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Biopolymer-based Nanocomposites: Processing and Properties

Thesis for the degree of philosophiae doctor

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Norwegian University of
Science and Technology
Faculty of Engineering Science and Technology
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Abstract

The aim of this study was to produce biopolymer-based nanocomposites using extrusion as an industrially adaptable manufacturing process, and to study how this production process influenced the structure and properties of the nanocomposites produced. Cellulose nanowhiskers (CNWs) were prepared and used as nanoreinforcement in two different biopolymers, polylactic acid (PLA) and cellulose acetate butyrate (CAB). The CNWs were added to PLA and CAB in order to improve the thermal and mechanical properties of these polymers. Two different preparation methods of CNWs were used; isolation by sulfuric acid hydrolysis and isolation by hydrochloric acid hydrolysis. Different feeding procedures were used and evaluated during compounding. The CNW suspension was either freeze-dried and dry-mixed with the polymer prior the extrusion, or fed as a suspension directly into the extruder during compounding. However, the CNW suspension required modification in order to prevent re-aggregation of the whiskers as the dispersing medium was removed and to uniformly disperse the whiskers in the polymer matrix. In order to improve the dispersion of the CNWs in the matrix, a surfactant and a water soluble polymer were used for PLA, and a plasticizer was used for CAB. No major improvements in mechanical or thermal properties were seen for the PLA/CNW nanocomposites, either because of degradation of the matrix or poor dispersion of the whiskers. The material system of CAB/CNW was more successful and showed great improvements in mechanical and thermal properties. This study demonstrated that it is possible to produce nanocomposites by pumping a suspension of CNWs into the extruder during compounding, but compatibility between the CNWs and the matrix is required.

Preface and Acknowledgments

This work was carried out at the Norwegian University of Science and Technology (NTNU), at the Department of Engineering Design and Materials from November 2003 to February 2007. It was a part of the NANOMAT program and was financially supported by the Research Council of Norway (NFR), which has been greatly appreciated. This work was carried out with the supervision of Professor Kristiina Oksman and I wish to express my deepest gratitude to her for making my research possible. I also wish to thank her for her guidance and enthusiasm throughout my work.

I would also like to thank Cargill Dow, USA, for providing our bio-composite group with polylactic acid and Borregaard ChemCell, Norway, for providing us with microcrystalline cellulose, as well as their support regarding their product.

Furthermore, I would like to thank Aji Mathew for all her help and valuable discussions, especially during the beginning of my studies, and Ingvild Kvien for enjoyable collaboration and all her microscopy work. I would also like to thank the other current and former members of the bio-composite group: Peder Syre, Dr. Bjørn Steinar Tanem, Magnus Bengtsson, Linnea Petersson, and Marie Le Ballif, for all their help, support, and great times together. Special thanks to my former roommate Magnus Bengtsson for all our discussions, laughter, and efforts in fly fishing. I am also very grateful to all my former and current colleagues at the Department of Engineering Design and Materials for their friendship, interesting discussions, and technical support. Part of my research was performed at Polymer Technology at Chalmers University of Technology in Sweden, and I would like to thank the people there, including my former fellow students, for their discussions and for providing equipment. I almost forgot to thank King Bore for giving me the opportunity to snowboard and skiing during periods of tough studies!

Finally and most importantly, I would like to thank my family, friends, and my lovely Silje for all their support and patience. You are all very important to me and make me realize how privileged I am.

List of Appended Papers

The thesis is based on work reported in the following papers, referred to by Roman numerals in the text.

I. Daniel Bondeson, Ingvild Kvien and Kristiina Oksman. Strategies for preparation of cellulose whiskers from microcrystalline cellulose as reinforcement in nanocomposites. In: Cellulose nanocomposites; processing, characterization and properties, Edited by Kristiina Oksman and Mohini Sain, ACS Symposium series vol. 938. Oxford: Oxford University Press, 2006. p.10-25.

II. Daniel Bondeson, Aji Mathew and Kristiina Oksman. Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. Cellulose 2006;13(2):171-180.

III. Daniel Bondeson, Ingvild Kvien, and Kristiina Oksman. Bio-nanocomposites based on cellulose whiskers. 6th Global Wood and Natural Fibre Composites Symposium, Kassel, Germany, April 5-6, 2006.

IV. Daniel Bondeson and Kristiina Oksman. Dispersion and characteristics of surfactant modified cellulose whiskers nanocomposites. Accepted for publication in Composite Interfaces.

V. Daniel Bondeson and Kristiina Oksman. Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol. Submitted to Composites Part A: Applied Science and Manufacturing.

VI. Daniel Bondeson, Peder Syre and Kristiina Oksman. All cellulose nanocomposites produced by extrusion. Accepted for publication in Journal of Biobased Materials and Bioenergy.

The PhD research has also contributed to the following seminars, papers, and conferences:

Daniel Bondeson and Kristiina Oksman. Nanokompositter/biopolymerer – Framtidens materialløsninger, Emballasjeforsk, 20-21 April 2004, Langesund, Norway.

Daniel Bondeson and Kristiina Oksman. Optimization of the preparation of nano crystals from microcrystalline cellulose in aqueous suspension. Poster presentation at 229th ACS National Meeting, 13-15 March 2005, San Diego, CA, USA.

Daniel Bondeson and Kristiina Oksman. Optimization of the preparation of nano crystals from microcrystalline cellulose in aqueous suspension. Oral presentation at 229th ACS National Meeting, 13-15 March 2005, San Diego, CA, USA.

Kristiina Oksman, Aji P Mathew, Daniel Bondeson and Ingvild Kvien. Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. Composite Science and Technology 2006;66(15):2776-2784.

Kristiina Oksman, Peder Syre, and Daniel Bondeson. Patent appl. NO20065147.

Kristiina Oksman, Peder Syre, and Daniel Bondeson. Patent appl. US 10/560190.

Kristiina Oksman, Aji P Mathew, Linnea Petersson, Ingvild Kvien, Daniel Bondeson, and Bjørn Steinar Tanem. Processing of cellulose nanocomposites, Functional Fillers for Plastics, 15-17 September 2004, Hamburg, Germany.

Kristiina Oksman, Aji P Mathew, Linnea Petersson, Daniel Bondeson, Ingvild Kvien, and Bjørn Steinar Tanem. Activities on cellulose based bio-nanocomposites in Norway, Symposium on Green Composites, 18 November 2004, RISH, Kyoto University, Kyoto, Japan.

Kristiina Oksman, Ingvild Kvien, Linnea Petersson, and Daniel Bondeson. Cellulose nanocomposites; Challenges to overcome, NSF Workshop, 22-23 September 2005, Georgia Tech. Atlanta, USA.

Kristiina Oksman, Ingvild Kvien, Linnea Petersson, Daniel Bondeson, and Aji P Mathew. Bio-nanocomposites, COMAT 2005, International Conference on Science and Technology of Composite Materials, 11-14 December 2005, Buenos Aires, Argentina.

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1. Introduction

1.1 Nanocomposites

The interest in nanocomposites has increased markedly in recent years due to the great potential associated with this relatively new group of materials. Nanocomposites are defined as composites with reinforcement in the nanometer range (<100 nm) in at least one dimension. Nanocomposites can be divided into three groups, depending on the geometrical shape of the nanoreinforcement. *One-dimensional nanocomposites* are polymers reinforced with sheets with a thickness in the nanometer range. Examples of nanoreinforcement in this group are different kind of clays[1] and graphite[2]. *Two-dimensional nanocomposites* are reinforced with tubes or whiskers with a diameter in the nanometer range; examples are carbon nanotubes[3], cellulose[4], and chitin whiskers[5]. The third group, *three-dimensional nanocomposites*, are reinforced by spherical particles in the nanometer range. Examples of nanoreinforcement in this group are nanosized metals[6], metal oxides[7], silica[8], and carbon[9].

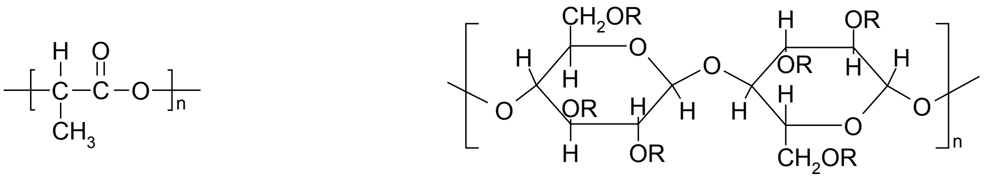
Depending on the nanoreinforcement used and the composition of the nanocomposite, it is possible to design materials with improved abrasion and wear resistance, dimensional and thermal stability, electrical conductivity, permittivity and breakdown strength, and mechanical, barrier, and flammability properties[10]. The possibilities for these improvements, often at a nanoreinforcement content of 5 – 10 wt%, originate from the properties and the nanometric size of the reinforcement. The likelihood of finding defects, such as grain boundaries, voids, dislocations and imperfections, in nanosized particles is greatly reduced compared to its micro or macro sized counterpart, which leads to significantly enhanced properties in the composite. Additionally, by moving from microscale to nanoscale, the interfacial area of the reinforcement increases tremendously and the number of possible interaction sites between the reinforcement and the matrix increases dramatically. For example, 15-nm particles at a loading of 10 vol% have an interparticle spacing of only 10 nm[10]. Even if the interfacial region between the nanoparticle and the polymer is only a few nanometers, the entire polymer matrix is affected by the interface of the nanoparticle. As a consequence, the entire polymer matrix will have different behavior than the bulk. The chain mobility of the polymer at the interface can be either facilitated, if the interaction is weak, or restricted, if the interaction is strong[10]. Therefore, by controlling the degree of the interaction between the polymer and the nanoreinforcement, the size of the interfacial region and hence the properties of the entire matrix can be controlled[10].

Another unique property of nanocomposites is the ability to preserve the optical clarity, or transparency, in the material after addition of the nanoreinforcement. The reason for this is the matrix can be reinforced with a relatively low nanoreinforcement content, and the reinforcement particles themselves are of extremely small size. In general, particles much smaller than the wavelength of light do not scatter light, thus preserving the optical clarity[10]. Another major difference from traditional composites is that nanosized reinforcements do not create large stress concentrations and thus do not compromise the ductility of the polymer[10].

1.2 Biopolymers

Biopolymers as an alternative to petroleum-based polymers are of great interest both in the academic world and in industry. Limited resources of crude oil, global warming, environmental consciousness and new standards are some of the factors that have led to this growing interest. Biopolymers are fully renewable, do not contribute to an accumulation of carbon dioxide in the atmosphere after their life cycle, and are a part of the ecosystem. A number of biopolymers are also biologically degradable, thus reducing waste management problems. However, some properties like melt strength, impact strength, thermal stability, permeability, etc do not meet the demands for some end-use applications and must be improved[11]. One way to improve the properties of biopolymers and greatly enhance their commercial potential is to incorporate nanosized reinforcement in the polymer[12].

The biopolymers used in this study were polylactic acid (PLA) and cellulose acetate butyrate (CAB). PLA is a linear thermoplastic polyester produced from fermentation products from corn, sugar beets, and rice[11] and has excellent properties compared to many petroleum-based plastics[13]. This polymer can also be processed much in the manner of polyolefins, and is competitive with petroleum-based polymers on a cost-performance basis[13]. Today, there is a great deal of interest in using PLA in packaging, medical and automotive applications. However, the softening point, i.e. the temperature at which the modulus drops catastrophically, is fairly low for PLA. CAB is a cellulose ester used in a variety of plastic applications and is produced by esterification of cellulose derived from wood, cotton, recycled paper, and sugarcane[14]. The repeating units for PLA and CAB are shown in Figure 1.


polylactic acid (PLA)

cellulose acetate butyrate (CAB)

R = $-H$; $-C_2H_3O_2$; $-C_4H_7O_2$
(acetate) (butyrate)

***Figure 1.** The repeating unit for polylactic acid (PLA) and cellulose acetate butyrate (CAB)[11].*

1.3 Cellulose Nanowhiskers

Cellulose is the most abundant renewable polymer on earth and is found in plant cell walls, but it can also be synthesized by some bacteria[15] and animals[16]. The hierarchical structure of softwood is shown in Figure 2. From the left, the figure shows a coniferous tree, which is built of wood cells (fibres). The cell wall of the wood cells consists of different layers that consist of cellulose microfibrils aggregated into larger oriented structures embedded in a matrix of hemicellulose and lignin[17]. The microfibrils consist of elementary fibrils[18]. The elementary fibril itself consists of elementary crystallites bridged by amorphous phases[18]. It is the isolated elementary crystallites that are called cellulose nanowhiskers (CNWs). The term whisker refers to the needle-like structure of the elementary crystallite.

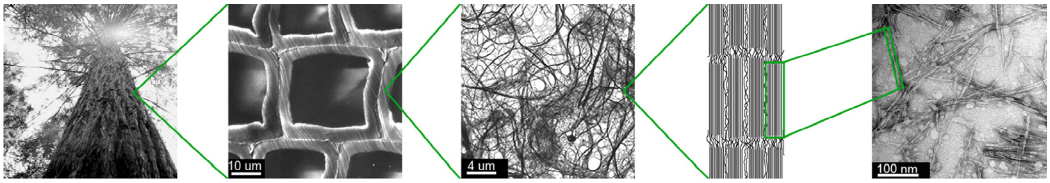


***Figure 2.** Hierarchical structure of wood showing from left: a tree, cross-section of wood cells, microfibrils, bundles of elementary fibrils, and cellulose nanowhiskers.*

The reinforcing capacity of crystalline cellulose is expected to be remarkable, with estimates of the elastic modulus along the chain axis of the crystalline cellulose reported to be 143 GPa[19] and 167.5 GPa[20]. Cellulose nanowhiskers from different sources have different geometrical characteristics, some of which are presented in Table 1.

Table 1. *Dimensions of cellulose whiskers from different sources.*

cellulose type	*cross section*	*length*
Wood[21,22]	3 – 5 nm	100 – 250 nm
Cotton[23,24]	5 – 15 nm	100 – 250 nm
Tunicate[25]	10 – 20 nm	100 nm – several μm
Algae (Valonia)[26,27]	10 – 20 nm	> 1000 nm
Bacterial[28,29]	6 – 10 nm by 30 – 50 nm	100 nm – several μm

1.4 Extrusion

Solution casting and in-situ preparation are the most common laboratory preparation methods used to prepare nanocomposites. These methods are both time consuming and produce a limited amount of material (few grams). Melt compounding, or extrusion, is a conventional method widely used in the industry to melt polymers and compound composites whereat the material is shaped through a die. Using extrusion to produce biopolymer-based nanocomposites could reduce manufacturing costs and make them competitive.

1.4.1 Extruder Classifications

Different kinds of extruders are available, such as single screw extruders, twin screw extruders, and multiple screw extruders[30]. The twin and multiple screw extruders can be classified by whether the screws rotate in the same direction, co-rotating; or in the opposite directions, counter-rotating; or a combination of both, for multiple screw extruders. Another classification of multiple screw extruders is according to the screw contact. The screws can be separated, tangential, partially intermeshing or fully intermeshing[30], as is illustrated in Figure 3.

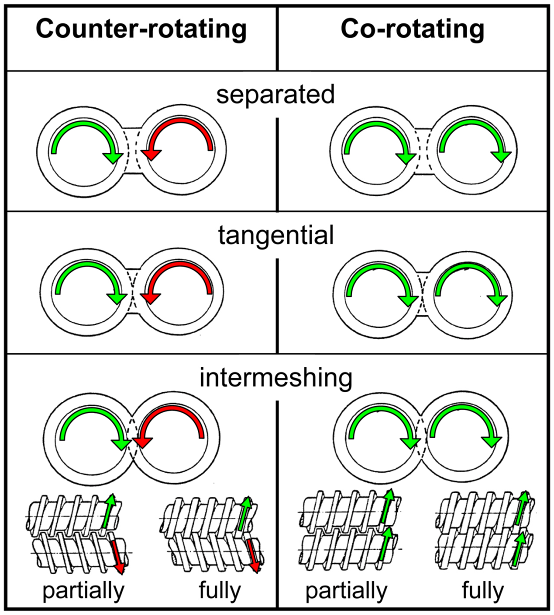


Figure 3. *Classification of extruders by rotational direction and screw contact*[30].

1.4.2 Screw Configuration

The screws in extruders are often designed with different zones with different functionalities. The *melting zone* functions to melt the polymer and is placed in the beginning of the screw. This zone is often constructed with a conveying element with a reversed pitch,[31] along with kneading elements. The conveying element with reversed pitch (backward pumping) is used for several reasons. It builds up the pressure and fills the screw channels to increase the shear. A typical heat balance for the melting section of a co-rotating twin screw extruder shows that approximately 55% of the energy reaching the material comes from the screws and 45% from the heater bands[31]. In addition, this element can be viewed as a mechanical barrier that prevents unmelted particles from moving downstream. The *feeding zone, a*s its name implies, functions to convey material in a forward direction. The *mixing zone* is used to distribute and disperse the nanoreinforcement in the polymer melt. Distributive mixing is the repeated rearrangement of components to reduce non-uniformities[30]. Dispersive mixing is the disintegration of agglomerates of solid particles[30]. Dispersive mixing can also be resembled as swelling of agglomerates with an increased interparticle distance as a consequence. The difference between distributive and dispersive mixing is illustrated in Figure 4.

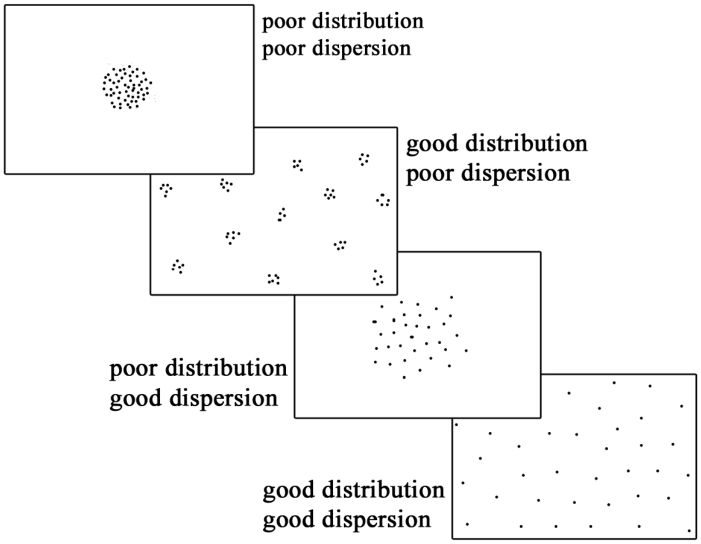


Figure 4. *Differences between distributive and dispersive mixing*[10].

There are many different screw elements designed for distributive and/or dispersive mixing, the composition and combination of which are very important to nanocomposite production. Kneading elements can provide a combination of both distributive and dispersive mixing. Wide block kneading elements are used for dispersive mixing but as the individual block gets narrower, the ability to provide distributive mixing increases. Turbine mixing elements and slotted conveying elements are examples of screw elements that provide distributive mixing during compounding.

1.4.3 Challenges

Extrusion is used as process method for short fibre reinforced composites, such as wood and glass fibre composites, but the operation procedure for these materials cannot be directly applied to biopolymer/CNW based nanocomposites. The reason for this is that biopolymers have in general a small process window and the combination of temperature, screw speed and screw configuration has to be such that the biopolymer is not degraded during processing. Additionally, some biopolymers need processing aids such as plasticizers to enable processing and to prevent degradation of the biopolymer and the CNWs. Feeding the CNWs as dry material is complicated due to the large differences in bulk density between the polymer and the CNWs. Freeze-dried CNWs are a very lightweight powder and dry mixing this powder with the polymer prior feeding is difficult. This problem could be solved by pumping the CNWs as a suspension directly into the polymer melt during extrusion. However, the dispersing medium has to be heated and evaporated during extrusion, which makes demands on the screw configuration and the venting/vacuum capability during extrusion. As the dispersing medium is evaporated, the CNWs have a strong tendency to re-aggregate and form strong hydrogen bonds. These hydrogen bonds are very hard to break with the shear forces produced in the extrusion process. There is also a risk that the dispersing medium will degrade the polymer at the elevated temperatures incurred during extrusion, a factor that must be taken into account. Another challenge lies in the extrusion process itself. In this continuous process, the CNWs must be dispersed in the matrix almost to a molecular level in less than two minutes.

1.4.4 Processing Strategies

Both dry feeding and liquid feeding were used in this study. When dry feeding was used, the CNW suspension was freeze-dried and dry mixed with the polymer prior extrusion. When liquid feeding was used, the CNW suspension was pumped into the polymer melt after the melting zone in the extruder. As the dispersing medium was removed during freeze-drying and liquid feeding, the CNWs had a strong tendency to re-aggregate and form strong hydrogen bonds between the whiskers. It was therefore important to find a substance that was soluble in the CNW suspension and that could prevent this re-aggregation of the whiskers during drying. This substance also needed to be miscible in the polymer and improve the dispersion of the whiskers in the matrix. It also needed to neither affect the CNWs or the matrix negatively. During liquid feeding, a long feeding zone was used together with two atmospheric venting sites to ensure that all dispersing medium was evaporated during compounding. A lowered screw speed and total throughput during extrusion was used to increase the capacity of evaporation. Excessive heating during compounding could cause degradation of the matrix and the CNWs and was avoided by using low heating and a screw configuration that produced relatively low shear forces during compounding.

1.5 Aim of Study

This thesis focuses on the production of nanocomposites based on cellulose nanowhiskers (CNWs) and polymers prepared from fully renewable resources. Until now, the majority of the research using CNWs as reinforcement in nanocomposites has been done with water-soluble polymers using laboratory scale preparation methods. This is not surprising, since using water-soluble polymers simplifies the production of these nanocomposites. In this study, nanocomposites using CNWs and non water-soluble biopolymers have been prepared by extrusion. Extrusion is widely used in the industry and could make it possible to produce these materials in a cost-effective manner for the commercial market. As can be seen in Figure 5, the nanocomposites' main constituents have either been derived from wood (i.e. CNWs) and maize (i.e. PLA) or wood/cotton alone (i.e. CNWs and CAB). Figure 5 summarizes the content of this thesis.

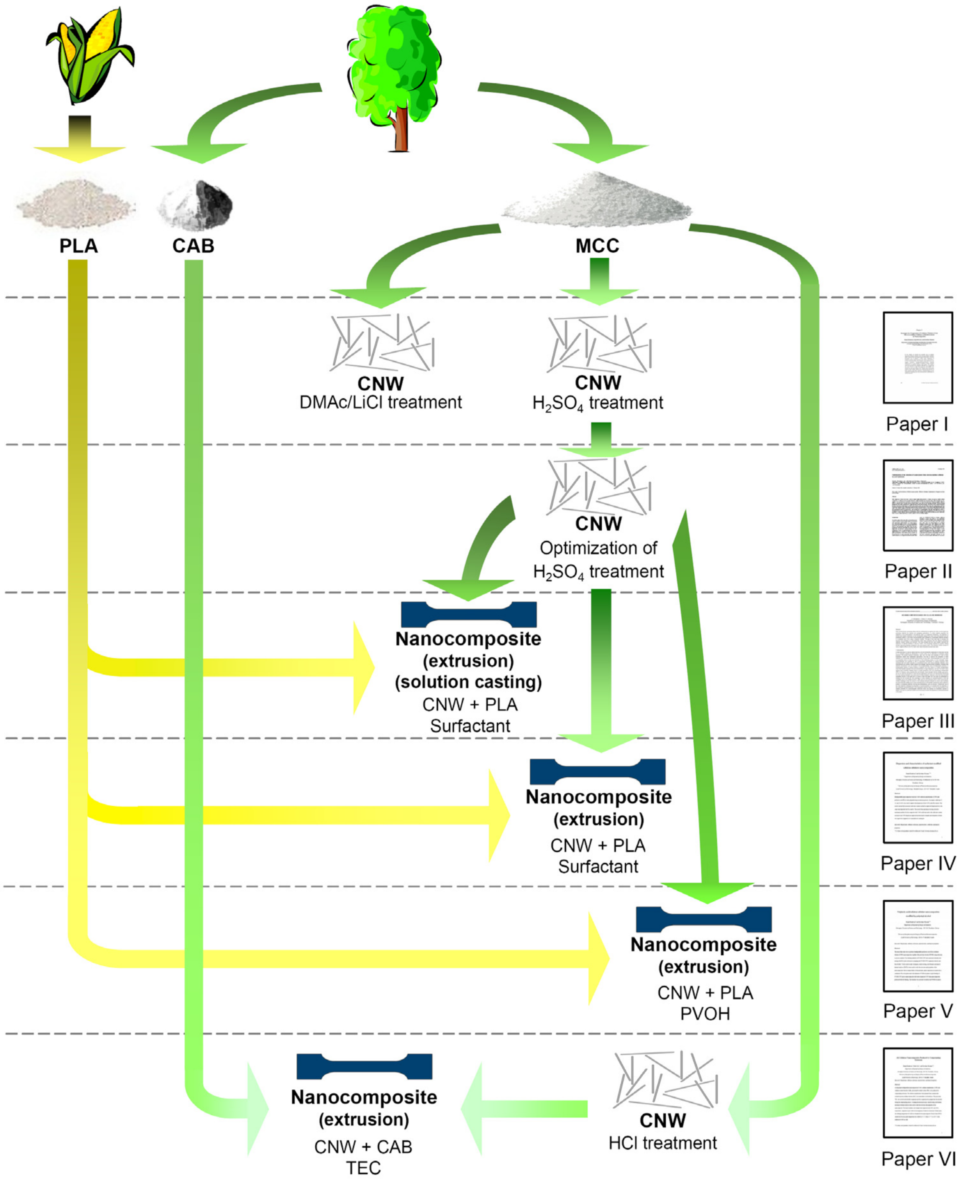


Figure 5. *Schematic overview of the contents of this thesis.*

2. Experimental

2.1 Preparation of Cellulose Nanowhiskers

Preparation of cellulose nanowhiskers (CNWs) by using sulfuric acid or hydrochloric acid is a well-known method for isolating CNWs[32]. The amorphous phase, which is more easily accessible for the acid, is hydrolyzed in this method leaving the crystalline part isolated in a suspension[32]. CNWs are not commercially available but can be prepared from microcrystalline cellulose (MCC), which has been used as starting material in this study. MCC is a commercial product prepared by hot-treating cellulose from wood with acid, vigorous agitation of the slurry and spray drying[33]. The MCC consist of CNWs, which have been re-aggregated by strong hydrogen bonds during the drying procedure[34]. To use CNWs as reinforcement, the hydrogen bonds between the whiskers must be broken in the MCC, which is achieved by using the acid hydrolysis process. Studies showed that the MCC used as starting material in this study also contained amorphous phases that were hydrolyzed during the preparation. The preparation procedure for CNWs is shown in Figure 6. Deionized water and MCC were mixed and placed in an ice bath and stirred while concentrated acid was added drop wise until desired concentration was reached. The hydrolysis was then completed by heating the suspension while stirring. Removal of excess acid was achieved by centrifugation and dialysis against deionized water. The suspension was then sonicated in an ice bath.

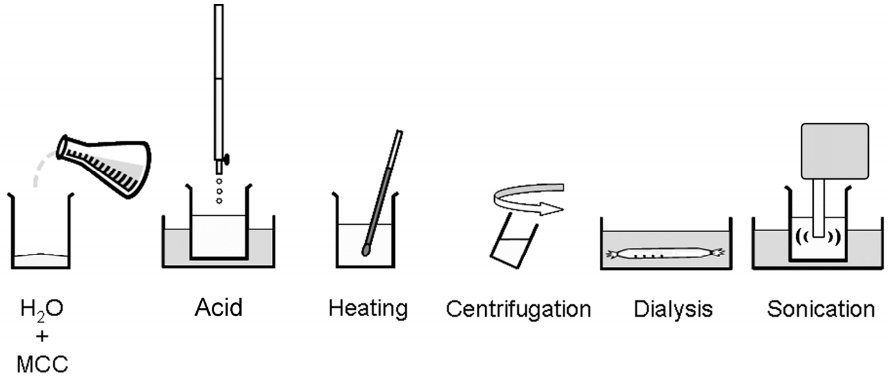


***Figure 6.** Preparation procedure for cellulose nanowhiskers.*

Hydrolysis with sulfuric acid gave the CNWs a negatively charged surface, which resulted from esterification of hydroxyl groups by sulfate ions[35], as is shown in Figure 7. After removal of the excess sulfuric acid, the sulfate groups on the surface of the whiskers became negatively charged as a consequence of increased pH in the suspension. This surface charging caused the whiskers to form a stable colloid suspension by electrostatic stabilization.

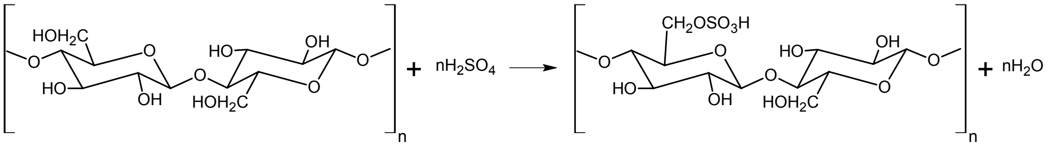


Figure 7. *Esterification of hydroxyl groups by sulfate ions from sulfuric acid treatment of cellulose*[35].

2.2 Processing of Nanocomposites

This study used co-rotating fully intermeshing twin screw extruders. This means that the screws were self-cleaning, and that there were no stationary zones in the barrel where the material could be trapped and degraded. The extruder used in Papers III and IV was a bench type extruder, a Haake MiniLab Rheomex CTW5. The screws were double-flighted, 109.5 mm in length and conical with a screw diameter of 14 mm at the beginning and 5 mm at the end, as is shown in Figure 8. The freeze-dried CNWs and the polymer pellets were dry mixed and fed batchwise during extrusion using a cylinder to pneumatically press the material into the extruder.

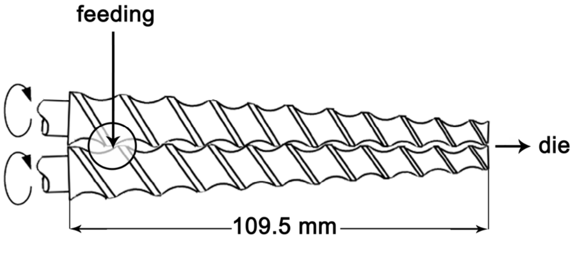


Figure 8. *Screw configuration with feeding site for the extruder used in Papers III and IV.*

The extruder used in Papers V and VI was a ZSK 25 WLE from Coperion Werner & Pfleiderer. The screws were double-flighted with a length of 1100 mm and a diameter of 25 mm, as is shown in Figure 9.

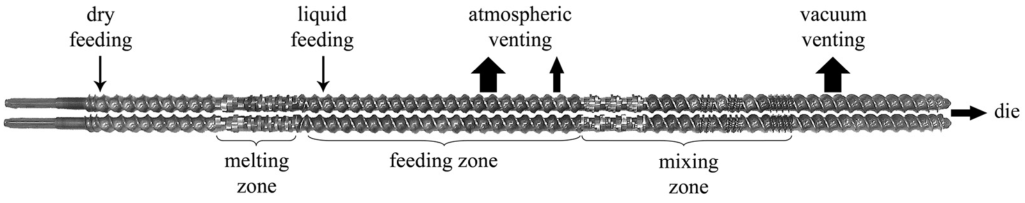


Figure 9. *Screw configuration with feeding and atmospheric/vacuum venting for the extruder used in Papers V and VI.*

Both dry feeding and liquid feeding were used during the compounding process for this extruder. The dry materials, i.e. the polymers and freeze-dried CNWs, were fed from the beginning of the extruder. When liquid feeding was used, the CNW suspension was pumped into the polymer melt in the beginning of the feeding zone. The long feeding zone was needed in order to heat and evaporate the dispersing medium before the melt reached the mixing zone. No mixing elements were used in this section because these would act as a barrier for the suspension and prevent the dispersing medium from reaching the atmospheric venting channels. Two atmospheric venting channels at the end of the feeding zone ensured that all of the dispersing medium was able to evaporate before the mixture reached the mixing zone. The mixing zone was composed of kneading elements to provide dispersive mixing, as well as ZME and SME elements (as labelled by Coperion Werner & Pfleiderer) to provide distributive mixing. Vacuum venting was used after the mixing zone to remove entrapped air and volatile substances in the compound.

2.3 Characterization Methods

The following characterization methods were used to study the CNWs or the materials produced. Flow birefringence and optical microscopy were used to study the effectiveness of the isolation process by acid hydrolysis. Thermogravimetric analysis was used to study the thermal stability of CNWs. Dynamic mechanical thermal analysis, field emission scanning electron microscopy, and tensile testing were used to study how the production process influenced the structure and properties of the materials produced.

2.3.1 Flow Birefringence

It is known that a suspension of cellulose whiskers forms liquid crystalline phases, either a chiral nematic (cholesteric) ordering or a flow-induced nematic ordering[23]. In order to determine if the preparation of whiskers was successful, i.e. if the suspension contained isolated crystalline cellulose, polarization filters were used to investigate flow birefringence. In this technique, the sample is placed between the polarization filters, one rotated 90° relative to the other in order to extinguish the light. During flow the whiskers will align with the long axis in the flow direction[23], which enables these macroscopic liquid crystalline phases to be seen as bright areas, as is shown in Figure 10.

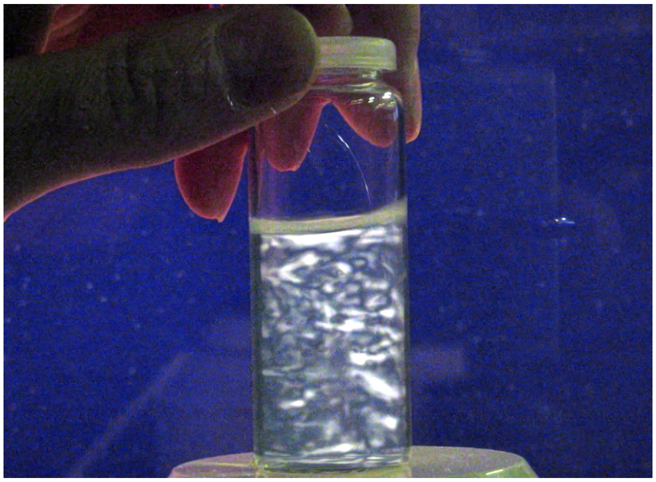


Figure 10. *Flow birefringence of a whisker suspension seen between two crossed polarization filters. (Vial is 24 mm in diameter)*

2.3.2 Optical Microscopy

Optical microscope was used to detect larger cellulosic particles after the microcrystalline cellulose had undergone different separation/isolation techniques. The detection of cellulose particles in an optical microscope indicates that the separation/isolation process has not been adequate enough to obtain a suspension of only whiskers. The optical microscope uses visible light and a system of lenses to magnify images of small samples.

2.3.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to measure the thermal stability and decomposition of the cellulose nanowhiskers. TGA is a procedure in which the sample is progressively heated and then changes in the weight of the material are recorded. The sample is placed on an arm of a recording microbalance inside a furnace and a gas flow is introduced into the furnace[36]. Air or argon was used as gaseous environment in this study. In order to remove moisture and absorbed water in the sample, the temperature was raised to an isotherm and held there for a specified time. Thereafter the analysis was started, using two different thermogravimetric analysis procedures. In the first procedure, the temperature was increased at a predetermined rate and the weight loss was measured versus temperature. The second method used the measurement of the weight loss versus time at a constant temperature (isotherm).

2.3.4 Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) was used to measure the thermal transitions and temperature dependence of the materials' mechanical properties. It was also used to determine if the CNWs were dispersed in the matrix, the extent of the interaction between the CNWs and the matrix, the extent of miscibility between polymer blends, and if the matrix was degraded during the process. DMTA examines the behaviour of viscoelastic materials according to temperature and frequency dependent behaviour. During measurement, the material is subjected to a sinusoidal stress (σ). The resulting strain (ε) is also sinusoidal with the same frequency but is somewhat retarded due to the viscous component in the material[37]. This phase lag is expressed as an angle, δ, as is shown in Figure 11.

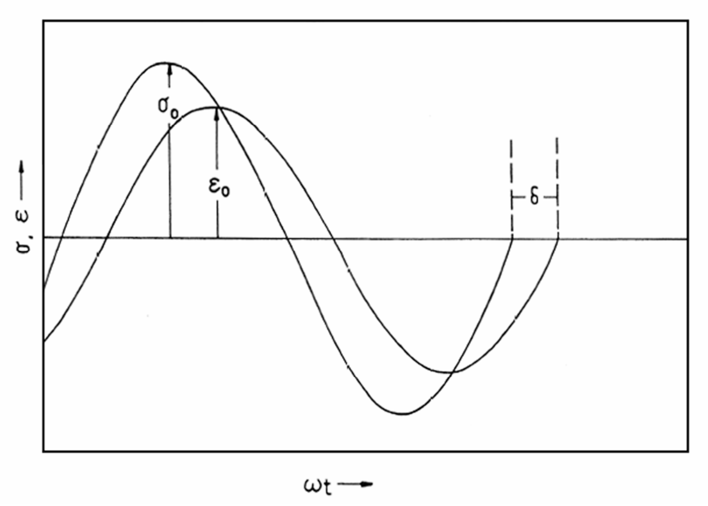


Figure 11. *Stress-strain relationship for a viscoelastic material.*

To describe the data from DMTA, a complex modulus, E*, is defined as:

$$E^* = E' + iE'' \qquad (1)$$

The complex modulus, E*, is separated into two responses of which *E′* is the in-phase component or storage modulus and *E′′* is the out-of-phase component or loss modulus[38]. The letter *i* stands for the square root of -1. In order to evaluate E*, the stress is separated into its two components, one that is in-phase with the strain and one that is out-of-phase:

$$\sigma = \sigma_0 \sin(\omega t + \delta) = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \qquad (2)$$

Equation (2) can be re-written by introducing the storage modulus, *E′*, and loss modulus, *E′′*:

$$\sigma = \varepsilon_0 E' \sin \omega t + \varepsilon_0 E'' \cos \omega t \qquad (3)$$

where *E′* and *E′′* are defined as:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \qquad (4)$$

$$E' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \qquad (5)$$

The damping in the system or the energy loss per cycle can be measured from the loss tangent, tan δ, which is a measure of the internal friction and is related to the complex moduli by[39]:

$$\tan\delta = E''/E' \qquad (6)$$

Any peak in the tan δ corresponds to a region where the material properties are changing very rapidly and the material is undergoing transitions. During a DMTA temperature ramp test, it is common to plot E', E'', and tan δ versus temperature, as is shown in Figure 12.

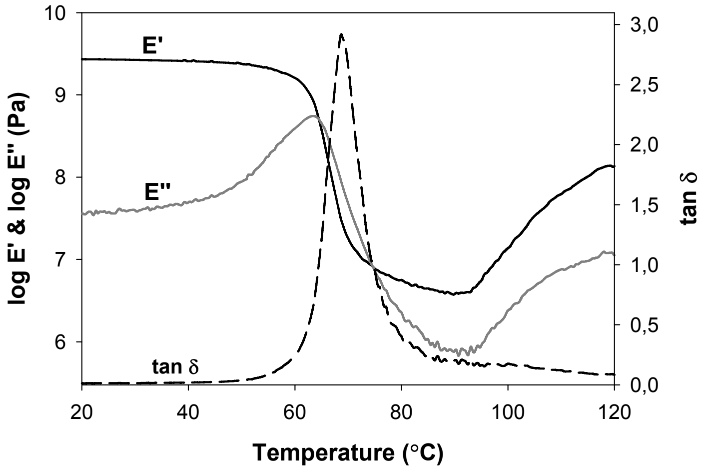


Figure 12. *An example of a DMTA temperature ramp test showing a plot of E', E'', and tan δ versus temperature for polylactic acid (PLA).*

DMTA is a good tool to use in order to find the temperature zone in which a material can be used. Figure 12 shows how the storage modulus, *E'*, drops catastrophically at a certain temperature interval. This is also seen as a peak of the tan δ curve. DMTA was also used to provide information about the level of dispersion of the CNWs in the matrix. An increase of the *E'* and a shift of the tan δ peak to higher temperatures could be an indication of well-dispersed CNWs with good matrix interaction. With strong interaction between the CNWs and the matrix, the polymer motion of the matrix is restricted[10]. This restriction is more apparent if the CNWs are well-dispersed, which gives a larger surface area and associated possible interaction sites. The intensity of the tan δ peak is also an indication on the number of segments participating in the transition. For a matrix with well-dispersed nanoparticles, it is common to see a broader tan δ peak for the nanocomposite than for the pure matrix.

This indicates that the temperature span or distribution of the transition has increased. If the tan δ peak shifts to lower temperatures, this could be an indication of weak interaction between the CNWs and the matrix, plasticizer in the matrix, or degradation of the matrix. As the polymer chains are cut due to degradation, more polymer ends are available, which generate more free volume than segments in the chain interior, so that less energy is required to rotate the chain ends[39].

2.3.5 Field Emission Scanning Electron Microscopy

The morphology of fractured and microtomed samples was investigated with field emission scanning electron microscopy (FESEM). Field emission refers to the filament used to emit electrons, which are accelerated, focused and scanned on the sample to provide an image of the surface[40]. When the electron beam hits the surface of the sample, a variety of signals will be emitted, such as secondary electrons, backscattered electrons, Auger electrons, photons, and characteristic and continuous X-rays[41], as is shown in Figure 13. Signals from the secondary electrons were used in this study to get an overview at a microscale of the prepared composites' structure. If no whisker aggregates were seen in FESEM, this could indicate uniform dispersion of the whiskers. The biobased materials investigated were not conductive and surface coating with platinum was often needed to prevent charging of the surface. A disadvantage with surface coating is that the platinum layer covers the original structure, and if the layer is too thick, the real structure could be misinterpreted and details could be overlooked. For that reason, the samples were coated over a short time period to assure a thin platinum layer. The surfaces of uncoated samples were also investigated, but the accelerating voltage had to be lowered to prevent charging. This was problematic because a lower accelerating voltage results in a lower image resolution. Precise instrumentation was required to get an image.

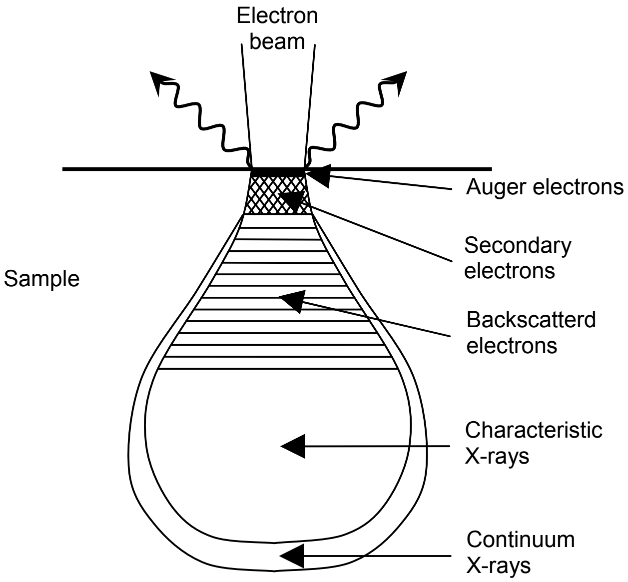


Figure 13. *Resolution of different signals emitted from the sample in FESEM analysis*[41].

2.3.6 Tensile Testing

Tensile testing was done to measure the mechanical properties of the materials. With uniform dispersion of the cellulose nanowhiskers and strong interactions with the matrix, the tensile modulus and strength is expected to increase. Tensile testing can also be used to characterize the toughness of a material. The area under the stress-strain curve is directly proportional to the amount of energy a material can absorb, i.e. the toughness[42]. A difference between micro- or macrocomposites is that nanosized reinforcements do not create large stress concentrations and thus do not compromise the ductility of the polymer[10]. Improvements in tensile modulus and strength together with preserved toughness of the material could therefore indicate that the CNWs are uniformly dispersed in the matrix and are not re-aggregated microscopic particles. The testing was performed with a miniature material tester (MiniMat) and the samples were held fast in the tensile testing equipment by 20 mm-long clamps. The measurements were done without using an extensometer and the strain was calculated by the rotational movement of the drive shaft. The test results obtained should therefore be considered for reciprocal comparison and not as absolute values. The tensile modulus (E), stress (σ), and strain (ε) were calculated according to the following equations:

$$E = \frac{\Delta\sigma}{\Delta\varepsilon}\text{, initial linear part of the curve} \qquad (7)$$

$$\sigma = \frac{F}{A} \qquad (8)$$

$$\varepsilon = \frac{\Delta L}{L_0} \times 100 \qquad (9)$$

where F is load (N), A is the cross-sectional area of test specimen (m^2), ΔL is elongation (m), and L_0 the original length of the test specimen (m).

3. Summary of Appended Papers

Paper I.

Strategies for preparation of cellulose whiskers from microcrystalline cellulose as reinforcement in nanocomposites.

This paper present two possible techniques for preparing cellulose nanowhiskers (CNWs) from microcrystalline cellulose (MCC) derived from Norwegian spruce (Picea abies). These whiskers were intended for use as reinforcement in biopolymer based nanocomposites. The first procedure was to swell the microcrystalline cellulose and partially isolate cellulose nanowhiskers by using *N,N*-dimethylacetamide (DMAc) with and without lithium chloride (LiCl). The second procedure was to prepare a stable water suspension of cellulose whiskers after hydrolysis with sulfuric acid (H_2SO_4). Treatment with DMAc, with and without LiCl, gave a suspension with whiskers but also contained MCC particles. Treatment with H_2SO_4 gave a stable colloidal suspension of only cellulose whiskers with a size between 200-400 nm in length and less than 10 nm in width.

Paper II.

Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis.

Microcrystalline cellulose (MCC) treated with *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) could not be used as swelling/separation agent for MCC due to the degradation of PLA. Using cellulose nanowhiskers prepared from sulfuric acid might be more suitable as the reinforcement in PLA. However, the preparation of whiskers with sulfuric acid is a tedious process and large quantities are required, since these whiskers are designed to be used in an extrusion process with a relatively high output. The objective in this paper was therefore to optimize this hydrolysis process regarding yield and preparation time. Microcrystalline cellulose (MCC) derived from Norway spruce (Picea abies) was used as the starting material. The processing parameters were optimized by using response surface methodology. With a sulfuric acid concentration of 63.5% (w/w), it was possible to obtain cellulose nanowhiskers with a length between 200 and 400 nm and a width less than 10 nm in approximately 2 h with a yield of 30% (of initial weight).

Paper III.

Bio-nanocomposites based on cellulose whiskers.

In this work, 5 wt% cellulose nanowhiskers, prepared as described in Paper II, were used as the reinforcement in PLA. An anionic surfactant (20 wt%) was used as a chemical modifier in order to prevent re-aggregation of the whiskers during drying and to improve the dispersion of the whiskers in the PLA. Two different processing methods were used, solution casting and extrusion. The study showed that the surfactant improved the dispersion of the cellulose whiskers in the PLA matrix for both processing methods. The nanocomposites prepared by solution casting showed improved properties compared to the pure polymer matrix. However, this was not the result for the nanocomposites produced by extrusion. The surfactant was shown to degrade the PLA matrix at the elevated temperatures associated with the extrusion process.

Paper IV.

Dispersion and characteristics of surfactant modified cellulose whisker nanocomposites.

In this study, 5 wt% cellulose nanowhiskers, prepared as described in Paper II, were used as the reinforcement in PLA. The same surfactant as in Paper III was used to prevent re-aggregation of the whiskers and to improve the dispersion of the whiskers in the PLA. The influence of a surfactant content that varied from 5 to 10 or 20 wt% on the structure and mechanical properties of the nanocomposites was investigated. The results from mechanical testing showed a maximum modulus for the composite with 5 wt% surfactant, and as the surfactant content increased, the CNW dispersion improved and the tensile strength and elongation at break was improved compared to its unreinforced counterpart. The results showed that increased surfactant content improved dispersion but degraded the PLA matrix at the same time. This surfactant was not suitable for use with PLA in the extrusion process even at lower concentrations due to degradation.

Paper V.

Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol.

In this work, 5 wt% cellulose nanowhiskers, prepared as described in Paper II, were used as the reinforcement in PLA. A water-soluble polymer, polyvinyl alcohol (PVOH), was solved in the whisker suspension with the aim of preventing re-aggregation of the whiskers during drying and improving the dispersion of the whiskers in the PLA. The nanocomposites were prepared by compounding, and two feeding methods of PVOH and CNWs were used and evaluated; dry mixing with PLA prior to extrusion, or pumping as a suspension directly into the extruder. The PVOH content was 30 wt% in the nanocomposites. Due to the immiscibility of the polymers, phase separation occurred with a continuous PLA phase and a discontinuous PVOH phase. The whiskers were primarily located in the PVOH phase and only a negligible amount was located in the PLA phase. This inadequate dispersion of whiskers in the PLA phase was probably the reason why no improvements in thermal properties were seen. The relatively small improvements in tensile modulus, tensile strength, and elongation to break for the nanocomposites also indicated that it was principally the PVOH phase, not the PLA phase, which was reinforced with whiskers.

Paper VI.

All cellulose nanocomposites produced by extrusion.

A transparent nanocomposite of 5 wt% cellulose nanowhiskers (CNWs) and cellulose acetate butyrate (CAB), plasticized by triethyl citrate (TEC), was produced by melt extrusion. The cellulose nanowhiskers were prepared from commercially available microcrystalline cellulose (MCC) using hydrochloric acid hydrolysis. The plasticizer, TEC, was solved in the whisker suspension and the subsequent suspension was pumped into the extruder during the compounding process. The tensile modulus and strength were improved by 300% and 100%, respectively, compared to unreinforced CAB, but the elongation at break was decreased. The improvements in mechanical properties could not be given with statistical significance but showed the potential of this material combination. Furthermore, the softening temperature of CAB was extended for the nanocomposite. Results from DMTA showed that the tan δ peak temperature was shifted by 31 ˚C, from 117 °C to 148 ˚C with the addition of CNWs in CAB.

4. Conclusions

Cellulose nanowhiskers (CNWs) were prepared from microcrystalline cellulose (MCC) as a reinforcement for polylactic acid (PLA) and cellulose acetate butyrate (CAB). Nanocomposites were produced by extrusion, and due to the large quantities of CNWs required, the CNW hydrolysis process using sulfuric acid was optimized for preparation time and yield. Isolated whiskers were prepared by hydrolysis in 63.5 wt% sulfuric acid in approximately 2 h with a yield of 30% (of initial weight). Preparation of CNWs by sulfuric acid rendered the CNWs acidic, which made them less thermally stable than MCC. Neutralization of the whiskers did not completely solve this problem. Preparation of CNWs by hydrochloric acid gave more thermally stable CNWs than CNWs prepared by sulfuric acid, and no neutralization of this suspension after preparation was needed.

A surfactant, an acid phosphate ester of ethoxylated nonylphenol (APEENP), and polyvinyl alcohol (PVOH) were used to improve the dispersion of CNWs in PLA. APEENP and PVOH were solved in the CNW suspension in order to prevent re-aggregation of the whiskers as the water was removed during freeze-drying or when the suspension was pumped into the hot polymer melt during extrusion. APEENP improved the dispersion of CNWs in PLA, and the tensile modulus, tensile strength and elongation at break were increased for the nanocomposites compared to the reference materials without CNWs. However, the APEENP degraded the PLA at elevated temperatures during extrusion and the surfactant was therefore not suitable for use together with PLA. Dispersed whiskers were seen in PLA when PVOH was used, but due to immiscibility between the PLA and PVOH, the whiskers were primarily located in the PVOH phase. The tensile modulus, tensile strength and elongation at break were increased for the nanocomposites as compared to the reference materials without CNWs. No improvements were seen in the dynamic mechanical thermal properties due to inadequate dispersion of whiskers in the PLA.

Triethyl citrate (TEC) was used as a plasticizer for CAB and was solved in the CNW suspension prior to feeding. The suspension was pumped into the hot polymer melt during extrusion and TEC prevented re-aggregation of the whiskers as the water/ethanol evaporated. The whiskers were assumed to be well dispersed in the matrix due the large improvements seen both in mechanical and thermal properties.

5. Future Work

This study has been done with the aim of finding an industrial and economical way to produce nanocomposites based on biopolymers. It has been shown that it is possible to feed the reinforcement into the extruder as a suspension during compounding. Feeding the reinforcement as a suspension could be advantageous from both an economic and environmental point of view. An understanding of the chemistry at the interphase is very important for controlling the level of dispersion of the CNWs in the matrix. Uniform dispersion of the CNWs in the matrix is a key to achieve the improved properties associated with nanocomposites. Therefore, it would be interesting to further investigate the possibility of using different polymers soluble in a CNW suspension that are also miscible with the polymer used as matrix. Chemical modification or grafting of the surface of the cellulose, with polyethylene glycol (PEG) for example, would also be very interesting to investigate in order to increase the compatibility between PLA and the whiskers. The CAB/CNW system was found to have a great deal of potential, and it would be fascinating to further investigate this system regarding the choice of plasticizer, process conditions, and composition in order to increase its mechanical and thermal properties further.

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Papers

Paper I.	Strategies for preparation of cellulose whiskers from microcrystalline cellulose as reinforcement in nanocomposites.
Paper II.	Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis.
Paper III.	Bio-nanocomposites based on cellulose whiskers.
Paper IV.	Dispersion and characteristics of surfactant modified cellulose whisker nanocomposites.
Paper V.	Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol.
Paper VI.	All cellulose nanocomposites produced by extrusion.

Paper I

Paper I is not included due to copyright.

Paper II

Paper II is not included due to copyright.

Paper III

BIO-NANOCOMPOSITES BASED ON CELLULOSE WHISKERS

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Abstract

New nanostructured composites where both the reinforcement as well as the matrix are bio based are promising materials for medical and packaging applications. To obtain desired properties the dispersion of the reinforcement in the polymer matrix is of significant importance. The dispersion is among other factors influenced by the compatibility between the matrix and reinforcement and the processing method. In this study nanocomposites were prepared by incorporating cellulose whiskers in a polylactic acid (PLA) using a chemical modifier. The goal of this work was to compare the structure and properties of nanocomposites which were produced with two different processing methods, solution casting and extrusion. The study showed that the used modifier improved the dispersion of cellulose whiskers in the PLA matrix. The composites prepared by solution casting showed improved properties compared to the pure polymer matrix. The chemical modifier showed to have a negative effect on the PLA matrix when high temperature process was used.

1. Introduction

Limited resources of crude oil, global warming, and environmentally awareness of consumers has led to an increased interest for biopolymers in recent years as an alternative to petroleum based polymers. The present low-level production, high cost, and often low properties of most of these biopolymers restrict their widespread applications. One way to improve the properties of these materials is to incorporate nanosized reinforcement into the matrix. Nanocomposites are a new class of composites where at least one dimension of the reinforcing phase is in the nanometer range. Nanocomposites are expected to lead to remarkable improvement of material properties when compared with the matrix polymers or conventional micro- and macro-composite materials. Such improvements can include a higher modulus and strength, improved barrier properties, increased heat distortion temperature, and an increase in the biodegradability rate of biodegradable polymers. A biodegradable polymer of special interest is polylactic acid (PLA) which is a readily biodegradable linear thermoplastic polyester derived by fermentation of sugar feedstocks, corn etc. PLA has in many aspects basic properties between those of crystal polystyrene (PS) and polyethylene terephthalate (PET) [1]. However, some properties like melt strength, impact strength, thermal stability, gas barrier, etc do not meet the demands for some end-use applications and has to be improved [2]. Reinforcing PLA with cellulose whiskers may solve some of these problems. Cellulose is also the most abundant renewable polymer in the world and it is found in plant cell walls, but it can also be synthesized by bacteria [3] and animals [4]. One challenge of using cellulose as nanoreinforcement is that the crystallites have to be isolated and this is often done by acid hydrolysis which is time consuming [5]. Another challenge to take into account is that cellulose whiskers prepared by sulfuric acid hydrolysis are more thermally instable due to acidic sulphate groups on the whisker surfaces [6], which might be a problem in processing methods involving high temperatures, such as extrusion. Furthermore, one of the most important challenge for preparation of nanocomposites is to succeed with the dispersion of the hydrophilic nanoreinforcement in the hydrophobic polymer matrix. If not, the improvements of the material properties for nanocomposites mentioned above will probably be remarkably reduced or absent. The use of a chemical modifier can be one way to control the dispersion of nanoreinforcement in the matrix.

The goal of this work was to prepare nanocomposites of cellulose whiskers and PLA with two different processing methods, solution casting and extrusion and compare the structure and properties of these two composites. In difference from solution casting, high temperature is involved in extrusion processes and requires thermally stable cellulose whiskers. The thermal stability of freeze-dried whisker suspensions with different pH was investigated with thermogravimetric analysis. An anionic surfactant was used to modify the dispersion of the cellulose whiskers in the PLA polymer. The structure of prepared whiskers and composites were studied using atomic force microscope (AFM), transmission electron microscope (TEM) and scanning electron microscope (SEM). The polymer and composite properties were measured using dynamic mechanical thermal analysis (DMTA).

2. Experimental

2.1 Materials

Polylactic acid (PLA), NatureWorks™ (Cargill Dow LLC, Minnetonka, MN, USA) was used as polymer matrix. Microcrystalline cellulose from Norway spruce (Picea abies) with a particle size between 10 to 15μm (Borregaard ChemCell, Sarpsborg, Norway), was used as starting material for the preparation of the cellulose whiskers. The Beycostat A B09 (CECCA S.A.), an acid phosphate ester of alkyl phenol ethoxylate, was used as a chemical modifier.

2.2 Materials processing

2.2.1 Preparation of cellulose whiskers

The different steps in the preparation process of cellulose nano whiskers are shown in Figure 1. The first step was to mix deionized water and MCC, 10g/100ml. The water/MCC-suspension was then put in an ice bath and stirred while concentrated sulfuric acid was added by drop until the desired acid concentration, 63.5wt%, was reached. The suspension was heated at 44°C in 130min while stirred. The suspensions were then washed with deionized water using repeated centrifuge cycles (10min at 13 000rpm, 18500g), i.e. the supernatant was removed from the sediment and replaced by new deionized water and mixed. The centrifugation step was continued until the supernatant became turbid. The last wash was conducted using dialysis with deionized water until the wash water maintained at constant pH. The samples were then sonicated for some minutes to fully disperse the cellulose whiskers in the suspension.

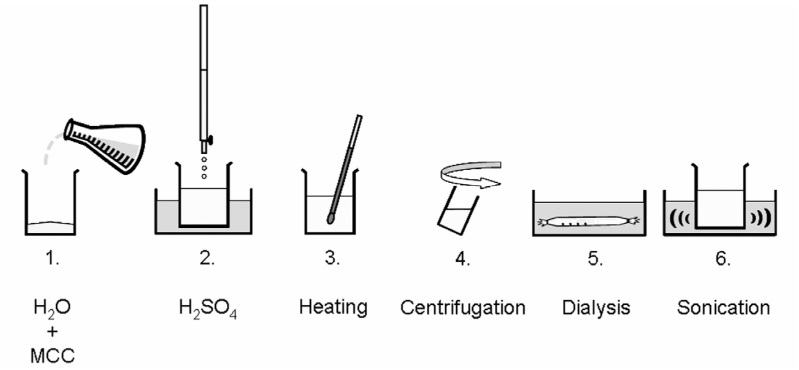

Figure 1. *The process steps in the preparation of cellulose whiskers.*

The prepared whiskers are seen in Figure 2 and were approximately 200 – 400nm in length and less than 10nm in width.

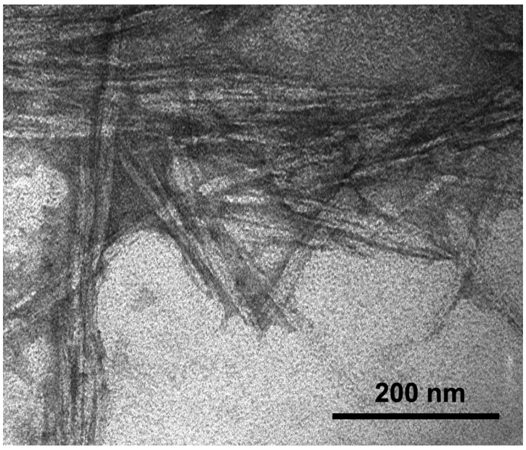

Figure 2. *TEM image of cellulose whiskers prepared from acid hydrolysis.*

2.2.2 Preparation of unmodified/modified cellulose whiskers for processing

Two different suspensions of cellulose whiskers were prepared before freeze-drying, one unmodified and one modified with surfactant. For the suspension without surfactant the pH was raised to approximately 7.5 by addition of 0.25mol/L NaOH prior freeze-drying. The suspension modified with surfactant was prepared with the ratio 4/1(w/w) of Beycostat A B09 to cellulose. A similar surfactant has also been used as a stabilizing agent to obtain stable dispersions of cellulose whiskers in nonpolar solvents [7]. This suspension was then vigorously mixed and the pH was raised to approximately 7.5 by addition of 0.25mol/L NaOH prior to freeze-drying. Freeze-drying of solely isolated whiskers in water suspensions has shown to be problematic due to the tendency of cellulose to agglomerate and form strong hydrogen bonds as the water sublimate. Figure 3 shows freeze-dried whiskers from a water suspension without surfactant and the whiskers were no longer isolated but agglomerated into large flakes. The surfactant used in this study hindered agglomeration and formation of strong hydrogen bonds between the whiskers.

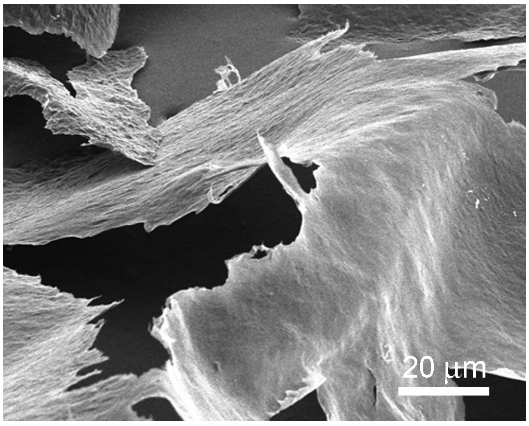

Figure 3. *FESEM image of freeze-dried cellulose whiskers without surfactant at 5kV acceleration voltage. Whiskers have aggregated into larger flakes.*

2.2.3 Nanocomposites prepared by extrusion

Extrusion might be the most suitable process method for industrial production due to continuous and relative fast processing. The process is also economical and simple and comparing to solution casting, no or little environmental hazardous organic solvent has to be removed to get the desired product. But several difficulties occur and one is to overcome the problem with dispersion of nano reinforcement in the polymer matrix [8, 9]. The reinforcement has to be compatible enough with the polymer to allow polymer chains to diffuse into the interspace of agglomerates and form either a partially or uniformly dispersed nanocomposite. Also the process conditions have to be optimized to ease the dispersion.

A co-rotating, intermeshing twin screw extruder (Haake, MiniLab Rheomex CTW5) was used to prepare the composites and reference materials. The cellulose content was held constant at 5wt% in the composites. The screws were conical and double-flighted with a length of 109.5mm and with a diameter of 14mm at the beginning and 5mm at the end. No atmospheric or vacuum venting zones were accessible on the extruder. Feeding was performed by adding 4g batchwise of the material into the feeder and then pneumatically pressed into the extruder by a cylinder. The screw speed was 100rpm and the barrel temperature 175°C during extrusion. The cellulose, with and without surfactant, was dry-mixed with PLA before compounding and all materials were kept in a desiccator until compounding. Materials were run three times through the extruder, with a pelletizing step between the first and second run, in order to improve the dispersion of surfactant and cellulose whiskers.

The extruded materials were compression moulded to 0.25mm thick plates at 180°C and 45.5MPa. The compositions of the extruded materials, along with the solution casted, are seen in Table 1.

Table 1. *Formulations and material abbreviation of extruded and solution casted materials.*

Process method	PLA (wt%)	Cellulose (wt%)	Surfactant (wt%)
extrusion	100	-	-
extrusion	95	5	-
extrusion	75	5	20
solution casting	80	-	20
solution casting	75	5	20

2.2.4 Nanocomposites prepared by solution casting

Solution casting is the most common lab scale processing method for the preparation of cellulose nanocomposites. Here, the nanoreinforcements are uniformly dispersed in a solvent in which the polymer, or prepolymer, is soluble. The solvent is then evaporated (or the mixture precipitated) and the polymer adsorbs onto the particles [10]. This technique has been widely used for polymers soluble in water [11]. Combining a nanoreinforcement and matrix with differences in hydrophilicity/hydrophobicity increases the demands on using a suitable solvent and/or compatibilizer agent.

In this study the freeze-dried whiskers were redispersed in chloroform by ultrasonic treatment at 2×15min. The concentration of cellulose whiskers was 1wt% in these suspensions. PLA was dissolved in chloroform, preparing a 10wt% solution of PLA, at 60°C for 6h with mechanical stirring. The prepared cellulose whisker suspension with surfactant was added to the PLA solution, and the composites were cast in a Petri dish. The chloroform was allowed to evaporate at ambient conditions and a film with 5wt% cellulose whiskers of approximately 0.3mm in thickness was obtained. The compositions of the solution casted materials, along with the extruded, are seen in Table 1.

2.3 Characterization methods.

Thermogravimetric analysis (TGA) of freeze-dried suspensions of cellulose whiskers was performed using a TGA Q500 (TA Instruments). Prior freeze-drying, the pH of the suspensions was regulated by addition of 0.25mol/L NaOH. Prior analysis, the samples were kept at 105°C during 10min in order to remove sorbed water. The temperature was then raised with 40°C/min to 180°C and the samples were heated in 37min under an atmospheric air flow of 90mL/min.

Fractured surfaces of the materials were studied using a field emission scanning electron microscope (FESEM), Hitachi 4300S, at 5kV acceleration voltage. Fractured surfaces were generated after cooling in liquid nitrogen and these surfaces were sputter-coated with platinum before examination.

Transmission electron microscope (TEM) observations were performed using a Philips CM 30 operated at 150kV. The whiskers from the suspension was prepared for TEM analysis by placing a droplet of the suspension on a copper grid covered by a thin carbon film and allowed to dry at 80°C overnight. The composites were cut and polished to rectangular sheets, embedded in epoxy and allowed to cure overnight. They were then trimmed in a Reichert-Jung ultramicrotome with freshly cleaved glass knives to obtain a rectangular block surface. Thin foils being approx. 50nm in thickness were cut using a diamond knife and gathered into a copper grid. All samples were stained with a 0.2wt% uranyl acetate solution for 2 minutes.

Atomic force microscopy (AFM) observation was performed using a NanoScope IIIa, Multimode™ SPM from Veeco. All scans were performed in air with commercial Si Nanoprobes™ SPM Tips. Height- and phase images were obtained simultaneously in tapping mode at the fundamental resonance frequency of the cantilever with a scan rate of 0.5 line/s using j-type scanner. The free oscillating amplitude was 3.0V, while the set point amplitude was chosen individually for each sample.

The viscoelastic behaviour of the PLA matrix as well as the nanocomposite films were studied using a DMTA V (Rheometrics Scientific) in tensile mode. The measurements were carried out at a constant frequency of 1Hz and a temperature range of 15-100°C.

3. Results and Discussion

3.1 Thermal stability of cellulose whiskers.

Sulfuric acid treatment of the MCC rendered the cellulose more thermally unstable but neutralizing the suspension by NaOH improved the thermal stability. The suspension with pH 7 before freeze-drying gave the most thermally stable whiskers (1.0% weight loss). The suspensions with lower pH showed decreased thermal stability for the whiskers and the weight loss was greatest for the unmodified whiskers, which had the lowest pH (2.9% weight loss at pH 4 and 9.0% weight loss at pH 2.5).

3.2 Microscopic characterization.

Figure 4 shows FESEM images of fractured surfaces of extruded composites (a) without surfactant and (b) with surfactant. There were large differences of the cellulose structure in these materials. In the composite without surfactant, the cellulose was agglomerated with poor interfacial interaction with the PLA matrix and the agglomerates had similar structure compared to agglomerates created during freeze-drying (compare with Figure 3).

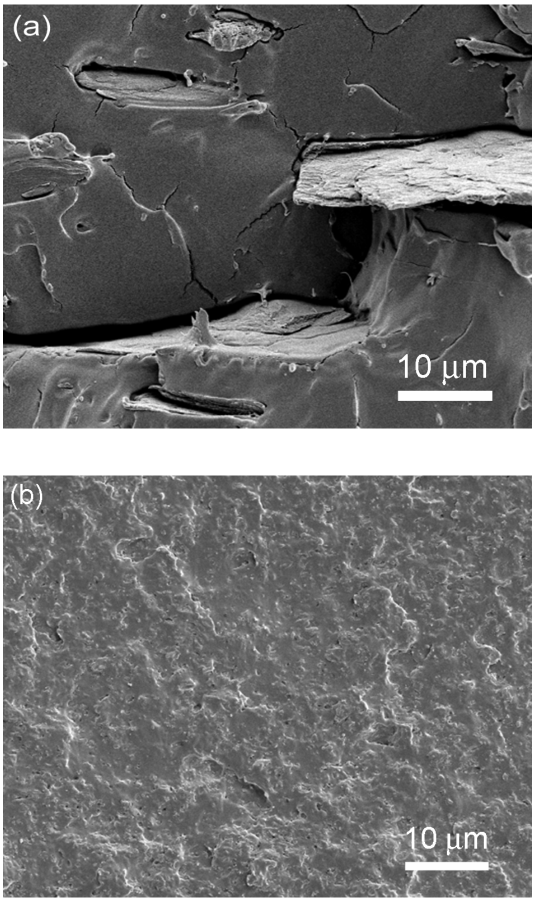

Figure 4. *FESEM images of extruded composite a) without surfactant and b) with surfactant. A remarkably improvement of the dispersion of the cellulose whiskers is seen when using the anionic surfactant.*

In the composite with surfactant, the dispersion of whiskers was dramatically improved. Figure 5 shows a TEM image of the extruded composite with surfactant. The whiskers are seen as needle like particles in the matrix. The dark color originates principally from the uranyl acetate staining medium. Figure 6 shows a topographic AFM image of the solution casted composite with surfactant and it is seen from the image that the whiskers were well dispersed in the matrix [12].

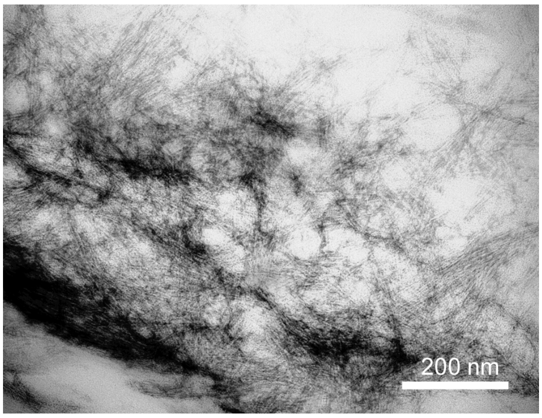

Figure 5. *The structure of extruded nanocomposite with surfactant.*

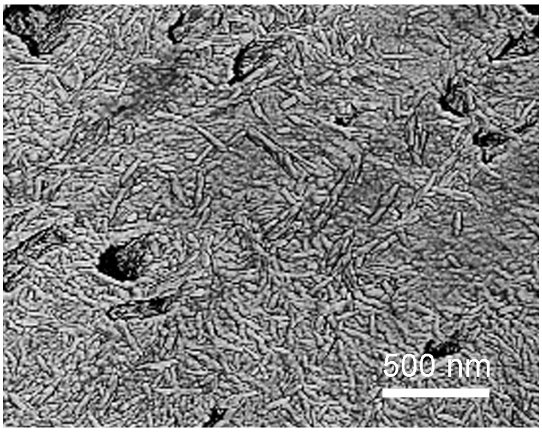

Figure 6. *The structure of solution casted nanocomposite with surfactant [12].*

3.3 Dynamic mechanic thermal analysis.

The DMTA curves of the solution casted materials are shown in Figure 7. It can be seen that the storage modulus was increased and the thermal stability was improved when whiskers were incorporated in the PLA/surfactant (PLA-S) matrix. The tan δ peak temperature for PLA with surfactant was increased from 59°C to 82°C when whiskers were added to the PLA-S matrix.

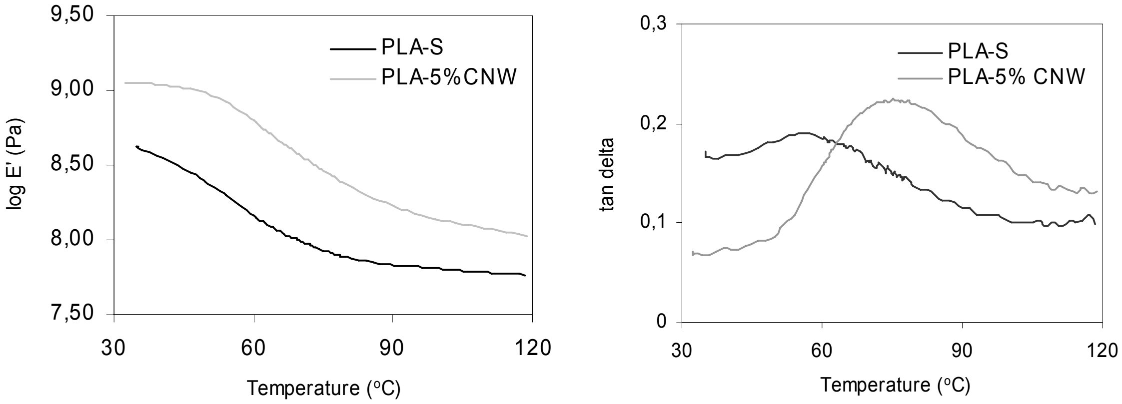

Figure 7. *DMTA curves for PLA-S and PLA-S/cellulose whiskers nanocomposite.*

The DMTA curves of the extruded materials are shown in Figure 8. If compared to solution casted materials in (Figure 7) it was not possible to test the PLA with 20% surfactant because this material was very brittle. The results show clearly that the surfactant had a negative effect on the storage modulus for extruded composites while addition of cellulose whiskers did not affect the storage modulus compared to pure PLA. Both cellulose whiskers and surfactant seems to decrease the tan δ peak temperature and effect was largest for the composite with the surfactant. The tan δ peak temperature was decreased from 66 °C for pure PLA to 48 °C for composite with surfactant. This decrease is believed to occur because of degradation of PLA caused by the surfactant at the elevated temperatures.

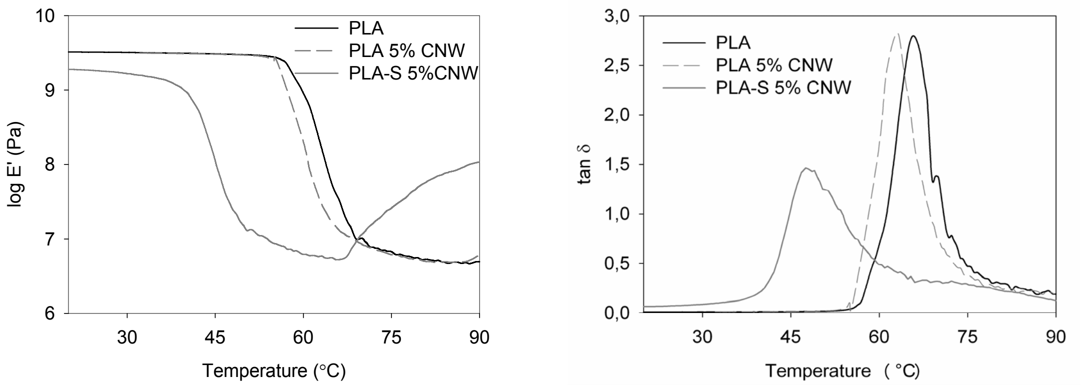

Figure 8. *DMTA curves for the extruded materials.*

4. Conclusions

Cellulose whiskers were prepared by sulfuric acid hydrolysis and were approximately 200 – 400 nm in length and less than 10 nm in width. The cellulose whiskers were made more thermally stable by neutralizing the whisker suspension by addition of NaOH. Freeze-drying the suspension with surfactant hindered the cellulose to agglomerate and form strong hydrogen bonds as the water sublimated during the freeze-drying process. The anionic surfactant was shown to act very effective as dispersant for the cellulose whiskers in the PLA. The composites prepared by solution casting had nanostructure and showed improved properties compared to the polymer matrix. The study showed that when high temperature process was used the surfactant improved the dispersion of cellulose whiskers in the PLA matrix but had a negative effect on the PLA matrix.

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Paper IV

Dispersion and characteristics of surfactant modified cellulose whiskers nanocomposites

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Abstract

Biodegradable nanocomposites based on 5 wt% cellulose nanowhiskers (CNW) and polylactic acid (PLA) were prepared using an extrusion process. An anionic surfactant (5, 10, and 20 wt%) was used to improve the dispersion of the CNW in the PLA matrix. The results showed that increased surfactant content resulted in improved dispersion but at the same time degraded the PLA matrix. The results from mechanical testing showed a maximum modulus for the composite with 5 wt% surfactant and as the surfactant content increased, the CNW dispersion improved and the tensile strength and elongation at break was improved compared to its unreinforced counterpart.

Introduction

The interest in using biopolymer as an alternative to petroleum based polymers has increased in recent years due to the limited resources of crude oil, environmental awareness of consumers and global warming. In order to be competitive compared to petroleum based polymers biopolymers need to have acceptable price, equally good performance and enable the same production methods as petroleum based polymers. The present low-level production and high cost for most of these biopolymers restrict their widespread applications [1, 2]. A biopolymer of special interest is polylactic acid (PLA), which is produced from renewable resources and readily biodegradable, and can compete with petroleum based polymers on a cost-performance basis [2, 3]. PLA is a linear thermoplastic polyester produced from fermentation products from sugar feedstock, corn etc [3, 4]. PLA has also excellent properties and comparable to many petroleum based plastics [4, 5]. However, some properties like melt strength, impact strength, thermal stability, gas barrier, etc do not meet the demands for some end-use applications and has to be improved [2]. One way to improve the properties of biopolymers and greatly enhance their commercial potential is to incorporate nanosized reinforcement into the polymer [6]. Biopolymer based nanocomposites have showed improvements in modulus [7-13], strength [11-14], heat distortion temperature [11-13], thermal stability [14], and barrier properties [11-14] compared to their pristine polymers. Several studies have been done with organically modified layered silicates as reinforcement in PLA and these materials has been produced by solution casting [15, 16], melt blending [17-20] or extrusion [10-13, 21, 22].

Using CNW as reinforcement in nanocomposites has numerous advantages. Its reinforcing capacity is expected to be remarkable. Theoretical evaluation of Young's modulus for native crystalline cellulose along the chain axis gave a value of 167.5 GPa [23] and experimental measurements of crystalline cellulose from a tunicate sea animal gave an elastic modulus of 143 GPa [24]. Theoretical calculation of the tensile modulus for CNW reinforced PLA showed great potential for this material combination [25]. Furthermore, cellulose is the most abundant renewable polymer on the earth and it is found in plant cell walls, but it can also be synthesized by some bacteria [26] and animals [27].

Preparation and incorporation of cellulose nanowhiskers from various sources, such as wheat straw and tunicin, in different matrixes has been reported in earlier studies [28-32]. However, the drawbacks of using cellulose whiskers are that the whiskers have to be isolated [33] and that the dispersion of the whiskers into the matrix has shown to be problematic, especially in extrusion processes [34]. Earlier work has shown that preparation of nanocomposites with solution casting resulted in well dispersed whiskers in PLA when using an acid phosphate ester of ethoxylated nonylphenol as surfactant [36, 37]. The same surfactant has also been utilized as a stabilizing agent to obtain stable dispersions of CNW in nonpolar solvents [38]. Another risk when using CNW prepared by sulfuric acid hydrolysis is that the cellulose will be more thermal instable due to acidic sulphate groups onto the whisker surfaces [35]. This might be a problem when using extrusion as a production method due to the elevated temperatures associated with this process.

The goal of this study was to prepare PLA/CNW nanocomposites by extrusion and study the influence of increased surfactant content on the dispersion of CNW in the matrix and the mechanical properties of the composites. In this study the whisker suspension, together with surfactant, is freeze-dried and dry-mixed with PLA before extrusion.

Experiment

Materials

Polylactic acid (PLA), NatureWorks™ 4032D (Cargill Dow LLC, Minnetonka, MN, USA) was used as polymer matrix. PLA have a glass transition temperature of 68 °C, melt temperature at 160 °C, and density of 1.25 g/cm^3. Cellulose nanowhiskers (CNW) were used as reinforcement and prepared as described elsewhere [39]. Microcrystalline cellulose (MCC) from Norway spruce (Picea abies) with a particle size between 10 to 15 μm (Borregaard ChemCell, Sarpsborg, Norway), was used as starting material for the preparation of the cellulose nanowhiskers. The surfactant used was Beycostat A B09 (CECCA S.A., France), an acid phosphate ester of ethoxylated nonylphenol, see Figure 1.

Preparation of materials

Four different sets of CNW were prepared, one unmodified and three modified with surfactant. For the CNW without surfactant the pH was raised to approximately 7.5 in the suspension prior freeze-drying by addition of 0.25 mol/L NaOH. The addition of NaOH to the suspensions was made in order to enhance the thermal stability of the whiskers. Figure 2 shows thermogravimetric curves at 180 °C (TGA Q500, TA Instruments) for freeze-dried CNW from suspensions without (pH 2.5) and with (pH 7) added NaOH and a clear improvement of the thermal stability is seen for the neutralized whiskers. The CNW modified with surfactant were prepared by adding Beycostat A B09 to the CNW suspension with the ratio 1/1, 2/1, and 4/1 (w/w) Beycostat A B09 to cellulose. These suspensions were then vigorously mixed and the pH was raised to approximately 7.5 by addition of 0.25 mol/L NaOH prior freeze-drying.

Extruded materials were prepared using a Haake (MiniLab Rheomex CTW5, Karlsruhe, Germany), co-rotating, intermeshing twin screw extruder. The screws were double-flighted, 109.5 mm in length and conical with a screw diameter of 14 mm at the beginning and 5 mm at the end. A schematic figure of the extruder is shown in Figure 3. No atmospheric or vacuum venting zones were accessible on the extruder. Processing temperature was 175 °C and the screw speed 100 rpm. Feeding was performed batchwise by adding 4 g of the material into a feeder whereupon it was pneumatically pressed into the extruder by a cylinder. The CNW, with and without surfactant, was dry-mixed with PLA before compounding and all materials were kept in a desiccator until compounding. Materials were extruded three times with a pelletizing step between the first and second run. This was done in order to improve the dispersion of surfactant and cellulose whiskers in the matrix. The cellulose nanowhisker content was constant at 5 wt% in all composites and the material formulations are shown in Table 1.

The extruded materials were compression molded to plates of 0.25 mm thickness using a laboratory press (Fontijne Grotnes B.V., Vlaardingen, the Netherlands). Prior pressing, the extruded strands were dried 1 day at 50 °C in a vacuum oven. Short strands of the extruded material were then placed in a mold to ensure constant thickness and preheated in the press for 2 minutes at 180 °C. After preheating, the materials were pressed for 30 seconds at 180°C and 15 MPa. The materials were then immediately cooled by pressing at 3 MPa and 20 °C.

Characterization methods

Gel permeation chromatography (GPC) analyses of extruded materials were performed at room temperature with a Knauer HPLC pump (type 364), five PL-gel 5µm columns, and a Knauer differential refractometer (type 198) detector. Tetrahydrofuran (THF) was used as eluent with a flow rate of 1 mL/min. Prior analysis samples were dissolved in THF and filtered through a Millipore filter (Millex FH) with a pore size of 0.45 µm. The molecular weight of the polymers were calculated based on the calibration with monodisperse polystyrene standards.

Tensile testing was performed using a miniature material tester (MiniMat2000, Rheometric Scientific) with a load cell of 1000 N. Test specimens were cut into stripes measuring 100×6×0.25 mm from the compression molded samples. Initial grip distance was 60 mm and tensile modulus, tensile strength, and elongation were determined at a crosshead speed of 3 mm/min. The measurements were done without using an extensometer and the results should rather be seen as comparable to each other than true values.

Dynamic mechanical thermal analysis (DMTA) was performed using a Rheometric Scientific DMTA V in tensile mode. The samples were prepared by cutting stripes measuring 30×5×0.25 mm from the compression molded samples. The measurements was carried out at a constant frequency of 1 Hz, a strain amplitude of 0.05%, a temperature range of 15 – 90 °C, a heating rate of 3 °C/min and gap distance of 20 mm.

Fractured surfaces of the materials were studied using a field emission scanning electron microscope (FE-SEM), Hitachi 4300S, at 5 kV acceleration voltage. Fractured surfaces were generated after cooling in liquid nitrogen and these surfaces were sputter-coated with platinum before examination.

Transmission electron microscope (TEM) observations were performed using a Philips CM 30 operated at 150kV. The materials for analysis were cut and polished to rectangular sheets, embedded in epoxy and allowed to cure overnight. They were then trimmed in a Reichert-Jung ultramicrotome with freshly cleaved glass knives to obtain a rectangular block surface, 50 x 500 μm^2 in cross-section. Thin foils, approximately 50 nm in thickness, were cut by a diamond knife and gathered onto cupper grids. The materials were then stained by allowing the grids to float in a 2 wt% solution of uranyl acetate for 2 min.

Results and discussion

Processing of materials

Figure 4 shows the maximum torque during the last extrusion cycle of different material combinations. The torque shows the resistance the materials exhibit to flow due to internal friction and therefore the maximum torque values are expected to give indirect information about the dispersion of the nanowhiskers. Addition of unmodified CNW into the PLA did not affect the torque which indicates poor dispersion of the whiskers in the PLA. The addition of surfactant into the PLA decreased the torque significantly which might be due to degradation of PLA but also to the surfactant acting as a lubricant for the polymer. In the materials with surfactant, unreinforced and CNW reinforced, the torque was higher for all nanocomposites compared to the corresponding surfactant treated PLA. This indicates improved distribution and dispersion of the nanoreinforcement but it can also be due to less degradation of the matrix in the nanocomposites.

Dispersion

Prior extrusion, the CNW suspension has to be prepared in such a way that it is possible to dry-mix them together with the polymer. This is done by freeze-drying and freeze-drying of cellulose whiskers has shown to be problematic due to their tendency to agglomerate and form strong hydrogen bonds as the water sublimate. Figure 5a shows freeze-dried CNW from a water suspension without surfactant and the whiskers are no longer isolated but have agglomerated into flakes. This freeze-drying step is critical for the production of nanocomposites. Therefore, one possible solution to avoid agglomeration can be to use a surfactant that will cover the CNW and thereby hindering the whiskers to agglomerate and create strong hydrogen bonds as the water sublimate during the freeze-drying [37]. Figure 5b shows freeze-dried CNW from a water suspension with 4/1 (w/w) Beycostat A B09 to cellulose and the CNW flakes appear to be thicker compared to the freeze-dried CNW without surfactant. The surfactant and CNW formed a sticky mixture whereas the CNW without surfactant was fluffy in texture after freeze-drying.

Figure 6 shows FE-SEM images of fractured surfaces of different cellulose reinforced PLA composites. Figure 6a shows the composite without the surfactant, PLA-CNW, and the CNW are agglomerated and can be seen as flakes in the PLA matrix. These CNW flakes are formed during the freeze-drying and the shear force during the extrusion is not enough to disperse them. There is an obvious similarity between these flakes and the flakes in Figure 5. This material is not a nanocomposite but a microcomposite due to the micrometric size of the cellulose. Figure 6b shows that the whisker dispersion is dramatically improved with 5 wt% addition of surfactant and in this composite there are no longer any visible flakes of CNW. Figures 6b, 6c and 6d show that with an increased level of surfactant the surface roughness increases. The roughness is caused by smaller inclusions which most likely consist of cellulose nanowhiskers and surfactant.

TEM images of the nanocomposite with 20 wt% surfactant are shown in Figure 7. As can be seen in the overall view in Figure 7a, the whiskers are not homogeneously distributed in the PLA matrix but are located in indistinct accumulations. In Figure 7b a more detailed view shows well separated nanowhiskers in the accumulation. This means that the surfactant is effectively hindering the aggregation of the whiskers in the freeze-drying step. However, due to reduced miscibility of the surfactant in the PLA matrix and insufficient shear forces during compounding from the bench type extruder used in this study, it was not possible to completely disperse the whiskers.

Mechanical properties

The results from tensile testing are given as values in Table 2 and comprehensively shown in Figure 8. The PLA-S20 was too brittle to handle during testing and was for that reason excluded from the test results.

The composite without modification (PLA-CNW) did not show improvements in tensile modulus compared to PLA. Also, the tensile strength and elongation at break decreased for this composite compared to PLA and these results verify the conclusions that this material is a microcomposite rather than a nanocomposite.

With 5 wt% surfactant modification the dispersion of the whiskers were greatly enhanced and the composite showed a clear improvement in tensile modulus and tensile strength, and a slightly higher elongation at break (PLA-CNW-S5 versus PLA-S5). The strength increased from 35 MPa for PLA-S5 to 52 MPa for the nanocomposite.

Increasing the surfactant content further, to 10 wt%, the tensile modulus for the composite (PLA-CNW-S10) was lowered and equal to the unreinforced reference material (PLA-S10). In addition, this increased amount of surfactant improved the elongation at break for the composite and thus toughened the material. The decrease in strength and elongation at break for PLA-S10, which also was seen for PLA-S5, could be due the reduced miscibility between the surfactant and the polymer and degradation of the PLA matrix by the surfactant. GPC-measurements of the weight average molecular weight (M_w) and polydispersity (M_w/M_n) for PLA, PLA-S10, and PLA-CNW-S10 showed a three-fold decrease in M_w for PLA-S10 compared to PLA (see Table 3). The degradation of PLA-CNW-S10 was less severe which most probably was due to more surfactant localized at the interface of the cellulose thus lessen the amount of surfactant in the matrix available for the hydrolysis of ester bonds in the PLA. It is known that acids and bases catalyze the chain scission of PLA [40].

As mentioned before, the PLA-S20 was too brittle to handle during testing and therefore no test results are available for this material. The PLA-CNW-S20 on the other hand showed a great elongation at break, larger than 100%, but a decrease in tensile modulus and tensile strength.

Dynamic mechanical thermal analysis

Figure 9 shows the storage modulus (E') and tan δ for unreinforced and CNW reinforced materials with different surfactant contents. For all materials at temperatures below the plastic region the polymer was in the glassy state and the modulus slightly decreased with increased temperature but remained approximately constant. Also, an increase of the storage modulus was seen at 20 – 30 °C above the tan δ peak which was a result of a cold crystallization process. This crystallization process is activated and favored by the increased chain mobility in the plastic region and was seen for all materials except for the PLA-S20 which failed due to irreversible chain flow.

As can be seen in Figure 9a-c, the materials with 0, 5, and 10 wt% surfactant, respectively, the CNW reinforced PLA showed almost the same properties as the unreinforced PLA. Minor improvement of the storage modulus in the plastic region prior the cold crystallization region could be observed for PLA-CNW-S5 and PLA-CNW-S10. In Figure 9d the PLA-S20 and PLA-CNW-S20 are shown. As mentioned before, the experimental setup failed to measure the storage modulus for PLA-S20 at temperatures above the tan δ peak due to irreversible chain flow. This behavior was not seen for PLA-CNW-S20 probably because of less degraded polymer matrix but also due to the reinforcing capability of the whiskers.

The influence of surfactant regarding temperature shifts of plastic region and tan δ peak can be seen by comparing the curves in Figure 9a-d. An increased surfactant content shifted the plastic region and the tan δ peak towards lower temperatures. The reason for this could due to, firstly, a facilitated segmental mobility of the polymer chains due to the surfactant thus lowering the temperature for the tan δ peak and cold crystallization. Secondly, a decreased molecular weight of PLA caused by polymer degradation will also lower the temperature for the tan δ peak and cold crystallization [41, 42]. As the PLA chains are cut due to degradation, more polymer ends are available which generate larger free volume than segments in the chain interior and less energy is required to rotate these chain ends [43]. Also, the chain mobility is increased with decreased molecular weight and the ability for the polymer to crystallize in the plastic region is increased [42].

Conclusions

An increased amount of surfactant improves the dispersion of the CNW in the PLA matrix but the surfactant has also a negative effect such as polymer chain degradation of the PLA. Also, the surfactant was not completely miscible in the PLA matrix. Control during the freeze-drying step is also crucial in order to prevent agglomeration of the whiskers and a modification of the CNW suspension, such as addition of surfactant, prior freeze-drying is therefore needed. The thermal stability of the cellulose whiskers can be improved by rendering the whisker suspension neutral by adding NaOH before freeze-drying. The mechanical testing of the produced materials showed that the composite with 5 wt% surfactant had highest modulus and as the surfactant content increased, the CNW dispersion improved and the tensile strength and elongation at break was improved compared to its unreinforced counterpart. The dynamic mechanical analysis showed that the softening temperature was shifted towards lower temperatures with an increased surfactant content. Reinforcement of CNW gave a slight improvement of the storage modulus in the plastic area prior the cold crystallization region. In future studies it would be interesting to use a cationic surfactant which do not degrade the PLA and create ionic bindings to the negatively charged surface of the cellulose.

Acknowledgements

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Table 1. Formulations of materials used in this study.

Material abbreviations	*PLA (wt%)*	*Cellulose (wt%)*	*Surfactant (wt%)*
PLA	100	-	-
PLA-CNW	95	5	-
PLA-S5	95	-	5
PLA-CNW-S5	90	5	5
PLA-S10	90	-	10
PLA-CNW-S10	85	5	10
PLA-S20	80	-	20
PLA-CNW-S20	75	5	20

Table 2. Results from tensile testing.

Material	*Tensile modulus (GPa)*	*Tensile strength (MPa)*	*Elongation at break (%)*
PLA	2.65 ± 0.08	62.8 ± 1.0	19.5 ± 9.7
PLA-CNW	2.69 ± 0.20	55.5 ± 2.9	9.7 ± 0.9
PLA-S5	2.60 ± 0.12	35.1 ± 3.6	1.8 ± 0.3
PLA-CNW-S5	3.10 ± 0.15	52.4 ± 0.4	3.1 ± 0.2
PLA-S10	2.34 ± 0.16	25.5 ± 3.8	1.4 ± 0.3
PLA-CNW-S10	2.36 ± 0.13	45.7 ± 0.9	20.5 ± 7.1
PLA-S20	-	-	-
PLA-CNW-S20	1.15 ± 0.03	23.5 ± 0.5	>100

Table 3. Gel permeation chromatography (GPC) measurements.

Material	M_w	M_w/M_n
PLA	162 200	2.0
PLA-S10	54 900	1.8
PLA-CNW-S10	136 200	1.9

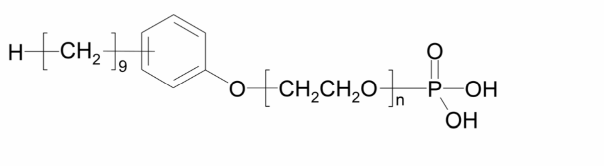

Figure 1. Chemical structure of the acid phosphate ester of ethoxylated nonylphenol used as surfactant in this study.

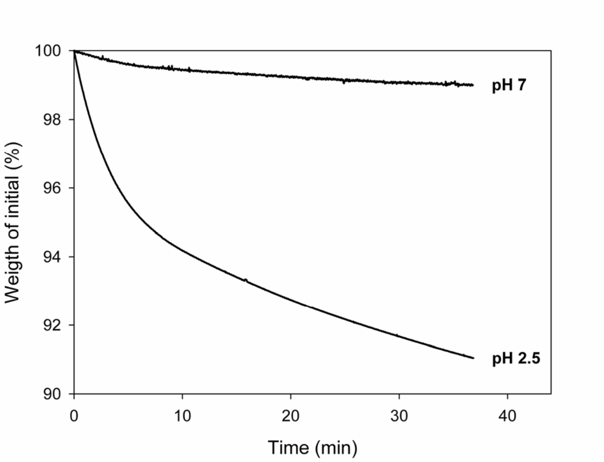

Figure 2. Thermogravimetric analysis at 180 °C of freeze-dried CNW from suspensions without (pH 2.5) and with (pH 7) added NaOH.

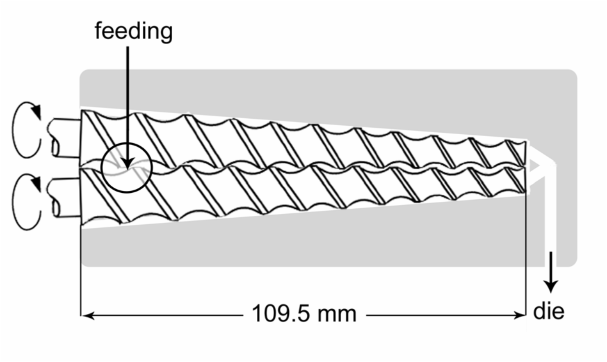

Figure 3. Schematic picture of the used extruder.

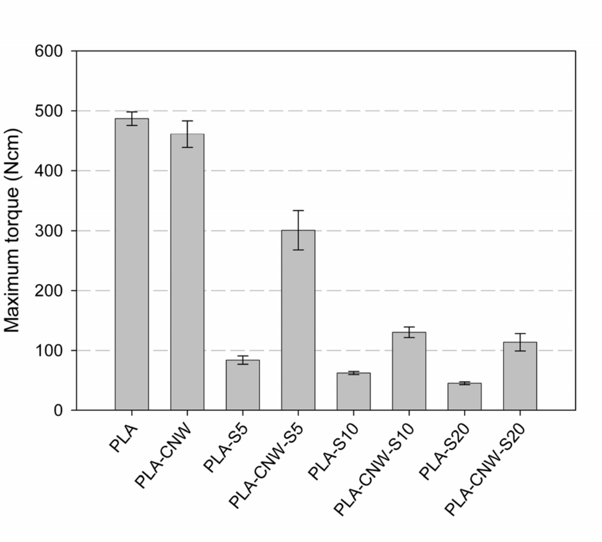

Figure 4. Maximum torques calculated from maximum values during the batchwise feeding cycles from the third extrusion.

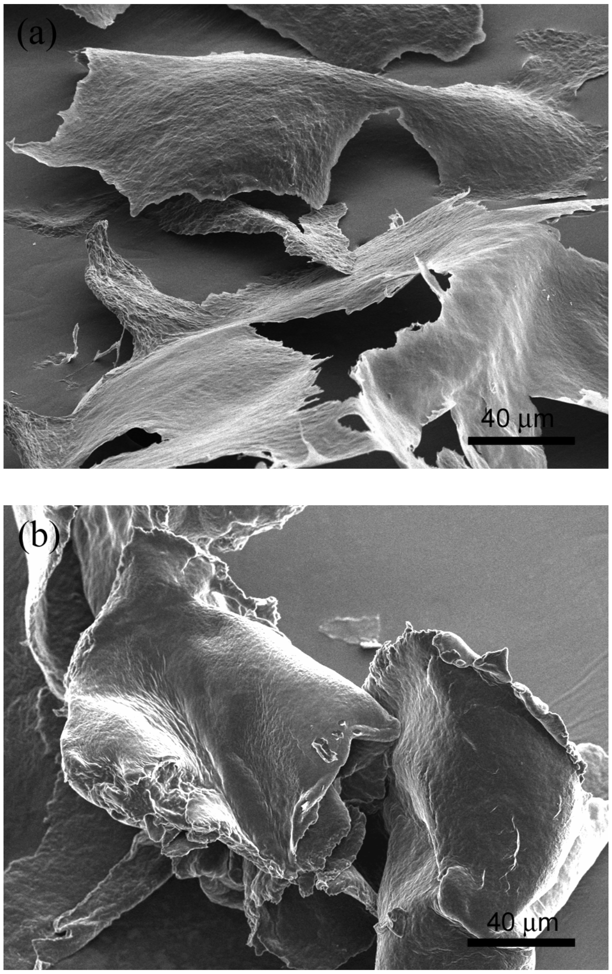

Figure 5. Structure of freeze-dried cellulose nanowhiskers a) without surfactant and b) with surfactant.

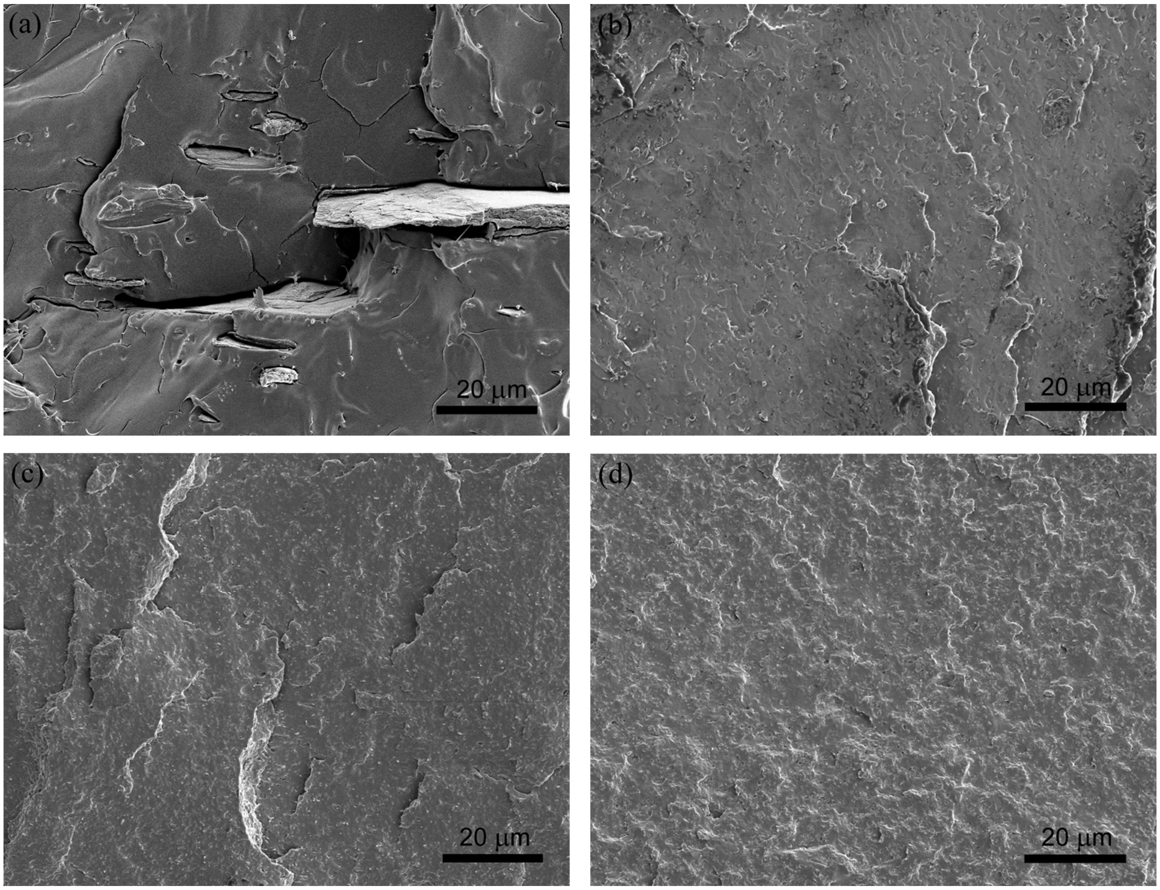

Figure 6. Fractured surfaces of a) PLA-CNW, b) PLA-CNW-S5, c) PLA-CNW-S10, and d) PLA-CNW-S20 showing an improved dispersion of the whiskers in the PLA matrix as the surfactant content increases.

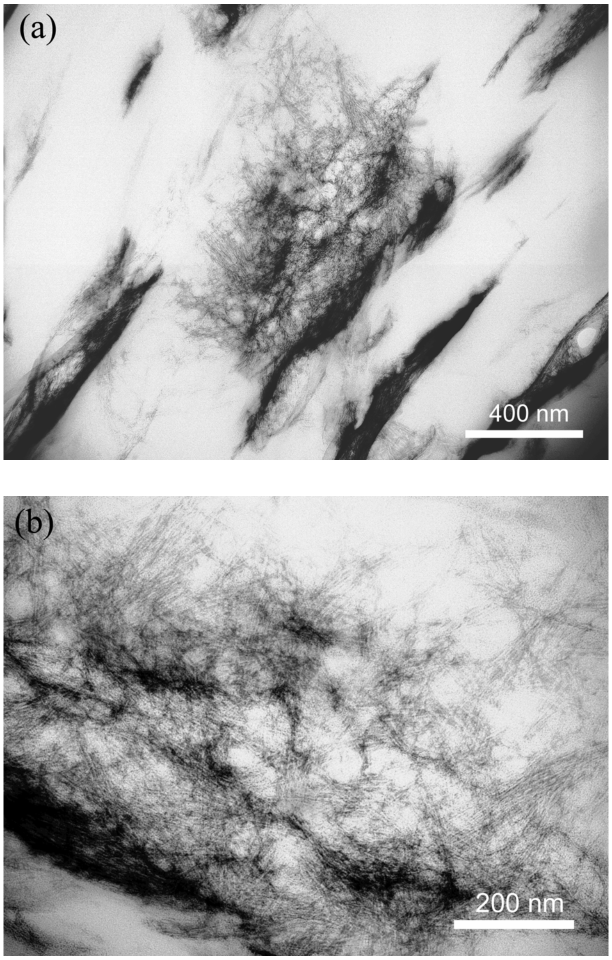

Figure 7. TEM image of PLA-CNW-S20. In a) an overall view of the structure is given and in b) separated whiskers are seen.

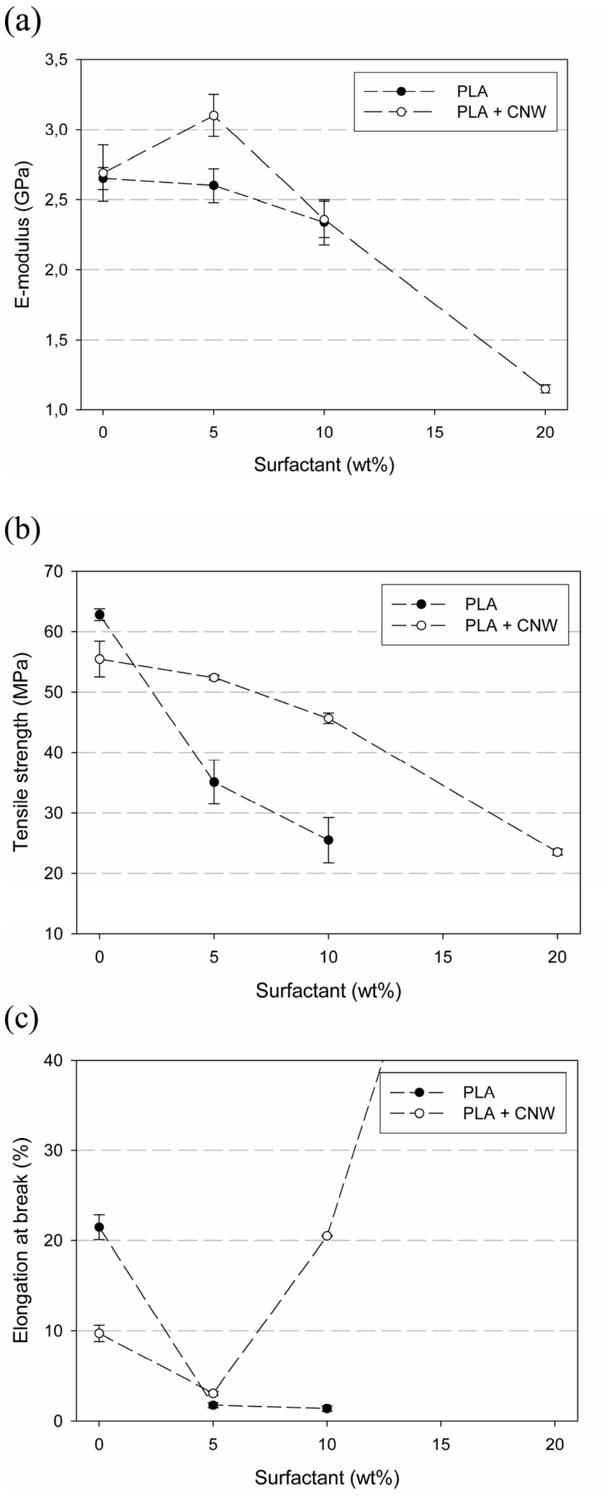

Figure 8. Mechanical properties of different material combinations showing the effect of increased surfactant content for a) elastic modulus, b) tensile strength, and c) elongation at break.

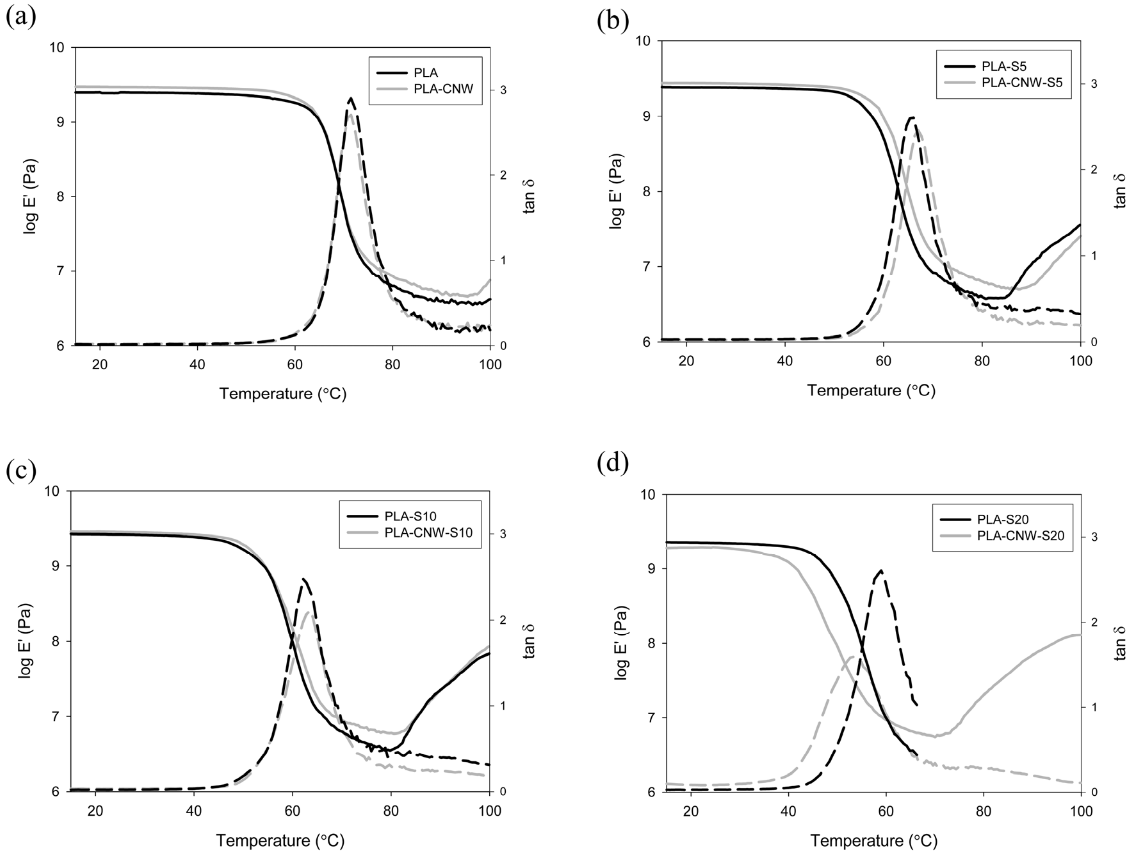

Figure 9. Storage modulus (continuous line) and tan δ (dashed line) as a function of temperature for materials with a) no surfactant, b) 5 wt% surfactant, c) 10 wt% surfactant, and d) 20 wt% surfactant.

Paper V

Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol

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Abstract

The aim of this study was to produce biodegradable polylactic acid/cellulose whisker nanocomposites by compounding extrusion and investigate the possibility to use polyvinyl alcohol to improve the dispersion of whiskers in the matrix. Two feeding methods of polyvinyl alcohol and cellulose nanowhiskers were used and evaluated, dry-mixing with polylactic acid prior extrusion or pumping as suspension directly into the extruder. Various microscopic techniques, tensile testing, and dynamic mechanical thermal analysis were used to study the structure and properties of the nanocomposites. Due to immiscibility of the polymers, phase separation occurred with a continuous polylactic acid phase and a discontinuous polyvinyl alcohol phase. The whiskers were primarily located in the polyvinyl alcohol phase and only a negligible amount was located in the polylactic acid phase. This inadequate dispersion of whiskers in the polylactic acid phase was probably the reason why no improvements in thermal properties were seen for the nanocomposites. The relative small improvements in tensile modulus, tensile strength, and elongation to break for the nanocomposites also indicated that it was principally the polyvinyl alcohol phase that was reinforced with whiskers but not the polylactic acid phase.

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Keywords: A. Nano-structures; B. Mechanical properties; B. Thermomechanical; E. Extrusion; Biopolymers

Introduction

Driven by a growing consciousness for the environment and new standards, there is a great interest to develop sustainable and environmentally friendly systems with enhanced performances. Several biodegradable biopolymers need to be modified to be competitive to petroleum based polymers in question of performance and cost. One way to improve the properties of biopolymers and greatly enhance their commercial potential is to incorporate nanosized reinforcement into the polymer [1]. There has been a growing interest for cellulose nanowhisker (CNW) based nanocomposites in the last decade and improvements in dynamic mechanical thermal properties, tensile strength, toughness, and elongation to break have been made possible by using CNW as reinforcement [2-5]. Its reinforcing capacity is expected to be remarkable and estimations of the elastic modulus of crystalline cellulose along its chain axis have been reported to be 143 GPa [6] and 167.5 GPa [7]. Furthermore, cellulose is the most abundant renewable polymer on earth and it is found in plant cell walls, but it can also be synthesized by some bacteria [8] and animals [9].

The use of cellulose whiskers in nanocomposites has mainly been limited to hydrophilic mediums due to the hydrophilic surface of the whiskers. Difficulties arise when the hydrophilic solvent or polymer is replaced with a hydrophobic one. To solve this problem, studies have been made to modify the whiskers and make them more susceptible to hydrophobic matrixes such as silylation [3,10], polyethylene glycol (PEG) grafting [11], acetylation [12,13], and use of surfactants [14-16]. The required modification together with the tedious procedure to isolate the whiskers from natural resources has often limited the production volume to low scale or laboratory scale. In order to make biodegradable cellulose based nanocomposites competitive on a cost basis research about production techniques that could be used industrially is important.

The biopolymer used in this study is polylactic acid (PLA) which is a readily biodegradable linear thermoplastic polyester with excellent properties and produced from fermentation products from sugar feedstocks, corn etc [17-19]. Today, there is a large interest to use PLA in packaging, medical and automotive applications where also properties other than stiffness and strength are important. Incorporation of cellulose whiskers is thought to improve the toughness, thermal stability and barrier properties of PLA. However, due to the strong tendency of cellulose whiskers to establish strong hydrogen bonds between the whiskers as the dispersing medium is removed, modification is needed to hinder this re-aggregation [20]. A possible approach to prevent re-aggregation of whiskers is to solve a water soluble polymer into the whisker suspension. This water soluble polymer is expected to encapsulate the single whiskers and prevent re-aggregation and formation of strong hydrogen bonds as the water is sublimated or evaporated, for example during freeze-drying or direct pumping into a polymer melt during extrusion. Polyvinyl alcohol (PVOH) is a large volume produced and water-soluble polymer with high tensile strength [21]. The hydroxyl groups on partial hydrolyzed PVOH are expected to interact with the hydrophilic surfaces of the cellulose and the residual vinyl acetate groups with the hydrophobic PLA. Ke et *al.* have studied the possibility to use PVOH together with a starch and PLA blend (50:50, w/w) to enhance the compatibility between the starch and PLA [22]. They found that PVOH formed a continuous phase with the starch and the mechanical properties increased when a partially hydrolyzed PVOH grade of low molecular weight was used.

The objective of this study was to improve the mechanical and thermal properties of PLA by using CNW as reinforcement together with PVOH. The nanocomposites were produced by extrusion and two different feeding methods were used, dry-feeding of freeze-dried PVOH/CNW pellets together with PLA or liquid feeding of PVOH/CNW suspension directly into molten PLA during extrusion.

Experiment

Materials

Matrix: Polylactic acid (PLA) with a D content less than 2%, NatureWorks™ 4032D, was supplied by Cargill Dow LLC, Minnetonka, MN, USA. The glass transition temperature (T_g) is 58 °C, the melting point (T_m) is 160 °C, and the molecular weight (M_w) is between 220 000 – 240 000 g/mol.

Modifier: A partially hydrolyzed (87.1 ± 1.0 mol-%) polyvinyl alcohol (PVOH), Mowiol 4-88, was supplied by Kuraray Specialities Europe GmbH, Frankfurt am Main, Germany. The glass transition temperature (T_g) is 68 °C and the molecular weight (M_w) is 31 000 g/mol (corresponds to a viscosity of 4 ± 0.5 mPas for a 4 wt% aqueous solution at 20 °C).

Reinforcement: Microcrystalline cellulose from Norway spruce (Picea abies) with a particle size between 10 to 15 µm (Borregaard ChemCell, Sarpsborg, Norway), was used as starting material for the preparation of the cellulose whiskers. The cellulose whiskers were prepared as described elsewhere [23].

Processing of cellulose nanocomposites

Preparation of materials prior to extrusion

The CNW concentration was increased to 21.0 wt% (forming a gel) by dialysis against a water solution of polyethylene glycol 35000 (Merck Schuchardt OHG, Hohenbrunn, Germany). A PVOH solution was made for mixing with the CNW gel prior extrusion. A part of this PVOH solution was also kept unmixed to produce reference materials. The PVOH solution was produced by solving granules of PVOH in deionized water to a concentration of 27.0 wt% by stirring and heating at 80 °C. A mixture with the ratio 6/1 (w/w) PVOH to CNW was prepared by adding the PVOH solution to the CNW gel. The pH of this PVOH/CNW suspension was raised to neutrality by addition of 0.25 mol/L NaOH. Half the volume of this mixture was kept as suspension for liquid feeding, i.e. pumping of the suspension into the polymer melt during extrusion, and the other half was freeze dried (Heto LyoPro 6000, Jouan Nordic A/S, Allerød, Denmark). The freeze-dried materials were then pelletized and dry-mixed with dried PLA (4 h at 80 °C) prior extrusion.

Extrusion

The materials were compounded using a co-rotating and fully intermeshing twin screw extruder, Coperion Werner and Pfleiderer ZSK 25 WLE (Stuttgart, Germany) with a gravimetric feeding system for dry materials (K-Tron AG, Niederlenz, Schwitzerland). The PVOH solution and the PVOH/CNW suspension was fed by a peristaltic pump (PD 5001, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) into heating zone 3 and prior pumping the solution/suspension was heated to 65 °C. The pumping rate was 4.44 kg/h for the PVOH solution and 5.40 kg/h for the PVOH/CNW suspension. The screw configuration used in the extruder is seen in Figure 1 and is designed to give relative low shear forces during compounding to minimize the risk of degradation of the materials. The kneading elements early in the screw, the melting zone, have the function to melt the polymer. This melting zone was followed by a feeding zone of two-flighted conveying elements with the function to vaporize the water during liquid feeding. The melt was then compounded in the dispersive mixing zone by kneading elements followed by a distributive mixing zone. The distributive mixing zone was composed of ZME and SME elements as labeled by Coperion Werner & Pfleiderer. Figure 2 shows a schematic picture of the compounding process. The extrusion was carried out in a temperature range of 170 – 200 °C, the screw speed was 150 rpm, the melt pressure at the die was 5 – 8 bar for the materials, and the total output was 4 kg/h. Atmospheric venting at zone 5 and 6 was used to remove the water as steam when the suspension was pumped into the extruder. Vacuum venting at heating zone 9 was used to remove entrapped air and remaining moisture in the compound. Table 1 summarizes the processing parameters and Table 2 the formulations of the extruded materials. The PVOH content was 30 wt% for all the materials and the CNW content was 5 wt% in the nanocomposites.

The extruded materials were compression molded prior analysis and molds were used to ensure a constant thickness of 0.25 mm and 0.75 mm. The materials were preheated in the press for 2 minutes at 180 °C thereafter pressed for 30 seconds at 180 °C and 15 MPa. The materials were then immediately cooled by pressing at 20 °C and 3 MPa. Test specimens were prepared by cutting 6 mm wide stripes from the compression molded samples. The samples were carefully packed and stored in freezer at -32 °C prior testing.

Characterization methods

Microscopy

Microtomed and fractured samples were studied using a field emission scanning electron microscope (FE-SEM), Zeiss SUPRA 55 VP (Carl Zeiss NTS GmbH, Oberkochen, Germany), at 0.8 kV acceleration voltage. The microtomed surfaces were prepared by cutting with a diamond knife in a Reichert-Jung ultramicrotome and the fractured samples were fractured in liquid nitrogen. The FE-SEM study was performed without surface coating of the samples. Transmission electron microscope (TEM) observations were performed using a Philips CM 30 (Royal Philips Electronics N.V., The Netherlands) operated at 150kV.

Tensile testing

Tensile testing of test specimens measuring 100×6×0.25 mm was performed using a miniature material tester (MiniMat2000, Rheometric Scientific Ltd, Leatherhead, UK) with a load cell of 200 N. Initial grip distance was 60 mm and tensile modulus, tensile strength, and elongation was determined at a crosshead speed of 3 mm/min. At least five test results were used to calculate an average value for each material. Deviating results, due to for example flaws in specimen or failure outside the gage length, were not used for the calculation of average values. The measurements were done without using an extensometer and the results should be considered for comparison and not as absolute values.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) of test specimens measuring 30×6×0.75 mm was performed using a Rheometric Scientific DMTA V (Rheometric Scientific Ltd, Leatherhead,UK) in tensile mode. The measurements was carried out at a constant frequency of 1 Hz, a strain amplitude of 0.01%, a temperature range of 15 – 100 °C, a heating rate of 3 °C/min and gap distance of 20 mm.

Results and discussion

Extrusion

Production of cellulose nanocomposites by extrusion renders many challenges. The tendency for cellulose whiskers to re-aggregate and establish strong hydrogen bonds between the whiskers as the dispersing medium is removed has to be taken under consideration. By just pumping a CNW suspension without any sort of modification into a polymer melt during extrusion will re-aggregate the whiskers once the water is removed as steam [20]. The same is valid for the freeze-drying process, as water is sublimated from a frozen unmodified suspension whiskers will re-aggregate [18]. The modifier used in this study is PVOH which is expected to encapsulate the single whiskers and hinder re-aggregation as the water is removed. During extrusion the PVOH is believed to melt and blend with PLA and fully disperse the whiskers in a PVOH/PLA matrix. A previous study has also shown that PVOH can act as a compatibilizer between PLA and starch and the compatibility was improved with decreased molecular weight of PVOH due to better flowability [22]. Another challenge lies in the liquid feeding procedure. Large amount of water has to be removed as steam during extrusion and the PVOH solution may foam during contact with the hot polymer melt as the water boils and evaporate. These problems were solved by using several separate venting systems to remove the steam and by keeping the total throughput low. There are not only disadvantages by feeding the whiskers as a suspension. From an economical point of view it could be beneficial with liquid feeding. Supplementary treatment of the suspension before extrusion, such as freeze-drying, will involve additional expenses like investment costs for equipments and prolonged preparation times.

Dispersion

Figure 3 show FE-SEM images of microtomed surfaces and fractured surfaces of the nanocomposites. No aggregates of cellulose were seen in these materials during FE-SEM investigations which strongly verify the possibility of dispersed CNW in the matrix. As seen in the micrographs from the microtomed surfaces, Figure 3a-b, the miscibility between the polymers was poor and phase separation occurred with a continuous PLA phase (bright in the image) and a discontinuous PVOH phase (dark in the image). The PVOH phase was smaller in size and better distributed in the PLA-PVOH/CNW5$_{dry}$ than in the PLA-PVOH/CNW5$_{wet}$. This is also seen for the fractured surfaces, Figure 3c-d. The cavities, much smaller in the PLA-PVOH/CNW5$_{dry}$ than in the PLA-PVOH/CNW5$_{wet,}$ are thought to be imprints of the PVOH phase and indicate that there is poor interfacial adhesion between the PLA and PVOH. It is believed that the cellulose nanowhiskers are preferably located in the PVOH phase due to its greater affinity to PVOH than PLA.

Figure 4 show TEM images of the nanocomposites at different magnifications. The dispersion of the whiskers was best in the PLA-PVOH/CNW5$_{wet}$, Figure 4b and 4d, even though FE-SEM showed better distribution of the PVOH phase in the PLA-PVOH/CNW5$_{dry}$. Further, the whiskers were not as tightly tied to the PVOH phase as first anticipated but were also spread in the PLA phase for both the nanocomposites. The bright circular areas in Figure 4 are artifacts that evolve during TEM observation and originate from the staining medium being exposed for the electron beam.

Mechanical properties

The results from tensile testing, except for PVOH which is given in accordance to reference [21], are given as values in Table 3. In order to distinguish between statistically significant differences in properties between the materials, a student two-tailed *t*-test at $\alpha = 0.05$ was performed for each material, expect for PVOH. Significant property differences between the materials, with a 95% probability, are denoted by different superscript letters (A, B, and C). The superscript A in Table 3 indicate the materials with the lowest values for a specific property and the superscript C the materials with the best values for a specific property. From this it is seen that the feeding technique, dry feeding or liquid feeding, is insignificant regarding the tensile properties for the reference materials (PLA-PVOH$_{dry}$ and PLA-PVOH$_{wet}$) and the nanocomposites (PLA-PVOH/CNW5$_{dry}$ and PLA-PVOH/CNW5$_{wet}$). Also, incorporation of CNW in the matrix will give a material with better tensile modulus, tensile strength, and larger elongation at break than its unreinforced counterpart.

Dynamic mechanical thermal analysis

The storage modulus (E’) of the produced materials is shown in Figure 5a and the tan δ is shown in Figure 5b. The polymers were in the glassy state at temperatures below the glass transition region. In this glassy region the modulus slightly decreased with increased temperature but remained approximately constant. Also, an increase of the storage modulus was seen at 20 – 30 °C above the tan δ peak which was a result of a cold crystallization process. This crystallization process is activated and favored by the increased chain mobility in the plastic region.

As seen in Figure 5, the reference materials (PLA-PVOH$_{dry}$ and PLA-PVOH$_{wet}$) and the nanocomposites (PLA-PVOH/CNW5$_{dry}$ and PLA-PVOH/CNW5$_{wet}$) all had roughly the same shape in the graphs. What is detected in DMTA and seen in Figure 5 is principally the polymer transitions in the PLA phase and the contribution from the PVOH phase, with or without whiskers, are too small to influence the storage modulus and tan δ curve. However, as seen from TEM images the whiskers in PLA-PVOH/CNW5$_{wet}$ were partially dispersed in the PLA phase and these whiskers could cause a change of the tan δ to higher temperatures due to restricted chain mobility of PLA at the PLA/CNW interphase. No such change in tan δ was seen and the reason for this could be that only a negligible part of the CNW was dispersed in the PLA phase, too small to influence the DMTA.

Conclusions

The goal of this study was to produce PLA/CNW nanocomposites by compounding extrusion and investigate the possibility to use PVOH to be able to uniformly disperse the CNW in the matrix. Two different feeding techniques of PVOH and CNW, dry feeding and liquid feeding, was evaluated. Analysis of microtomed and fractured samples in FE-SEM showed that PLA and PVOH formed two immiscible phases with a continuous PLA phase and a discontinuous PVOH phase. TEM analysis showed that the whiskers were better dispersed in the nanocomposite produced with liquid feeding, PLA-PVOH/CNW5$_{wet}$, and these whiskers were also partially dispersed in the PLA phase. However, the thermal stability of the nanocomposites was not improved compared to its unreinforced counterpart, probably because the majority of the whiskers were located in the PVOH phase and only a negligible amount was located in the PLA phase. The relative small improvements for the nanocomposites in tensile modulus, tensile strength, and elongation to break, compared to its unreinforced counterpart, was also an indication that it was primarily the PVOH phase that was reinforced but not the PLA phase. Using a screw configuration with more mixing elements would most probably have enhanced the mechanical and thermal properties of the nanocomposites due to better dispersion and distribution of both PVOH and CNW.

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Table 1. Processing parameters.

Parameter	Value
Main feeder (kg/h)	2.6 – 4
Pumping rate (kg/h)	4.44 – 5.40
Screw rotation speed (rpm)	150
Motor load (torque) (%)	35 – 60
Pressure at the die (bar)	5 – 8

Table 2. Formulations of prepared materials (wt%).

Material abbreviations	*PLA*	*Dry fed*		*Liquid fed*	
		PVOH	*CNW*	*PVOH*	*CNW*
PLA	100	-	-	-	-
PLA-PVOH$_{dry}$	70	30	-	-	-
PLA-PVOH$_{wet}$	70	-	-	30[a]	-
PLA-PVOH/CNW5$_{dry}$	65	30	5	-	-
PLA-PVOH/CNW5$_{wet}$	65	-	-	30[b]	5[b]

[a] The PVOH content in the solution was 27.0 wt% and 3.24 kg water/h was removed as steam during extrusion.

[b] The PVOH and CNW content in the suspension was 22.2 wt% and 3.7 wt%, respectively, and 4.00 kg water/h was removed as steam during extrusion.

Table 3. Results from tensile testing. The different superscript letters represent statistically significant differences in properties.

Material	*Tensile modulus (GPa)*	*Tensile strength (MPa)*	*Elongation at break (%)*
PLA	3.31 (±0.12)^{A}	71.9 (±2.0)^{C}	3.4 (±0.2)^{C}
PVOH*	-	24 - 79	0 - 300
PLA-PVOH$_{dry}$	3.31 (±0.09)^{A}	56.1 (±2.4)^{A}	2.0 (±0.2)^{A}
PLA-PVOH$_{wet}$	3.42 (±0.19)^{A,B}	54.2 (±5.0)^{A}	1.8 (±0.3)^{A}
PLA-PVOH/CNW5$_{dry}$	3.64 (±0.28)^{B,C}	67.7 (±0.8)^{B}	2.4 (±0.2)^{B}
PLA-PVOH/CNW5$_{wet}$	3.71 (±0.07)^{C}	66.5 (±2.7)^{B}	2.3 (±0.1)^{B}

* Values are given according to reference [21] for a 87 – 89 % hydrolyzed PVOH grade. The properties are very dependent on the moisture content in the PVOH.

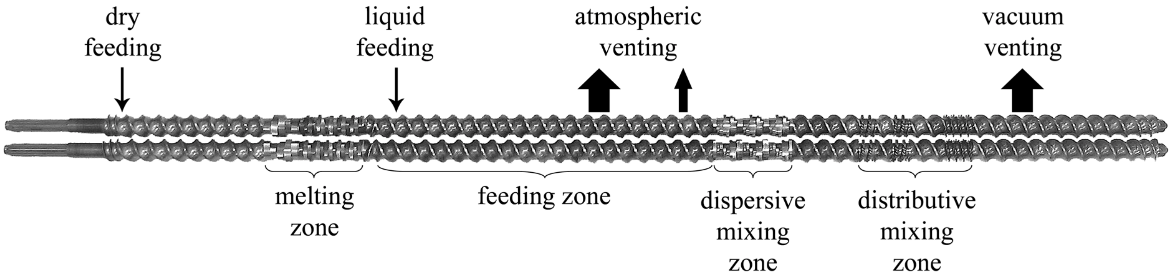

Fig. 1. Screw configuration used in the extruder.

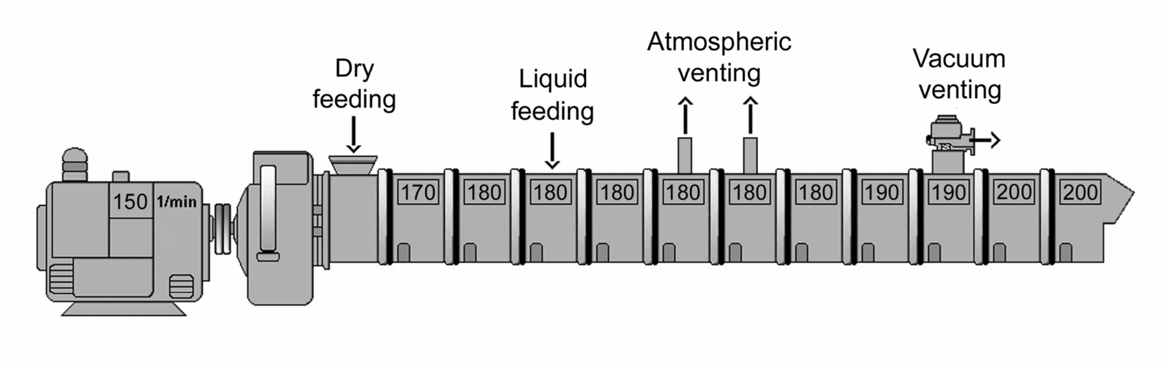

Fig. 2. Schematic picture of the extruder with feeding and venting zones.

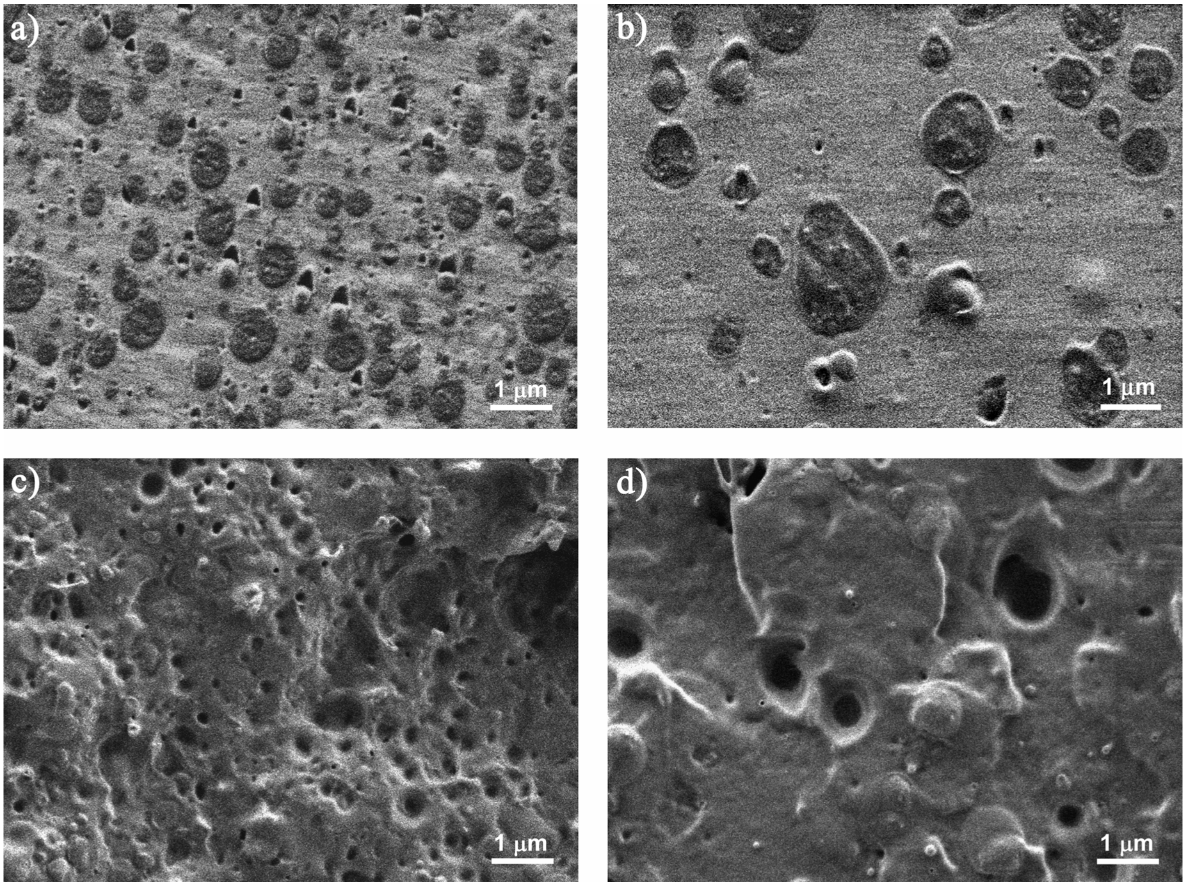

Fig. 3. Microtomed surface of a) PLA-PVOH/CNW5$_{dry}$ and b) PLA-PVOH/CNW5$_{wet}$, and fractured surface of c) PLA-PVOH/CNW5$_{dry}$ and d) PLA-PVOH/CNW5$_{wet}$. (Photo by Tor A. Nilsen, NTNU)

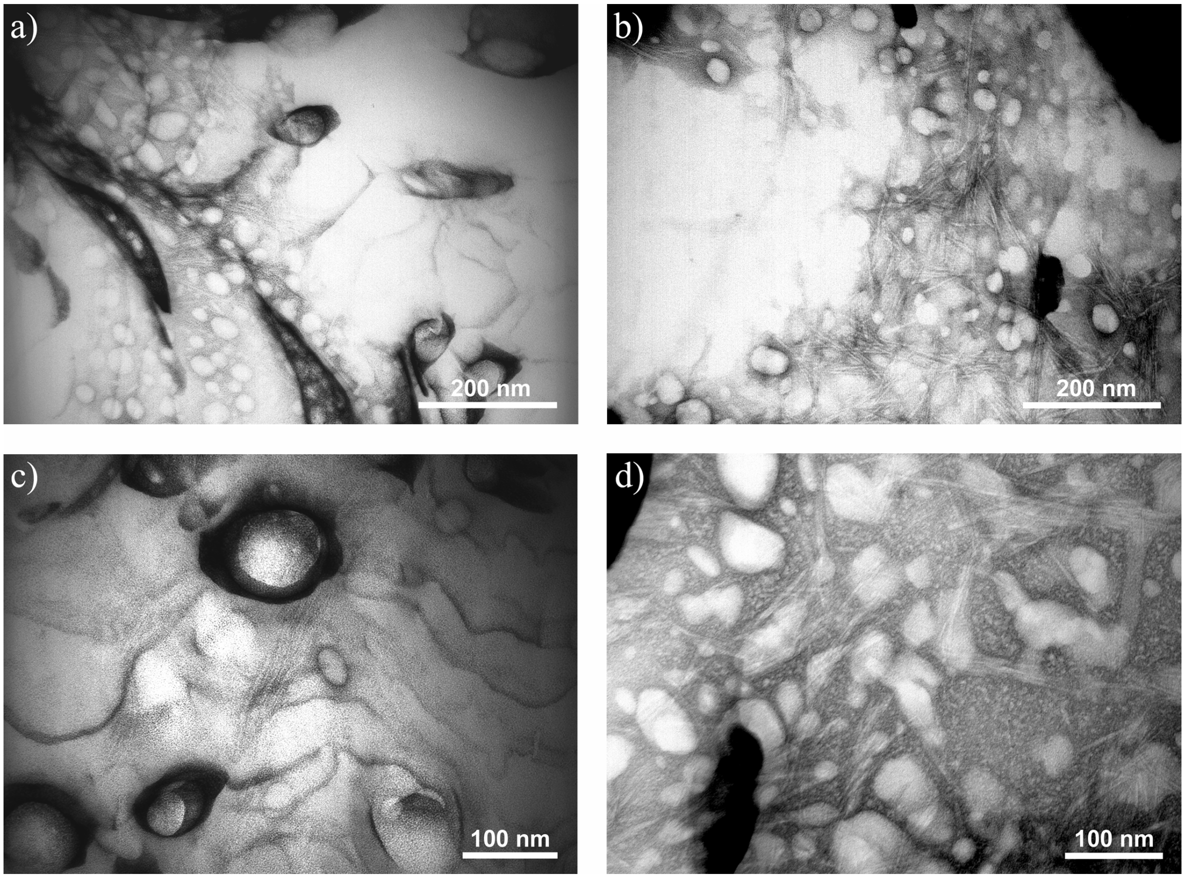

Fig. 4. TEM image of whiskers at ×89 000 for a) PLA-PVOH/CNW5$_{\text{dry}}$ and b) PLA-PVOH/CNW5$_{\text{wet}}$, and at ×120 000 for c) PLA-PVOH/CNW5$_{\text{dry}}$ and d) PLA-PVOH/CNW5$_{\text{wet}}$.

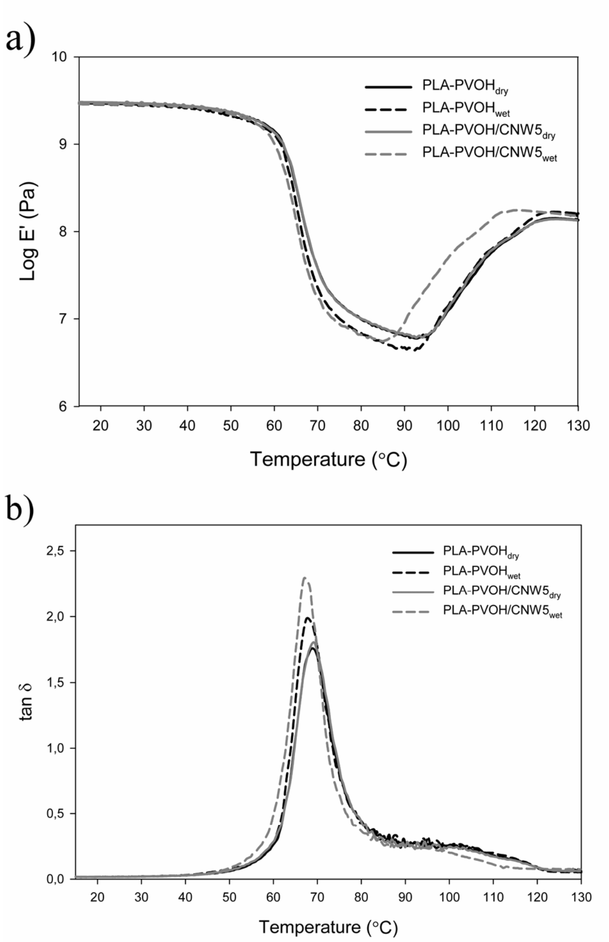

Fig. 5. Storage modulus a) and tan δ b) as a function of temperature for the reference materials and the nanocomposites.

Paper VI

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