be rather high and if the cellulose fibres start to degrade, the mechanical performance of the composite will deteriorate and additionally, the surface characteristics and the visual perception of the component can change.

1.1 Cellulose

Cellulose is the most abundant polymer on earth and is present in all plants. It can also be found in algae, fungi and some certain species of bacteria, but the majority of cellulosic materials is found in the plant cell wall. Cellulose is a linear homo-polysaccharide structured in crystalline and amorphous regions forming the cellulose microfibrils or nanofibrils. The fibrils are packed into bundles and form larger fibres within the plant cell wall. Cellulose is contributing with the strength and stiffness of plants, making it possible for tall thin structures and stems to withstand the stresses from the environment.

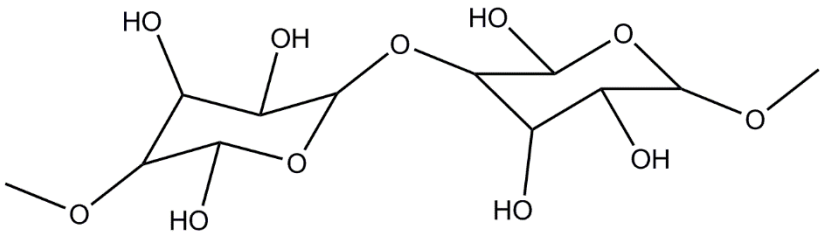

Figure 1: Cellulose molecular structure.

Wood is of special interest in this study and the Swedish forest is vast and the forest industry is of great importance for the nation. Approximately 40 % of the wood structure is cellulose, and the other main components are hemicelluloses (30 %), lignin (30 %) and some minor amounts of extractives. These components can be separated in various ways, following normal processes within the pulp and paper industry. (Henriksson et al. 2008)

The hydroxyl groups (-OH) of cellulose form hydrogen bonds both within the molecule and between the molecules, thus forming strong crystalline regions. The decomposition of cellulose takes place at temperatures lower than any melting and therefore it is not possible to process cellulose using thermoplastic techniques.

1.1.1 Cellulose as a reinforcing element

Cellulose have been and are continuously used in numerous applications and as a construction material throughout human history. There is an ongoing development of the use of this multifaceted material into new applications by different processing techniques or treatments as well as an additive into other material classes. For example, cellulose can be incorporated into concrete and isolation materials, it can be used as a thickener in food and viscous products like paint and it can serve as a reinforcement or filler in thermoplastics and thermosets. (Ardanuy 2015, Bandyopadhyay-Gosh 2015, Deckner 2016) The concept of using cellulose- or wood-based fillers in polymers composites is not new, cf e. g. Kokta et al. (1983), Klason et al. (1984), Miao et al. (2013), Pickering et al. (2016) and a substantial amount of work has aimed at optimizing the influence of natural fibres in such applications.

Both Kiziltas et al. (2013) and Pervaiz et al. (2016) looked in more detail into the possibilities and trends within the automotive industry with regard to the use of cellulose-reinforced composites. They noted a positive trend for such composites since the automotive industry is aiming for lighter cars and reduced fuel consumption but also to meet the request from the customers with more environmentally benign products and components.

Combining cellulose with a polymer gives great opportunities to both improve the mechanical properties of inherently rather weak and flexible polymers, and at the same time reduce the need for fossil-based materials. It might also be possible to replace some glass-fibre reinforcements with cellulosic materials in the future. Cellulose has potentially good mechanical properties as a reinforcing element with high specific stiffness and strength. In addition to the promising mechanical property profile and its low density, the main advantages of cellulose are of course

its renewability, biodegradability, low abrasion towards processing equipment and almost unlimited availability to a low cost if the replanting is continuous.

However, when using cellulose as a reinforcing material in polymer matrices, some challenges are faced. The hydrophilic nature of cellulose makes it prone not only to absorb water but also to repeal the most conventionally used polymers due to their, often, hydrophobic nature. The ability to absorb moisture impedes the processing into components since high moisture levels are not desired, and this possibly may also contribute to the formation of agglomerates. The fibre agglomerates are hard to break up and thus makes it difficult to distribute the fibres uniformly in the polymer matrix. The mismatch in hydrophilic/hydrophobic character between cellulose and most plastics can also result in a weak interphase region between the two components and thus to adhesion problems (Bledzki et al. 2005; Dalväg et al. 1985)

Another challenge when using cellulose as a reinforcement in polymer matrices is the thermal stability of cellulose. Elevated temperatures are needed when processing thermoplastic materials, but the degradation of the cellulose might start even below the required processing temperatures, depending on the choice of polymer matrix.

1.1.2 Cellulose nanocrystals – CNC

Cellulose structures with at least one dimension in the nanometer range is denoted nanocellulose. There are in general two different types of nanocellulose; cellulose nanofibrils (CNF) and cellulose nanocrystals. In this thesis, only CNC have been considered.

On a structural level, the cellulose fibre can be regarded as being built-up of nanofibrils containing both amorphous and crystalline regions. When removing the amorphous parts of the nanofibrils, densely packed crystalline particles (CNC) are obtained in the ideal case, which possess promising mechanical properties due to their dense and strong structure as well as a large surface area for adhering to the matrix. Values reported by Lee et. al. (2014) indicate the tensile strength for a CNC to be in the range of 0.3-22 GPa and the corresponding axial modulus to be between 58 and 180 GPa, which certainly account for the interest in using CNC as a reinforcing element in composite materials, sf e. g. Klemm et al. (2011). The removal of the amorphous regions could be accomplished by hydrolysis of the cellulosic fibres/fibrils using sulfuric acid. (Beck-Candanedo et al. 2005; Rånby 1951) The hydrolysis converts some of the surface hydroxyl groups on the CNC to negatively charged sulphate ester units, providing a stabilisation of CNC in aqueous dispersions and reducing the tendency to agglomerate. But the sulphate groups also promote thermal degradation through a dehydration process, starting already at 150 °C, which could be detrimental since commonly used engineering polymers require higher processing temperatures. (Roman and Winter 2004; Wang et al. 2007)

The CNCs used in this project are typically of the size 6 nm thick and approximately 200 nm long, hence having a thin needle-like structure. (Moberg et al. 2017). Figure 2 shows a micrograph, obtained using atomic force microscopy (AFM) of a dried CNC dispersion.

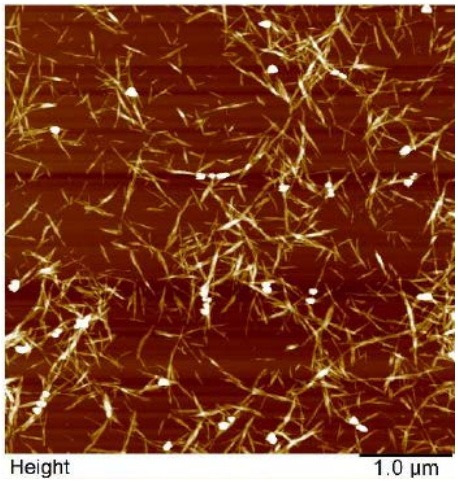

Figure 2: AFM micrograph of a dried CNC network (Moberg et al. 2017).

1.1.3 Surface grafted CNC

Trying to tailor the properties of the CNC, functional groups could be grafted onto the cellulose surface in order to reduce the effects of the previous mentioned challenges when using CNC as a reinforcement in polymer matrixes. By surface grafting, it is potentially possible to reduce the hydrophilic nature of cellulose, thus possibly improving the compatibility with a hydrophobic matrix. The chemical groups grafted onto the surface could also be tailored to the specific polymer that is intended to be used as the matrix in order to control the interaction between the components in the most profitable way. Furthermore, the thermal stability could be increased by grafting a functional group by shifting the initial degradation to a higher temperature. The idea of chemically surface-modify nanocellulose is not new, Börjesson and Westman (2015) have summarized some possible routes and processes used to customize the properties of CNC. In this project, a procedure using azetidinium salts have been used to graft functional groups onto the cellulose nanocrystals. This method is described in more detail in section 3.1.1.

1.2 Ethylene-acrylic acid copolymer (EAA)

Ethylene-acrylic acid is a copolymer consisting of ethylene and acrylic acid sections in the polymer chain, Figure 3. The copolymer combines the properties of ethylene (E) and acrylic acid (AA), where the ethylene segments provide crystallinity, flexibility and water resistance, whereas AA provides toughness and promotes adhesion properties and polarity. (Michelman 2018) In practise, the acrylic acid content decreases the melting temperature compared to pure polyethylene (approx. 80-110 °C for EAA depending on concentration of AA and 105-140 °C for polyethylene) but the AA content also makes the copolymer more hydrophilic than

polyethylene and hence potentially more easily mixed with the hydrophilic cellulose. (Michelman 2009)

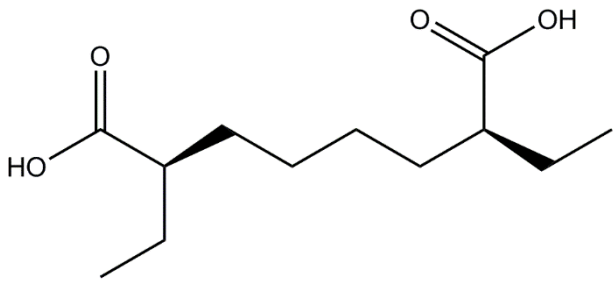

Figure 3: EAA molecular structure with alternating ethylene repetitive units and acrylic acid sections.

1.3 Compression moulding

Compression moulding is a commonly used processing technique, enabling a wide variety in product shape and processing settings. Being the main processing method for polymers in the beginning of the 20th century, but it is nowadays to a large extent replaced by the injection moulding processes which can provide higher production rates giving a lower cost-to-performance level. (Rosato et al. 2004) The compression moulding technique is however still commonly used, especially for small volume production.

During compression moulding cycle, the plastic raw material is simply converted into finished products by compression in a mould to the desired shape using elevated temperatures and high pressures. A metered sample, in the form of polymer granulates or similar, are placed in the heated mould cavity before closing the mould. When reaching the target temperature, the cooling will start while maintaining high pressure until the component have solidified and is ready to be ejected. Figure 4 is a photo of the compression moulding equipment used in the present study.

Figure 4: The compression moulding equipment used in the present study.

Compression moulding has the advantage of providing low tooling costs because of the usually simply used moulds. Furthermore, there is little or no wasted material since there are no spruce or runners as in the injection moulding process and when using a simple mould, a more or less uniform material with limited anisotropy in mechanical properties or distribution of fibres in the final component. (Rosato et al. 2004)

1.4 Aim

The aim of this project is to investigate the possibilities to develop composites with nanocellulose as the reinforcement by surface grafting the CNC to achieve desired properties, i. e. mechanical performance and effects on thermal stability as well as compatibility with a hydrophobic polymer matrix.

The long term goal is to reduce the amount of fossil-based materials used by replacing those currently used with equivalent renewable materials. This requires an increased understanding of how to utilize cellulose-based materials in composite materials and how to modify them (if required) to meet the demands in this type of application. An understanding of the interactions between the reinforcing elements and the polymer matrix is essential here. Such knowledge could possible also increase the possibilities for replacing fossil-based polymer matrices with bio-based matrices in the future.

There is also an interest from the society and forest industry to make relevant use of the great resources of wood in Sweden in order to reduce the impact on the environment in a sustainable way.

2 Materials

2.1 Cellulose nanocrystals (CNC)

The cellulose nanocrystals (CNC) were obtained by using sulphuric acid hydrolysis of microcrystalline cellulose (MCC), Avicel® PH101, with an average particle size of 50 µm, using a procedure described by Hasani et al. (2008). By hydrolysis of the MCC using sulphuric acid, the amorphous regions are removed leaving only the nanocrystals (in the ideal case). This treatment converts some of the hydroxyl groups on the CNC surface to negatively charged sulphate ester units, which contributes to the stability of the CNC in an aqueous dispersion by reducing the inclination of CNC to agglomerate.

2.2 Ethylene-acrylic acid copolymer (EAA)

The ethylene-acrylic acid copolymer (EAA) dispersion was obtained from BIM Kemi AB, Sweden. This grade had an acrylic acid content of 15 %, a melting point of 88 °C, a density of 0.994 g/cm^3 and a melt flow rate of 36 g/10 min (ISO 1133, 190 °C, 2.16 kg) according to the supplier. The dispersion had a solids content of 20 weight-% EAA and pH 9.7.

3 Experimental

Several experimental techniques have been used throughout the project and a short summary of each of them will follow. More in-depth descriptions of the techniques and the conditions used can be found in the two appended papers.

3.1 Manufacturing and processing

3.1.1 Surface grafting of CNC

The CNC prepared as described in section 2.1 using the procedure by Hasani et al. (2008) were surface modified by following a procedure outlined by Chattopadhyay et al. (2012) using substituted azetidinium salts to graft three different chemical groups onto the cellulose surface. In Paper I, these salts were N-morpholino-3-methoxyazetidinium, N,N-dihexyl-3-methoxyazetidinium and N,N-diallyl-3-methoxyazetidinium, denoted in the following as MorphOMe, diHexylOMe and diAllylOMe, respectively. The schematic molecular structure of the three different salts can be seen in Figure 5. The synthesis of the azetidinium salts is described in detail in Paper I

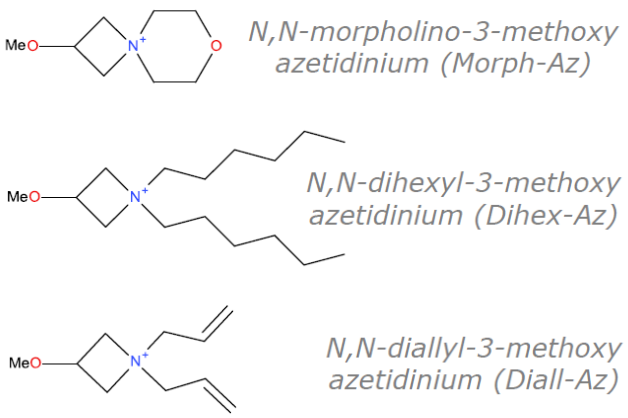

Figure 5: Schematic outlines of the molecular structures of the salts.

The grafting procedure described by Chattopadhyay et al. (2012) is based on the reaction between the azetidinium ion and the sulphate groups on the surface of the CNC. Previous work by Hasani et al. (2008) has shown that the dimensions of the CNC did not change significantly by this type of surface grafting.

The initial studies (Paper I), regarding the characterization of the CNC and the rheological behaviour of the corresponding dispersions, were performed with a grafting involving a methylation of the azetidinium salts, whereas for the production of composites (Paper II), the methylation was omitted. Experimental studies (mainly based on rheological measurements) indicated no significant differences in performance or characteristics of the surface-treated CNC due to this omission, but it made the modification procedure significantly more straightforward. The surface-grafted CNC produced with the process using no methylation, but

only hydroxyazetidinium (Paper II), are denoted CNC-Morph-OH, CNC-diAllyl-OH, CNC-diHexyl-OH, respectively, and their performance is compared with the same type of untreated CNC as in Paper I.

3.1.2 Mixing of CNC and EAA

The aqueous dispersions of CNC and EAA were blended to achieve three different concentration levels in the composite materials; 0.1, 1 and 10 weight-% CNC. This was the case for all three surface modifications as well as the unmodified CNC. An IKA T25 digital Ultra Turrax was used for 6 minutes at 7400 rpm to ensure throughout mixing. The mixed aqueous dispersions were then poured onto large plates and allowed to air-dry for approximately one week.

3.1.3 Compression moulding

Composite materials were obtained by compression moulding 12 g of the dried flakes of the EAA/CNC material using the hydraulic press (Buscher-Guyer KHL 100, Switzerland) shown in Figure 4.. In this study, quadratic plates of the composite, with an areal size of 100x100 mm^2 and a thickness of about 1 mm, were produced The compression moulding was performed at 105 °C and with a maximum pressure of 500 bar, for approximately 5 min. A detailed description of the moulding procedure can be found in Paper II.

3.2 Characterization methods

3.2.1 Rheology

The rheological properties of the aqueous CNC dispersions were assessed at 25 °C using an Anton Paar MCR 702 Rheometer (Graz, Austria) with a cone-plate configuration with a diameter 50 mm and cone-plate angle 1.991°. The measurements were carried out with two concentration levels of CNC, 0.65 and 1.3 wt-%. The starting dispersions had a somewhat higher concentration and were consequently diluted with deionized water to reach the two target concentrations. The applied shear rates were varied between 1 and 1000 s^{-1} and the steady-state shear viscosity was determined as a function of the shear rate. The dynamic-mechanical properties were measured during a strain-sweep at 1 Hz in which the storage modulus *G'* and the loss modulus *G"* were assessed as functions of the applied shear strain amplitude.

3.2.2 Thermal stability

Thermal gravimetric analysis, using a TGA/DSC 3+ Star system from Mettler Toledo, Switzerland, was applied in order to determine the onset temperature for thermal degradation. This characterisation was performed with the aqueous dispersions of CNC as well as for the composite material containing 10 weight-% CNC. Samples with the weight 10 mg were subjected to a heating ramp from 25 °C to 500 °C with a heating rate of 5 °C/min in nitrogen atmosphere at a flow rate of 20 mL/min (aqueous dispersions of CNC) or 50 mL/min (composite).

The composites were also examined visually using a Kopfler Bench, that provides a heat gradient, in order to compare discoloration effects and hence possibly also initiation temperatures for thermal degradation. Small samples of each composite with 10 weight-% CNC (surface treated as well as untreated) and a reference sample with pure EAA were placed at 120, 130, 140, 150 and 160 °C for 8 minutes.

3.2.3 Characterisation of the surface-grafting

To ensure that the surface grafting was successful, a number of characterizations methods was applied to the surface-treated CNC. These analyses were mainly performed by Karin Sahlin and Gunnar Westman from the Department of Chemistry and Chemical Engineering at Chalmers University of Technology, co-authors of Papers I and II. The methods employed are described in more detail in Paper I and will only be presented very briefly in the following.

Solid-state NMR (Nuclear Magnetic Resonance) analysis was performed using ^{13}C polarization transfer solid-state (Pt-ss) measurements on a 14.7 T Agilent Inova fitted with a 3.2 mm double-resonance MAS probe, were used to analyse the azetidinium-substituted CNC. The results were compared to a model reaction in which no grafting took place in order to verify the reaction.

The ζ-potential of the surface-grafted CNC were measured using a Zetasizer Nano ZS (Malvern Instruments, UK) based on the Laser Dopple Velocimetry technique. The measurements were performed at 25 °C using DTS1070 disposable folded capillary cells, with a 50 mW diode-pumped solid-state laser with a wavelength of 532 nm as light source.

Using conductometric titration (Eutech Instruments, Singapore), the sulphate half ester content could be determined. The conductivity was measured when 0.1 or 0.2 mL of 0.01 M sodium hydroxide was added at 60 second intervals to a pH adjusted sample volume of 100 ml 0.1 weight-% CNC dispersion (pH value below 3.5), until a pH value of 11 was reached.

Fourier-Transform Infrared (FTIR) spectroscopy was applied to freeze-dried CNC samples employing a Perkin Elmer Spectrum One instrument with the potassium bromide (KBr) pellet technique in order to obtain infrared spectra in the range 4000 to 400 cm^{-1}.

3.3 Mechanical properties

3.3.1 Tensile properties

The mechanical properties in tension (Young's modulus, tensile strength at yield, elongation at yield, tensile strength at break and elongation at break) were measured using a Zwick/Z2.5 tensile tester with a 500 N load cell. Test bars with a gauge length of 40 mm were cut from the compression moulded composite plates and kept in a conditioned environment at 55 % relative humidity and 25 °C for at least four days prior preforming the tensile tests. The tensile properties were measured at 25 °C with a strain rate of $2.5 \cdot 10^{-3}$ s^{-1} (6 mm/min) for six different specimens from each composite sample. Reported values are the average value of these six measurements.

3.3.2 Dynamic-mechanical analysis

Using a Rheometrics RSA II at 25 °C and a frequency of 1 Hz, the dynamic-mechanical properties of the composites were measured. The specimens were pre-strained with a constant tensional strain of about 0.15 % while a sinusoidal deformation with an increasing amplitude of 0.03 to 0.14 % was superimposed while measuring the storage and loss moduli as well as the mechanical loss factor of the specimen.

The mechanical loss factor (tan δ) of a composite material could be affected by a surface treatment of the filler particles. The adhesion between the reinforcing element and the polymer matrix or the friction between the polymer and filler particle could be associated with these effects (Nielsen 1974). The surface treatment thus could affect the interactions between the filler and matrix, giving an interphase region between the components with different properties compared to the bulk polymer. The influence if the interphase region on the mechanical loss factor could be estimated as described by Kubát et. al. (1990) using

$$\tan\delta_c = v_f \tan\delta_f + v_i \tan\delta_i + v_m \tan\delta_m \qquad (1)$$

where v denotes the volume fractions of the polymer matrix (m), filler (f) and the interphase region (i). Equation 1 gives a very simplified estimation of the mechanical damping of the composite, but could be useful when comparing the different surface treatments regarding the ability to adhere to the polymer matrix, e. g. giving higher increased loss factor if the interphase region is weak compared to a stronger interaction at the interface.

3.3.3 Differential scanning calorimetry

To access the crystallinity and the thermal transitions of the composite material, differential scanning calorimetry, DSC, was performed using a Perkin-Elmer DSC7. The endotherms were recorded when the temperature was increased from -20 to 150 °C at a scan rate of 10 °C/min in a nitrogen atmosphere.

The crystallinity (X_c) was evaluated using

$$X_c = \frac{\Delta H_c}{w_{EAA}\Delta H_o} \qquad (2)$$

where ΔH_c is the specific heat of fusion of the composite, w_{EAA} the weight fraction of EAA and ΔH_o the specific heat of fusion for 100 % crystalline polyethylene; 286.19 J/g (Wunderlich and Cormier 1967).

4 Summary of results

A summary of the most interesting findings is given in this section. The results will be divided into three sections; manufacturing and processing, characterization results and mechanical properties. The findings from the analysis of the CNC materials and the aqueous solutions in Paper I are presented alongside with the results from the evaluation of the properties and processing behaviour of the composite materials given in Paper II.

4.1 Manufacturing and processing

4.1.1 Surface grafting of CNC

Two batches of surface-grafted cellulose nanocrystals were used. The first batch, used for the initial characterisation of the CNC as well as for the rheological measurements, was produced using methoxyazetidinium salts for the grafting (as mentioned earlier). The process was then optimized and based on the lack of significant differences from the characterisation of the aqueous dispersions, surface grafting of the CNC using hydroxyazetidinium salts was used instead when producing the composite materials, providing an easier chemical procedure possible to use for larger volumes. The actual grafting procedure and synthesis of the salts are described in detail in Paper I.

The functional groups that could be grafted onto the CNC can be tailored to fit specific polymer matrices but also to yield different properties of the composites. The three functional groups used here were selected from discussions aiming at, first of all, improving the compatibility of the surface-treated CNC with EAA or polyethylene matrices as well as the thermal stability of the composite. The functional groups were also chosen based on their different molecular structure, possibly giving different effects on the interaction in between the grafted groups and not only on the adhesion between the polymer matrix and the surface-grafted CNC. For future work, it may be of interest to consider similar types of grafting onto CNC when polyamide-based matrices are used.

4.1.2 Mixing of CNC and EAA

The aqueous dispersions of CNC and EAA were easily mixed, and even though some minor foaming did occur during the mixing, the dispersions were considered homogeneously mixed. When dried at room temperature onto the large plates, the material cracked into thin flakes. The flakes were transparent, and no agglomerations of CNC particles could be visually observed. The mixing process and the flake formation are illustrated by the photographs in Figure 6 below.

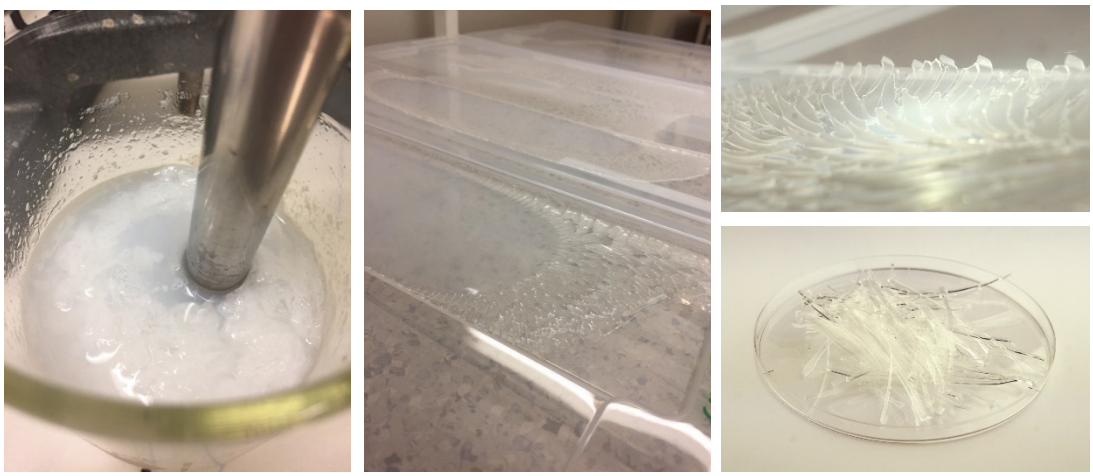

Figure 6: From left: Mixing of the EAA and CNC dispersions, the mixed dispersion being dried on the plates and then the final flakes of dried composite.

4.1.3 Compression moulding

After compression moulding of the dried flakes, the compression moulded plaques exhibited no visual aggregation of CNC elements or defects and were more or less transparent even up to a concentration of 10 weight-% CNC. An exception was the composite containing 10 weight-% CNC-Morph-OH, which exhibited a slight difference in colour compared to the other samples as can be seen in Figure 7. The pure EAA reference sample was totally transparent and both the composites with 10 weight-% CNC-diHexyl-OH and CNC-diAllyl-OH as well as the sample with untreated CNC displayed a similar visual appearance.

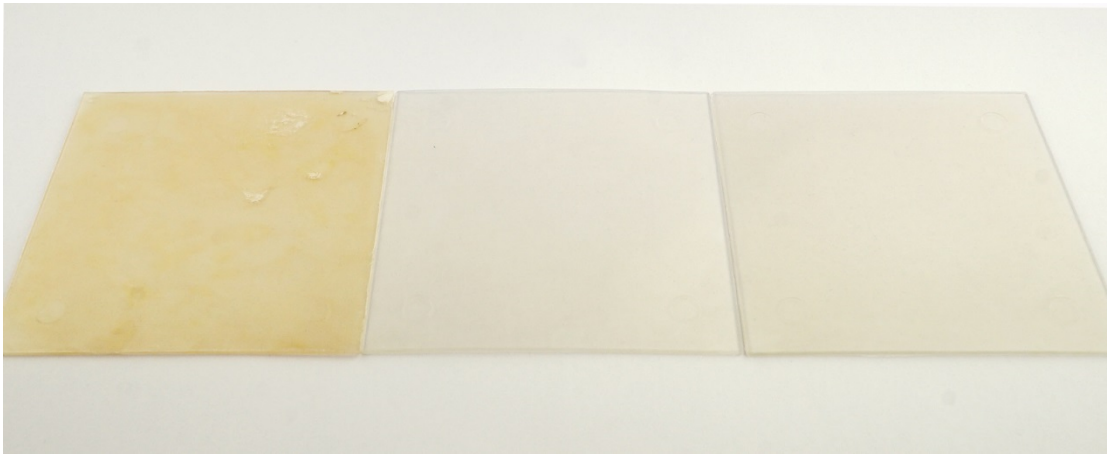

Figure 7: Composites with 10 weight-% CNC, from left; CNC-Morph-OH, CNC-diHexyl-OH and CNC-diAllyl-OH.

The composite containing 10 weight-% CNC-Morph-OH showed a more yellowish appearance and some visible defects after compression moulding. Studies reported by e. g. Allen et. al.

(1990) and Xiao et. al. (2008) indicated the amine structure to affect the yellowing; however this has not been further investigated in this study.

4.2 Characterization of the CNC-containing dispersions and composites

4.2.1 Rheological properties of the CNC-containing dispersions

Figure 8 shows the shear viscosity as a function of the shear rate in the region between 1 and 1000 s^{-1} for the dispersions containing untreated as well surface-grafted CNC at a concentration of 1.3 weight-%. All suspensions exhibited a pronounced shear thinning behaviour and the same was also noted at the lower concentration (0.65 weight-%), although the magnitude of the viscosities was, as expected, lower. In the low shear rate region of Figure 8, the dispersion containing the unmodified CNC exhibited the lowest viscosity, whereas the dispersions with CNC-morph-OMe and CNC-dihexyl-OMe displayed up to ten times higher viscosity in this region. The dispersion containing CNC-diallyl-OMe exhibited the highest viscosity at these low shear rates. However, as the shear rate increased, the viscosity curves for the different dispersions approached each other.

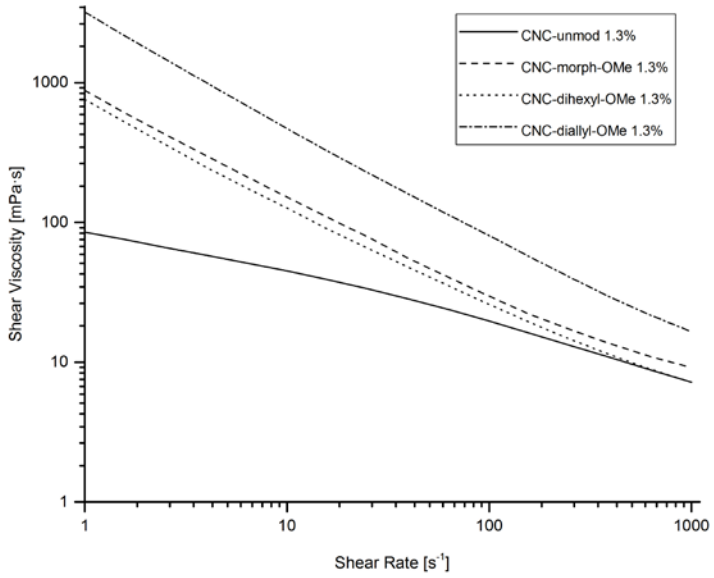

Figure 8: The shear viscosity of the CNC-dispersions at a concentration of 1.3 weight-% as a function of the shear rate.

In a similar way, the surface grafting onto the CNC increased markedly the dynamic-mechanical moduli *G'* and *G"* when compared with the corresponding values obtained for the dispersion with the unmodified CNC. This is exemplified in Figure 9 for the dispersions with a solids content of 1.3 weight-%.

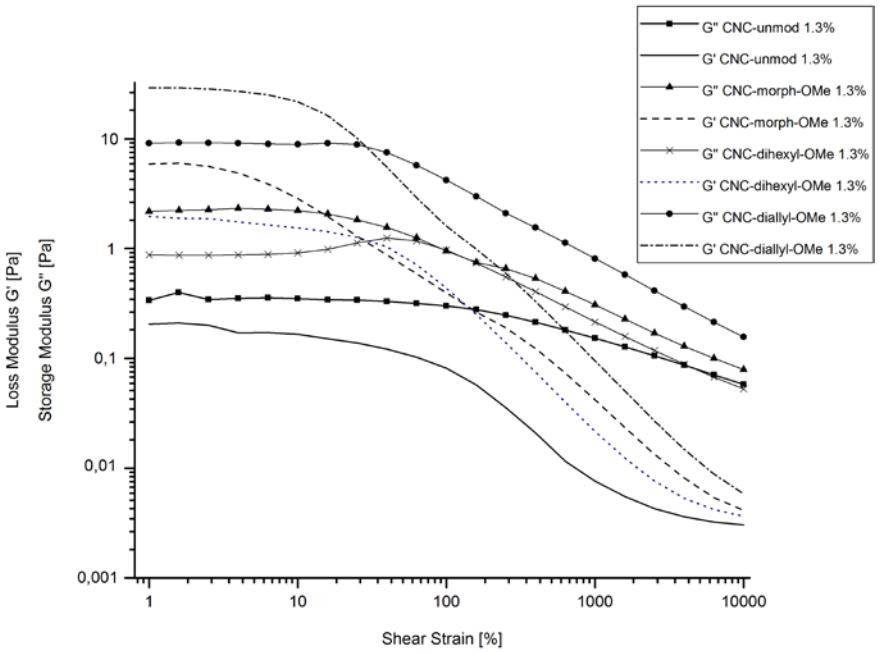

Figure 9: Dynamic-mechanical properties (at a frequency of 1 Hz) of the CNC dispersions as a function of the applied strain amplitude at 25 °C. The CNC-concentration was 1.3 weight-%.

These findings were substantiated by corresponding measurements of a decrease in the percolation threshold or gel point for the modified samples. The dispersions containing the unmodified CNC started to gel at approximately 2.5 weight-% CNC, whereas the dispersions with the surface-grafted elements showed a gel like behaviour already at 0.2 - 0.4 weight-%. The percolation threshold was determined as the concentration at which the storage and loss moduli overlapped over a significant region of the applied strain amplitude as exemplified in Figure 10 in case of the dispersion containing unmodified CNC.

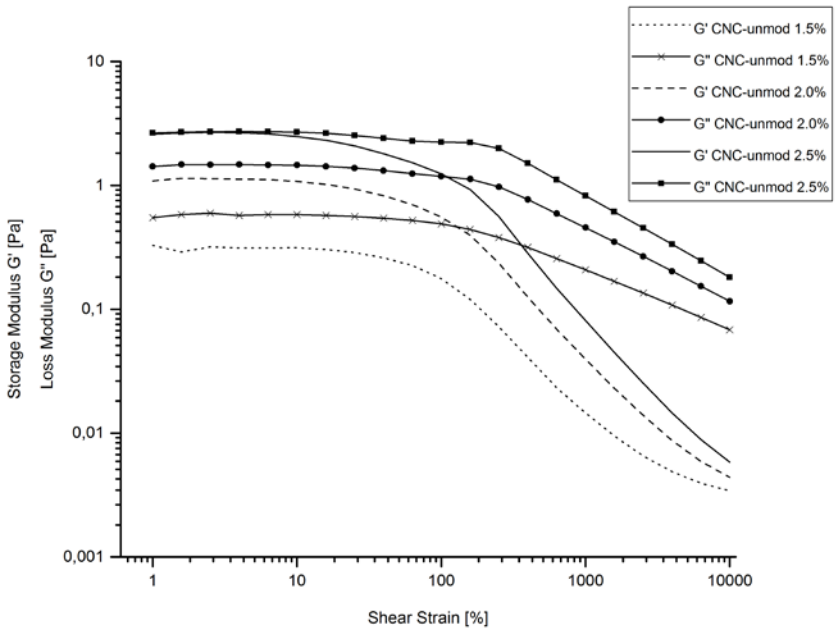

Figure 10: The dynamic mechanical moduli at a frequency of 1 Hz and 25 °C as functions of the applied shear strain amplitude for aqueous dispersion containing different concentrations of untreated CNC. At a concentration of 2.5 weight-% CNC, the storage and loss moduli coincide over a substantial part of the applied shear strain region.

The above results point to that the surface treatments do change the interactions between the nanocrystals in the aqueous dispersions. The treated particles formed network structures already at lower concentration levels, most likely due to stronger molecular interactions resulting in an increased viscosity and increased dynamic moduli. The grafted azetidinium salts are primarily lipophilic, compared to the otherwise hydrophilic nature of CNC. In the aqueous dispersions, the substituents are more prone to interact with each other than with the surrounding water, forming a network to minimize contact with water.

The different grafted azetidinium salts affect the rheological properties to different degrees, where the magnitude of the effect probably depends on the strength of the intermolecular bonding of the substituents. The main molecular interaction between alkyl groups is van der Waals forces, which applies for the MorphOMe and diHexylOMe substituents. Also the length of the substituents might cause differences to the shear viscosity, which might form a more flexible network for the longer diHexylOMe structure compared to the stiffer and smaller MorphOMe. The diAllylOMe showed significantly higher values of the shear viscosity, possibly associated with the stronger molecular interaction of π-π-bonds of the allyl functionality acting between the substituents.

4.2.2 Thermal stability

The thermal stability of the nanocrystals was assessed using thermal gravimetric analysis, TGA. As shown in Figure 11, the surface grafting onto the CNC surfaces shifted the onset temperature for thermal degradation from 150 °C (untreated CNC) to approximately 250 °C. The effect

might be due to the removal of the acidic hydrogen associated with the sulphate group which is removed through the grafting of the azetidinium substituents. The hydrogen facilitates the acid-catalyzed dehydration process, and when the hydrogen is removed the degradation is delayed. This could be compared to the results reported by Wang et. al (2007) showing that the acid catalysed dehydration could be inhibited by replacing the hydrogen ion associated with the sulphate group with a sodium ion. There were no greater difference in the onset temperature for thermal degradation between the different surface-modified CNC.

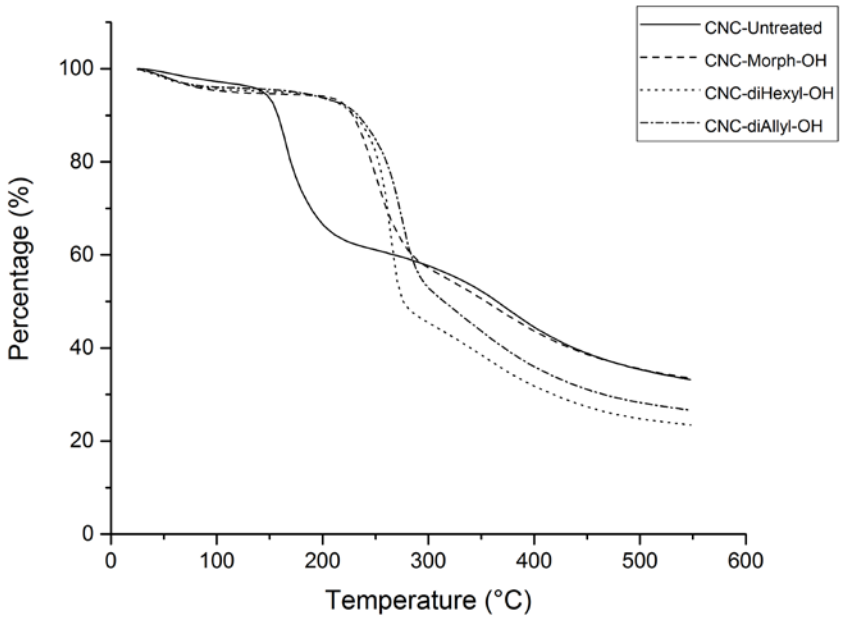

Figure 11: Thermogravimetric curves showing the thermal degradation of the unmodified CNC and of the azetidinium-grafted CNC. (Before mixing with polymer)

Using the same procedure for analysing the onset temperature for thermal degradation in case of the CNC-containing composites, the increase in degradation temperature for the composites containing the surface-treated CNC was not observed anymore. The degradation started at the same (lower) temperature for the modified as for the untreated CNC. Using the heat-gradient bench, the thermal stability and discolouration of the composites could be illustrated visually. There was no difference in discolouration between the different composites (containing untreated and surface grafted CNC) as can be seen in the upper photo in Figure 12. The discolouration apparently started at the same time and at the same temperatures for all composites. A reference sample with only EAA was tested in the same way without showing any discoloration.

However, a hypothesis could be that the alkalinity of the polymer dispersion (pH 9.7) might hamper the increase in thermal stability. The sulphate ester groups act as good leaving groups in the presence of nucleophiles, such as hydroxides and carboxylates, which are abundant in the alkaline environments, and the azetidinium salts will no longer stabilise the CNC towards a higher thermal resistance. The alkaline nature of the polymer dispersion was suggested to cause the degrafting of the azetidinium salts, lowering the thermal stability of the composites to its

original level for unmodified CNC. A model sample was then prepared with a neutralised mixture of EAA dispersion and 10 weight-% CNC-diAllyl-OH. For this model composite, the expected improvement in thermal stability was obtained; both in the TGA-curves, as can be seen in Figure 13, and also visually, as shown in Figure 12, lower photo.

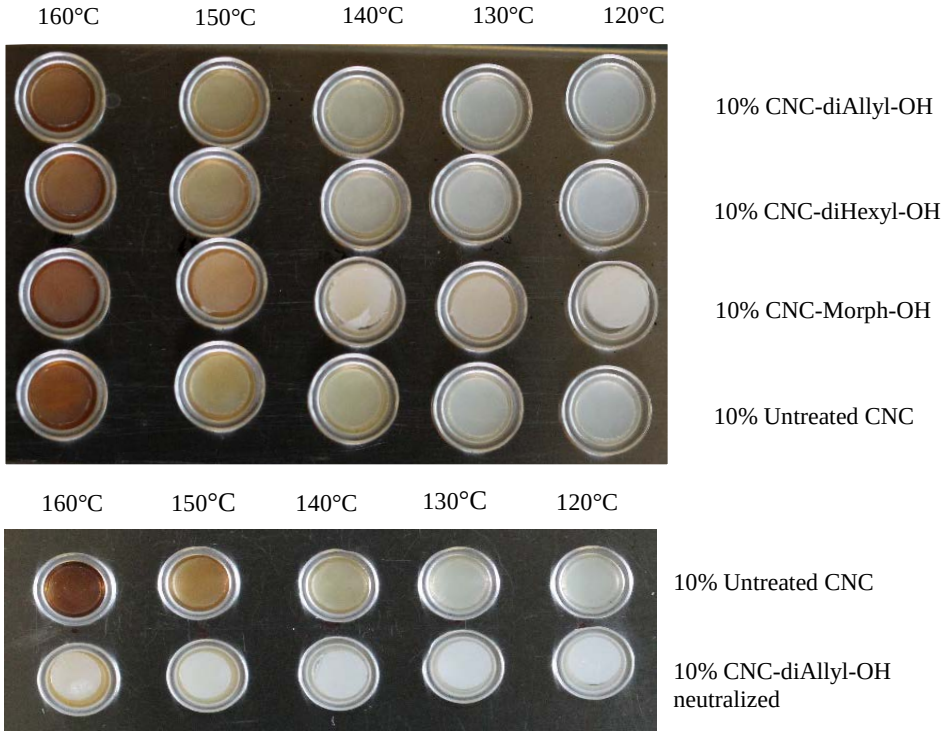

Figure 12: Upper photo: Visual appearance of the composites containing 10 weight-% CNC after exposing them to (from right to left) 120, 130, 140, 150 and 160 °C for 8 minutes. Lower photo: Visual appearance of the untreated CNC composite compared to the model sample produced under neutralised processing conditions, exposing them to (from right to left) 120, 130, 140, 150 and 160 °C for 8 minutes.

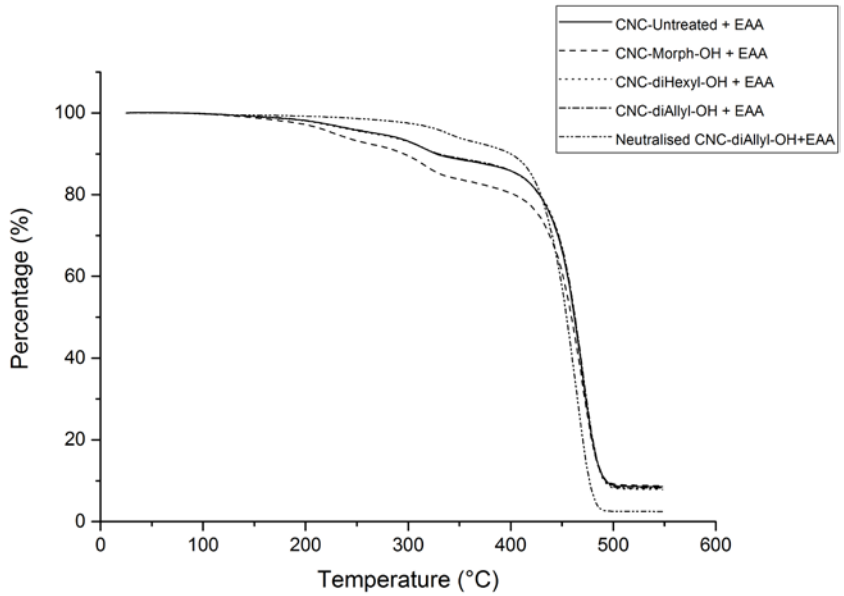

Figure 13: Thermogravimetric curves showing the thermal degradation of the composites containing unmodified CNC, the azetidinium-grafted CNC and a model sample produced under neutralised conditions.

Thus it was concluded that the alkaline character of the EAA dispersion was responsible for the degrafting of the functional groups at elevated temperatures, resulting in the reduced thermal stability. Further model experiments, described in Paper II, showed however that this kind of degrafting did not take place during the processing steps mixing, drying and compression molding at 105 °C. Hence it is plausible that higher temperatures than 105 °C are required to degraft the functional groups from the CNC surfaces. Using a neutralised polymer solution, the increased thermal stability from the initial TGA measurements of the surface grafted CNC could also be maintained when the CNC were incorporated into the EAA matrix.

4.2.3 Characterization of the surface-grafting

The detailed characterization of the surface-grafted CNC was performed by Karin Sahlin and Gunnar Westman at the Department of Chemistry and Chemical Engineering at Chalmers University of Technology in order to assess the surface grafting of the CNC using NMR, FTIR, ζ–potential measurements and conductometric titration. The detailed results of these measurements are reported in Paper I and only a brief summary is given below.

Using solid state NMR, it is possible to analyse the chemical environment close to, in this case, the carbon atom. The chemical environment will be affected by the surrounding atoms and would indicate if the grafting has occurred or not. When comparing the characteristic peaks from cellulose I of the unmodified sample with the additional peaks originating from the surface modifications, the result indicate a successful grafting onto the surface of the crystals.

Using FTIR and comparing the grafted samples with the unmodified sample, it was possible to assess a peak shift corresponding to a change in the sulphate ester bond absorption indicating a substitution on the sulphate ester and thus supporting that the grafting has occurred.

The results from ζ-potential measurements and the sulphate half ester content of the CNC determined by conductometric titration are given in Table 1. The lowest ζ-potential value was noted for the unmodified nanocrystals, indicating that the unmodified CNC had more sulphuric groups on the surface whereas the higher values for the modified CNC indicate that the grafting had occurred. Also the sulphate half ester content measured by conductometric titration indicates that grafting has taken place since the decreased values of surface charge of the surface-grafted samples shows that the azetidinium reagents have reacted with the negatively charged sulphate groups, lowering the negative surface charge

Table 1: The ζ-potential (standard deviation in parentheses) of the CNC-particles at a concentration of 0.05 wt-% and pH 3.5, the content of sulphate half esters on the surfaces of the CNC and the pH-values of the different dispersions at the two concentrations used for the rheological characterization

Type of CNC	ζ-potential (mV)	Sulphate half ester content (μmol/g)	pH at 0.65 wt-%	pH at 1.3 wt-%
CNC-unmod.	-71.7 (2.0)	350.4	2.7	2.3
CNC-morph-OMe	-45.6 (2.4)	101.8	4.4	5.0
CNC-dihexyl-OMe	-54.2 (2.0)	179.9	5.2	5.3
CNC-diallyl-OMe	-47.9 (1.9)	118.7	5.2	5.0

From these characterization analyses, it could be concluded that the surface grafting was successful, and the chemical groups were actually grafted onto the CNC surface to a large extent.

4.3 Mechanical properties of the composites

4.3.1 Tensile properties

The tensile properties were measured on six sample of each composite material, giving an internal variation as showed in Figure 14 in the case of the composite CNC-diAllyl-OH (1 weight-%). The unfilled EAA exhibited a clear yielding behaviour and hence also the composites did, at least at lower CNC contents. However, for the composites with highest CNC content (10 weight-%), it was hard to distinguish any yield point since the material became stiffer and more brittle. The values discussed in the following section are average values of the six measurements.

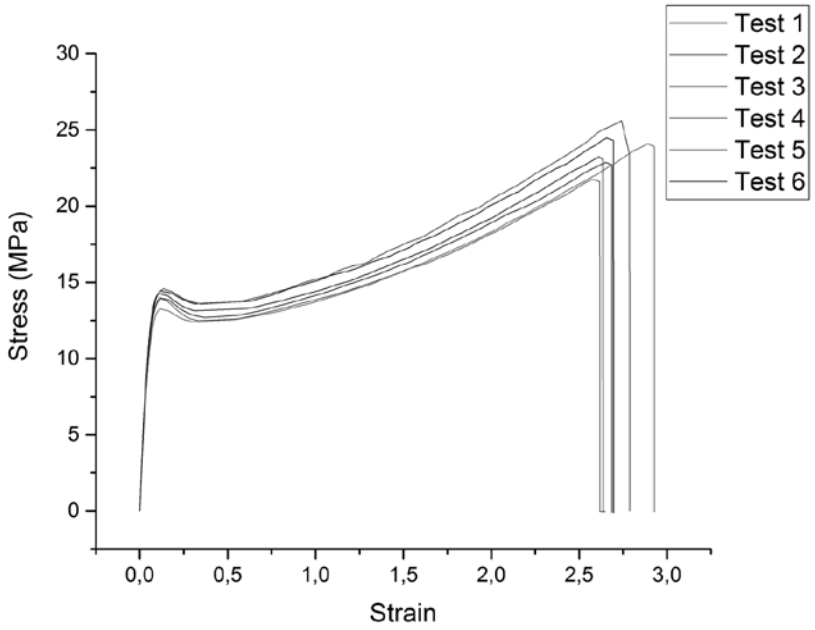

Figure 14:Tensile stress-strain behaviour of the CNC-diAllyl-OH composite (1 weight-% CNC). The different curves refer to different tests and illustrate the experimental scatter.

All results from the tensile testing are summarized in Table 2 giving the average values and the standard deviations in parentheses.

Tqble 2. The elastic modulus, the yield stress, the strain at yield, the failure stress and the strain at yield for the composite materials. The average values are given with the standard deviation in parentheses.

Material	Modulus, MPa	Yield stress, MPa	Yield strain, %	Failure stress, MPa	Failure strain, %
0.1 % CNC-Morph-OH	294 (28)	14.1 (0.5)	10.4 (0.6)	24.3 (0.8)	284 (11)
0.1 % CNC-diAllyl-OH	237 (25)	12.1 (1.0)	12.2 (0.4)	21.2 (1.3)	276 (11)
0.1 % CNC-diHexyl-OH	249 (24)	12.8 (0.6)	12.0 (0.8)	23.5 (1.4)	288 (15)
0.1 % untreated CNC	270 (13)	13.5 (0.3)	11.4 (0.8)	24.5 (0.7)	278 (6)
1 % CNC-Morph-OH	367 (22)	15.2 (0.6)	10.2 (0.4)	23.4 (1.3)	252 (10)
1 % CNC-diAllyl-OH	314 (21)	14.1 (0.6)	11.0 (0.5)	22.9 (1.0)	261 (10)
1 % CNC-diHexyl-OH	295 (16)	14.1 (0.4)	11.7 (0.9)	23.7 (1.2)	267 (10)
1 % untreated CNC	353 (18)	15.3 (0.5)	9.9 (0.2)	25.3 (1.7)	246 (7)
10 % CNC-Morph-OH	678 (46)	15.1 (0.4)	7.5 (0.4)	14.2 (2.3)	11 (10)
10 % CNC-diAllyl-OH	864 (32)	21.1 (0.7)	8.2 (0.8)	19.7 (0.8)	31 (22)
10 % CNC-diHexyl-OH	678 (21)	17.9 (0.4)	8.6 (0.7)	16.5 (1.0)	28 (15)
10 % untreated CNC	921 (64)	-	-	21.9 (0.9)	6 (1)
EAA	322 (5)	15.1 (0.6)	9.6 (0.6)	25.8 (1.2)	255 (6)

It is clear that the incorporation of CNC in the polymeric matrix gave a strong positive effect on the tensile modulus, *E*, of the polymeric material. As can be seen in Figure 15, the modulus increased from ca 300 MPa up to more than 900 MPa for the untreated CNC, closely followed by the composite containing CNC-diAllyl-OH, at a CNC content of 10 weight-%. This is a significant increase at these rather low reinforcing concentrations. However, at the lower concentration of 0.1 and 1 weight-%, the effect was limited. It can be seen that the CNC-Morph-OH appeared to have somewhat stronger effect in improving the modulus at low concentrations compared to the other CNC versions, whereas at 10 weight-%, the CNC-Morph-OH did not produce the greatest effect. This might be associated with the appearance of defects or discoloration that can occur in this sample at 10 weight-%, cf Figure 7.

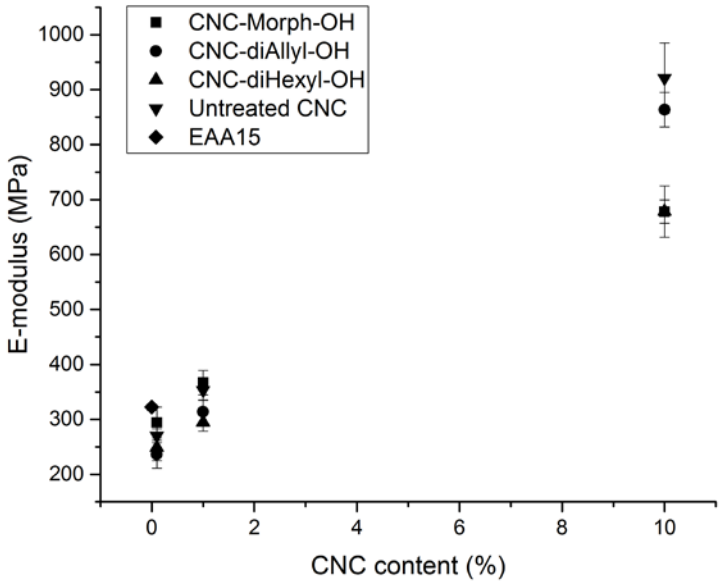

Figure 15: The elastic modulus of the composites as a function of the CNC-content.

At low concentrations of CNC, the material appeared to be more flexible (soft) than the EAA copolymer itself. This is also in a sense reflected in Figure 16 which shows the yield strain of the different composite materials versus the CNC concentration. The yield strain increased at low concentrations of CNC which is not common when adding fillers to a matrix, cf (Nielsen 1974). The increased ductility may be interpreted as a change in the interaction between the surface-modified nanocrystals and also between the nanocrystals and the matrix polymer, as discussed in more detail in Paper II.

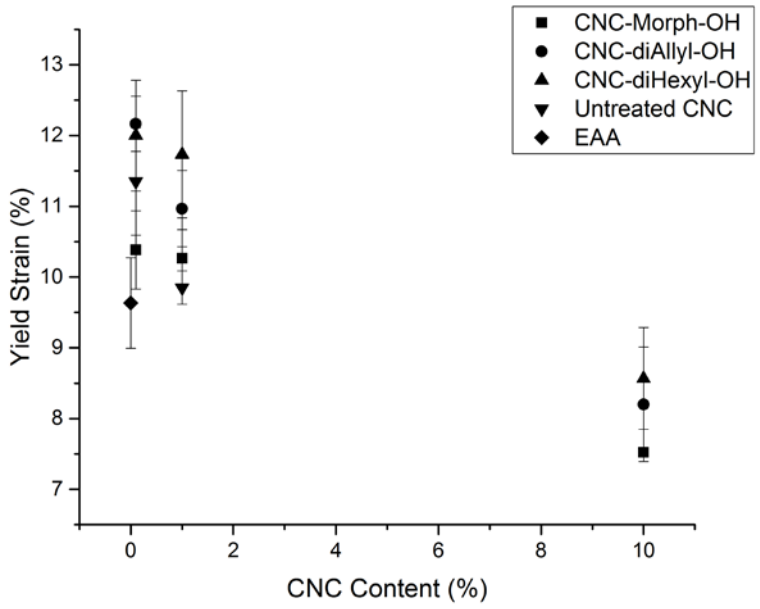

Figure 16: The yield strain of the composites as a function of the CNC-content.

At higher concentration of CNC, the elongation at yield and break decreased significantly. A closer inspection of the tensile properties (in particular the yield and failure strains) of composites containing 10 weight-% CNC (Table 2), reveals a more ductile behaviour in case of the CNC-diAllyl-OH and CNC-diHexyl-OH composites compared to those containing the untreated CNC. The composite containing 10 weight-% CNC-Morph-OH exhibited a less ductile behaviour but, as already mentioned, this could be due to defects in the material resulting from the processing.

In similarity with the elastic modulus, the yield stress of the composites increased significantly when 10 weight-% was incorporated into the polymer. However, the composites with 10 weight-% untreated CNC did not show any clear yield point before break and they are not included in Figure 17 below. The unfilled EAA had a yield stress value of approximately 15 MPa, whereas the composite reinforced with 10 weight-% CNC-diAllyl-OH reached 21 MPa before yielding.

As predicted when looking at the E-modulus values, the yield stress of the composites increases significantly when the concentration of CNC is 10 weight-%. However, the untreated CNC did not show any clear yield point before break and are not represented in figure x, as all other versions are. The pure EAA have a yield stress value of approximately 15 MPa, whereas the composite reinforced with 10 weight-% CNC-diAllyl-OH reached 21 MPa before yield. For the lowest concentrations of CNC, the trend with lower stiffness and as could be seen in figure x, higher ductility an elongation to yield is observed.

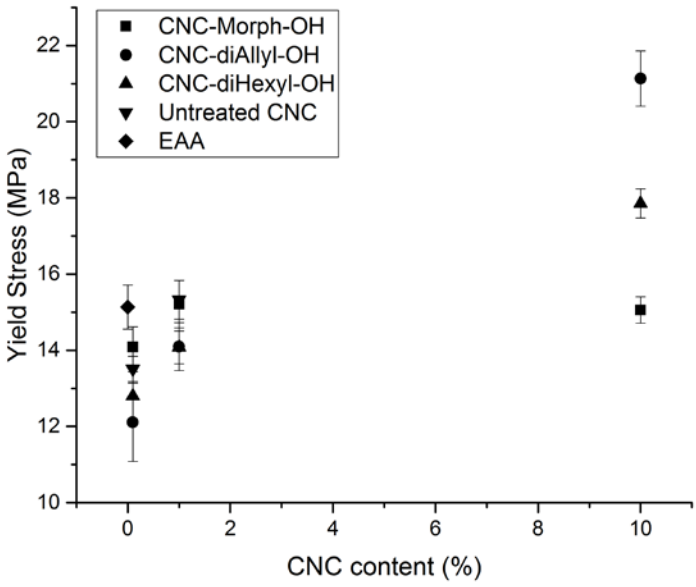

Figure 17: The yield stress of the composites as a function of the CNC-content.

The elastic modulus of CNC has in this work (Paper II) been estimated to be in the range of 55-60 GPa using the Cox-Krenchel equation (Matthews and Rawlings 1994, McCrum et al. 1997, Lee et al. 2014)

$$E_c = \eta_L \eta_O f E_f + (1 - f) E_m \quad (3)$$

where E_c is the tensile modulus of the composite, E_f the modulus of the CNC, E_m the tensile modulus of the EAA matrix and f the volume fraction of the CNC. If assuming random distribution of the nanocrystals in the plane, the factor η_o will have the value 3/8 (Matthews and Rawlings 1994). The factor η_L describes the effect of the finite length of the nanocrystals and could be expressed using the shear lag theory (McCrum et al. 1997):

$$\eta_L = 1 - \frac{\tanh(na)}{na} \quad (4)$$

with

$$n = \sqrt{\frac{2G_m}{E_f \ln(\frac{2R}{d})}} \quad (5)$$

The aspect ratio a of the CNC was taken to be 210/6 = 35 as reported by Moberg et al. (2017) and the shear modulus G_m was obtained from the tensile test of the unfilled EAA. Using the values of tensile moduli given in Table 2, and assuming perfect adhesion between the matrix and the CNC, the modulus of CNC could be estimated. The value of 55-60 GPa is rather high, approaching the value for glass fibre (70 GPa) and surpasses or is close to previous values

reported for the effective modulus of cellulose nanofibrils (CNF), e. g. 29-36 GPa (Tanpichai et al. 2012), 33-62 GPa (Ansari et al. 2014) and 25-42 GPa (Ansari et al. 2015).

4.3.2 Dynamic-mechanical analysis

The mechanical loss factor of the composites was here determined as a function of the applied strain amplitude. Comparing the tan δ-values of the composites containing 0.1, 1 and 10 weight-% untreated CNC with those of the unfilled EAA matrix, it is clear that the two lower concentrations of CNC did not appreciably affect the mechanical loss factor, as shown in Figure 18. However, the loss factor increased considerably for the composite containing 10 weight-% CNC when increasing the strain amplitude. This may indicate a break-up of formed CNC-aggregates or a decrease in the adhesion between the polymer and the CNC.

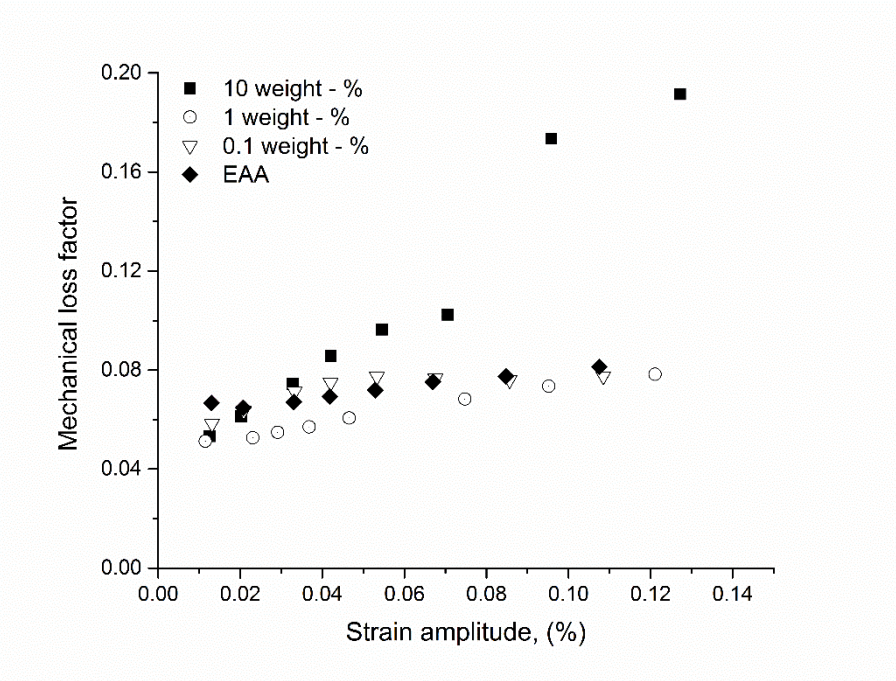

Figure 18: Mechanical loss factor as a function of the applied strain amplitude. The composites contained 0 (denoted EAA), 0.10, 1 and 10 weight-% untreated CNC.

The mechanical loss factor was assessed for all composites, but the effects on tan δ were more pronounced at a CNC-content of 10 weight-% and the discussion is focused on these in the following. Comparing the composites containing treated and untreated CNC, Figure 19, it is clear that the untreated CNC exhibited a larger increase in the loss factor as the strain amplitude was increased than any of the composites with the surface-treated nanocrystals. However, at lower strain amplitudes, the CNC-Morph-OH and CNC-diHexyl-OH composites both displayed a higher loss factor than the composite with the untreated CNC, but as already mentioned, not being as sensitive to the increase in strain amplitude. It might be due to the surface treatment promoting a rather flexible interphase region close to the CNC surface. In case of the composite containing 10 weight-% CNC-diAllyl-OH, a lower mechanical loss factor than with the same amount of untreated CNC and also a low sensitivity towards the increase of the strain amplitude. This may possibly be interpreted in terms of a rather a strong interphase region between the CNC and the polymer matrix. The CNC-diAllyl-OH composite even

exhibited lower loss factor values than the unfilled EAA over strain amplitude region used. This may be plausible if the adhesion between the CNC and the polymer is sufficient, since CNC is expected to have a lower loss factor than the EAA copolymer as discussed in Paper II.

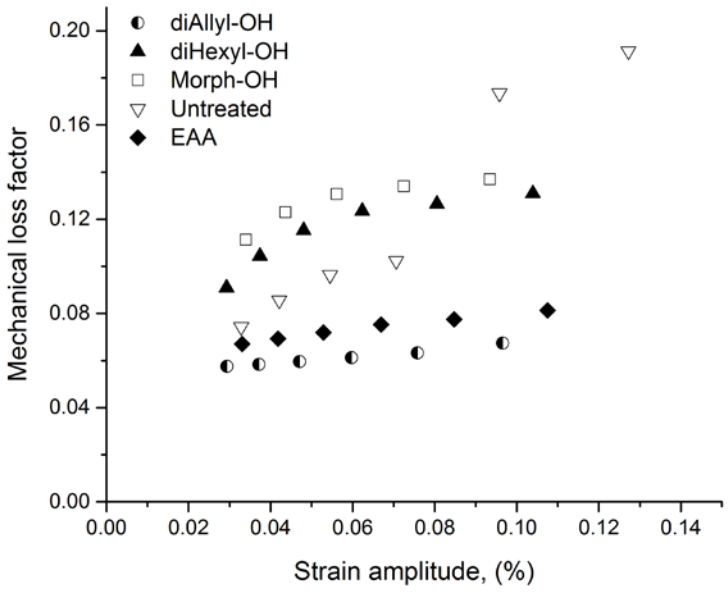

Figure 19: The mechanical loss factor as a function of the applied strain amplitude for composites containing 10 weight-% surface-treated CNC as well as 10 weight-% untreated CNC.

Thus, the measurement of the mechanical loss factor indicate that the grafted surface groups had a clear effect on the properties of the interphase region. This could be interpreted in terms of a change in the interactions between the polymer matrix and the grafted groups and/or between the grafted groups on different CNC entities.

4.3.3 Differential scanning calorimetry (DSC)

The peaks of the DSC endotherms (associated with polymeric crystalline structures) did not shift markedly in position along the temperature axis when the results relating to the composite containing the surface-grafted CNC are compared to those of the material with the untreated nanocrystals. This shown in Figure 20 when the CNC concentration was 10 weight-%. Similar curves were also obtained for the composites with lower concentrations of CNC as well as for the unfilled EAA. (Venkatesh et al. 2018)

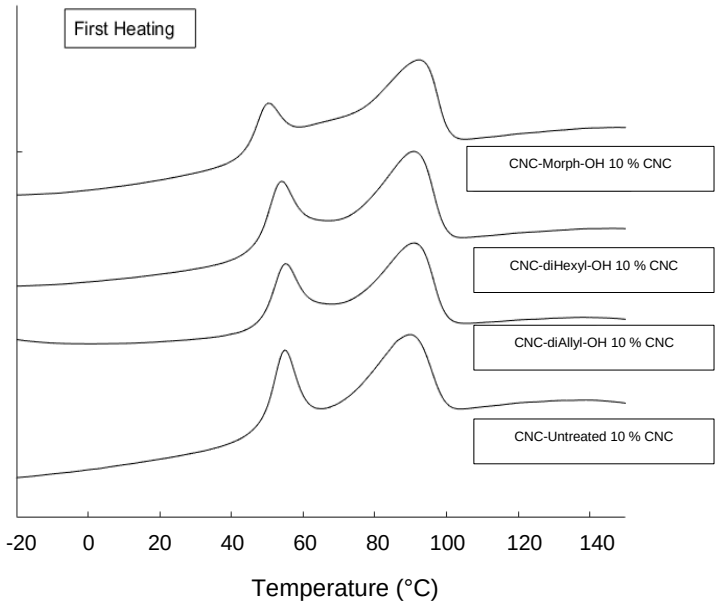

Figure 20: DSC endotherms for the composites containing surface-treated and untreated CNC (10 weight-%).

Using eq. (2), the total crystallinity corresponding to the multiple melting endotherms (shown in Figure 20) was evaluated, see Figure 21. The total crystallinity did not differ markedly between the unfilled EAA and the different CNC composites, but there was a slight tendency towards increased crystallinity for the composites containing the surface-treated CNC. However, this increase in crystallinity is considered too small to be associated with the improvement in mechanical properties, described in section 4.3.1.

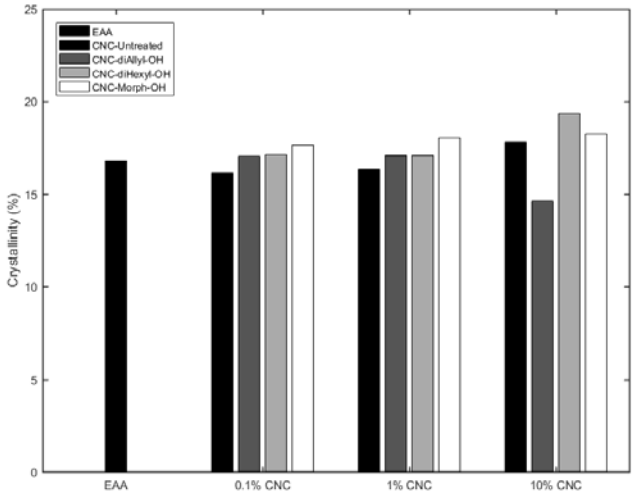

Figure 21: The total crystallinity of the unfilled EAA and the CNC-containing composites.

5 Conclusions

Already when evaluating the properties of the aqueous dispersions of CNC, it was obvious that the surface-grafting of the azetidinium groups affected the performance of material. The surface grafting promoted a higher dispersion viscosity and the dispersions became more prone to form a gel like substance, hence the percolation threshold was substantially lowered. Furthermore, the dynamic-mechanical moduli *G'* and *G"* increased significantly for the dispersions based on the surface-grafted CNC. It is possible that the grafted groups interact with each other and form a network structure in the aqueous dispersion. The more hydrophobic character of the surface-grafted CNC could also be beneficial when using it as a reinforcement in polymer matrix composites.

An interesting and potentially promising result was revealed by the thermal gravimetric analysis (Figure 11). The surface treatment improved the thermal stability of the cellulose nanocrystals compared to the unmodified reference, i. e. the onset temperature for thermal degradation increased from 150 °C to about 250 °C. This effect might be due to the removal of acidic hydrogen, which facilitates an acid-catalysed dehydration process, when the azetidinium substituents are grafted onto the CNC.

Based on the potentially good mechanical properties of CNC and the improved thermal stability associated with the surface grafting (Paper I), it is certainly of interest to produce polymer composites using CNC as the reinforcing elements. Here an ethylene-based copolymer (EAA) was chosen as the matrix material based on its compatibility with cellulose. Procedures were developed for producing composite materials involving mixing of CNC and EAA dispersions, drying and compression moulding. It was possible to produce almost fully transparent samples with up to 10 weight-% CNC as can be seen in Figure 7 and being more thoroughly described in Paper II.

The promising results of thermal stability from the TGA measurements on the isolated CNC particles (dried aqueous dispersions) were however not at hand after the mixing and compression moulding of the composite materials. The alkaline character of the EAA dispersion was suggested to be the reason to the absence of increase in thermal stability, causing a degrafting of the previously grafted functional groups on the CNC surface at high temperatures. Model experiments with pH-neutralized dispersions supported this hypothesis and the onset of thermal degradation once again was raised by almost 100 °C to 250 °C for the composites containing surface-grafted CNC. Further model experiments indicated that the degrafting did not take place during the production of the composite material (with a maximum temperature of 105 °C) when using the alkaline polymer dispersion.

With regard to the mechanical properties of these composites, it is clear that a strong reinforcing effect was attained when 10 weight-% CNC was incorporated into the EAA matrix, The elastic modulus increased in this case up to three times compared to the unfilled polymer (for some systems). Such an improvement corresponded to an elastic modulus of CNC of the order of 55-60 GPa according to model calculations.

The surface treatment of the CNC also affected the ductility, providing a higher elongation at yield when adding low concentrations of CNC into the EAA matrix. For the higher

concentration of CNC, the material became more brittle and the elongation at yield was reduced. However, even at the highest CNC concentration, some of the composites containing the surface-grafted CNC, especially CNC-diAllyl-OH, exhibited a higher ductility reflected in the failure strain than the composite containing untreated CNC. The surface treatments furthermore appeared to influence the properties of the interphase region between the CNC particles and the matrix, indicated by the measurements of the mechanical loss factor. The effects on the mechanical properties were interpreted as being the results from interactions, possibly both between the grafted groups and also between the grafted groups and the polymer matrix.

Thus, the surface grafting enabled both increased thermal stability by inhibiting the acid-catalysed dehydration process, when the azetidinium groups were grafted onto the CNC, and improved mechanical performance of the composite.

The results obtained in this study are important since they indicate possible routes for the production of composites containing cellulosic reinforcing components with enhanced mechanical and thermal performance using conventional processing techniques such as extrusion and injection moulding.

6 Future work

There are many possibilities for the future work based on the results from these initial studies. But selecting the most promising version or versions of the surface-grafted CNC and implement them when using different polymer matrices would be of great interest. It could also be worthwhile to adjust the surface modifications to customize them to more advanced and commonly used polymer matrices, for example polyamides. At the same time, it is important to look at this in a broader perspective, making it possible to use these techniques at larger scales and reducing the number of treatments/processing steps and chemicals needed to produce these modified CNC.

Mixing of dispersions has been a successful processing step in these experiments, but is it realistic to use for larger production volumes? Also the forming method, i. e. compression moulding, would preferably not be the main production method of the future. More conventionally used processing techniques such as injection moulding or extrusion are preferred for larger production volumes and reduced cycle times for manufacturing complex products. Here a better understanding of the requirements that the use of CNC enforces on the manufacturing methods is definitely needed. This relates also to the mechanical performance of the composite and the appearance of the final product.

Another part of the project has been running in parallel with the work reported here. It involves EAA reinforced with microsized cellulose fibres and the effect on the surface appearance and colour when injection moulding this compound. This work will continue and the goal is to connect the findings from that study with the results presented in this thesis. Of special interest is here the possibility to improve the thermal stability using suitable surface modifications or additives, i. e. a widening of the processing window for injection moulding, when CNC or cellulose fibres are used as reinforcing elements. Here, the mechanical performance as well as the appearance of the product is of great concern.

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