

Dispersion and Properties of Cellulose Nanowhiskers and Layered Silicates in Cellulose Acetate Butyrate Nanocomposites

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ABSTRACT: The aim of this work was to develop well dispersed nanocomposites, in a non water soluble polymer using a non aqueous, low polarity solvent as a dispersion medium. The nanoreinforcements were cellulose whiskers and layered silicates (LSs) and matrix was cellulose acetate butyrate (CAB). Before nanocomposite processing, a homogenizer was used in combination with sonification to achieve full dispersion of the nanoreinforcements in a medium of low polarity (ethanol). After processing, the cellulose nanowhiskers (CNW) showed flow birefringence in both ethanol and dissolved CAB, which indicated well dispersed whiskers. The microscopy studies indicated that the processing was successful for both nanocomposites. The CNW showed a homogeneous dispersion on nanoscale. The LS nanocomposite contained areas with lower degree

of dispersion and separation of the LS sheets and formed mainly an intercalated structure. The produced materials were completely transparent, which indicated good dispersion. Transparency measurements also indicated that the nanocomposite containing CNW showed similar performance as the pure CAB. Dynamic mechanical thermal analysis (DMTA) showed improved storage modulus for a wide temperature range for both nanocomposites compared with the pure CAB matrix. This study indicated that CNW have a potential application in transparent nanocomposites based on fully renewable resources. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2001–2009, 2009

Key words: nanocomposites; microscopy; solution casting; transparency; thermal properties

INTRODUCTION

Research groups all over the world are working on improving the properties of biopolymers to develop materials that can replace petroleum based plastics. This research has been triggered by an interest to reduce our dependency on fossil fuels.¹ Increasing the use of biopolymers is believed to be a path to receiving sustainable developments in the future. Biopolymers can be produced from byproducts or wastes from other industries, which will allow us to utilize our renewable resources to a greater extent. Biopolymers will after use degrade to form carbon dioxide, water, and biomass. The amount of carbon dioxide released into the atmosphere during degradation is the same amount as the renewable resource harnessed during its cultivation. As a result, biopolymers will have a positive effect on our environment.² Many applications of plastic materials today generate non-recyclable plastic waste and numerous

of these applications can benefit from the degradability that biopolymers offer.

To be able to exchange petroleum based commodity thermoplastics with biopolymers, the biopolymers need to have comparable properties and processing methods. One way of improving the properties of biopolymers is to produce biopolymer based nanocomposites. Nanoreinforcements have the ability to improve stiffness, strength, toughness, thermal stability, and barrier properties of the pure polymer matrix.³ Nanoreinforcements are also unique in that they will not affect the clarity of the polymer matrix, because they are smaller than the wavelength of visual light.³ Only a few percentages of these nanoreinforcements are normally incorporated (1–5%) into the polymer and the improvement is vast because of their large degree of specific surface area. The first research on polymer based nanocomposites was made by researchers at Toyota in Japan in the early 1990s.⁴ In their research, they utilized layered silicates (LSs) as nanoreinforcements and these materials have since received wide attention. The most commonly used LSs belong to the clay mineral family of 2 : 1 phyllosilicates, which include montmorillonite, saponite, and hectorite

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among others. The morphology of these materials is made up of two-dimensional layers containing two tetrahedral silicate sheets (Si, Al) and one octahedral hydroxide sheet $[\text{Mg}(\text{OH})_2]$ or $[\text{Al}(\text{OH})_3]$.³ The oxygen ions of the octahedral sheet are shared with the two tetrahedral sheets producing a sheet like material. These sheets have a thickness of around 1 nm and LSs are therefore characterized as nanoreinforcements. LSs form stacks that are held together by van der Waals forces and to produce nanocomposites polymer chains need to penetrate these stacks. LSs are today commercially available with different types of modifications to make them compatible with a large range of plastic materials. Unfortunately, LSs do not come from renewable resources.

There are a few research groups around the world focusing on producing biopolymer based nanocomposites based on fully renewable resources. Cellulose is one of the preferred materials for generating renewable nanoreinforcements, because it is abundant in nature and available in a large variety of resources.^{5,6} From cellulose two different types of nanoreinforcements can be produced, microfibrils and whiskers. Microfibrils contain both amorphous and crystalline regions of cellulose and unlike whiskers they have the ability to create entangled networks. Whiskers on the other hand are described as isolated monocrystalline regions of cellulose and they are believed to have a modulus equivalent to the theoretical modulus of cellulose (167.5 GPa⁷) because of their near perfect crystalline structure. As a result, cellulose whiskers have equally good mechanical properties as LSs (170 GPa).⁸ However, there are several obstacles remaining before cellulose whiskers can be commercialized. One of the major drawbacks with cellulose whiskers is that they are difficult to disperse in non-polar solvents because of their strong hydrogen bonds. Different chemical modifications have been used to try to overcome this problem, for example the use of a surfactant,⁹ poly(ethylene glycol) grafting,¹⁰ and partial silylation.¹¹ These treatments have overcome the problem with dispersion, but unfortunately the reinforcing effect of the whiskers has been reduced or lost.¹²⁻¹⁴ Examples of other drawbacks with cellulose nanowhiskers (CNW) and their nanocomposites is the low yield, which is associated with the production of these whiskers (~ 30 wt %)¹⁵ and the difficulty to produce the nanocomposites via melt compounding.¹⁶ Although cellulose nanocomposites are difficult to produce, they form an interesting group of materials because the cellulose is abundant and renewable. From experiments it is possible to see that cellulose whiskers have the ability to improve the stiffness and softening temperature of biopolymers.^{12,13,17-19} One study has also showed that incor-

porating cellulose whiskers into starch can reduce water uptake.²⁰

Cellulose acetate butyrate (CAB) belongs to the group of cellulose esters. These polymers are biopolymers produced from renewable raw materials such as wood or cotton. Cellulose esters are based on highly purified cellulose and plasticized they will act as thermoplastic polymers. Cellulose esters are stiff materials due to the stiff nature of the cellulose polymer backbone.²¹ Generally, cellulose esters are described as having moderate heat resistance, high moisture vapor transmission, grease resistance, clarity, and moderate impact resistance.²¹ CAB was introduced in the 1940s as a tougher version of cellulose acetate (CA).²¹ CAB is known to have lower water absorption and density than CA. CAB is today often used as coating, film, or in medical applications. CAB has in two prior studies been reinforced with CNW.^{13,17} When using whiskers from bacterial cellulose the storage modulus of the CAB was improved during dynamic mechanical testing.¹³ When using whiskers from microcrystalline cellulose (MCC) based on wood the tensile modulus, tensile strength, and storage modulus increased compared with the pure CAB matrix. No work has been reported where CAB has been reinforced with LSs. However, CA has been reinforced with organically modified LSs giving rise to large improvements in modulus and strength.^{22,23}

This work is a continuation of an earlier experiment where CAB was reinforced with MCC that had been swelled in dimethylacetamide/LiCl.¹⁸ The results showed that the dispersion was not at nano-level, the materials did not show transparency and unfortunately, the experiment also showed that the dimethylacetamide/LiCl had a negative effect on the CAB matrix. The aim was to disperse CNW and layerate silicates in a low polarity solvent, as well as developing nanocomposites using CAB as matrix polymer. The dispersion and structure of the produced materials was studied using, flow birefringence, field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM), and wide angle x-ray analysis. UV-Visual spectroscopy was also performed to measure the transparency of the produced materials. The nanocomposites thermo mechanical properties were studied using dynamic mechanical thermal analysis (DMTA).

EXPERIMENTAL

Materials

Matrix: CAB (CAB-553-0.4) was supplied by Eastman Chemical Company, Kingsport. The material had a butyryl content of 46 wt %, acetyl content of 2 wt %, and a hydroxyl content of 4.8 wt %. It had a

glass transition temperature of 136°C and a melting point in the range between 150 and 160°C.

Reinforcement: MCC, Avicel PH 102, was supplied by FMC BioPolymer, PA. Avicel PH 102 is commercially available and was used as a raw material for the production of CNW. Hectorite (LS) was supplied by Elementis Specialties, NJ. This smectite LSs was organically modified (dimethyl benzyl hydrogenated tallow treated) and was commercially available as Bentone 2004. It had a density of 1.8 g/cm³ and the dimensions 800 × 80 × 1 nm.

Chemicals: Sulfuric acid (95–97%) from Merck KGaA, Darmstadt, Germany was used during the CNW production. Polyethylene glycol (PEG) 1500 from Merck-Schuchardt, Hohenbrunn, Germany was used to remove water from the water/CNW suspension. Ethanol with 2% methylisobutylketone content from Arcus AS, Oslo, Norway, was used as solvent for the CAB.

Processing of cellulose nanowhiskers

CNW production: MCC, 10 g/100 mL, was hydrolyzed in 9.1 mol/L sulfuric acid at 44°C for 130 min. The excess of sulfuric acid was removed by repeated cycles of centrifugation, 10 min at 13,000 rpm (MR23i, Jouan, France). The supernatant was removed from the sediment and was replaced by deionized water. The centrifugation continued until the supernatant became turbid. After the centrifugation, the suspension containing the whiskers was dialysed against deionized water. The final water/CNW suspension had a pH of 5. To remove large quantities of water from the water/CNW suspension dialysis tubes containing the suspension were placed in a bath filled with deionized water and a high concentration of PEG 1500. After 7 days in the bath, the dialysis tubes were removed and a gel containing 34 wt % of whiskers had been obtained.

Dispersion of nanoreinforcements

The CNW and LS were added to ethanol forming two separate 3 wt % suspensions. These two suspensions were then exposed to sonification (UP200S, Hielscher Ultrasonics GmbH, Germany) twice for 3 min each to disperse the nanoreinforcements thoroughly. The suspensions were then stirred for 20 hr on a hotplate at room temperature. The suspensions were then passed through a homogenizer (APV2000, Rannie & Gaulin Homogenizers, Denmark) at 850 bar for ~ 15 cycles. The suspensions were then sonified for 3 min and exposed to another 15 cycles through the homogenizer at 850 bar. To avoid contamination, the homogenizer was thoroughly cleaned between processing the two different nanoreinforcements. The suspensions were placed in an

TABLE I
Prepared Formulations (wt %)

Materials	CAB	CNW	Hectorite
CAB	100	–	–
CAB/CNW	95	5	–
CAB/LS	95	–	5

ice bath in between each processing step to cool the suspensions.

Processing of nanocomposites

The nanocomposites were prepared by solution casting using ethanol as solvent. Each formulation in the experiment was prepared separately and the produced formulations can be seen in Table I. CAB was dissolved in ethanol forming 15 wt % solutions. The CAB was dissolved by stirring the ethanol solutions for 3 hr at 75°C. The dissolved CAB was then mixed with the suspensions containing the nanoreinforcements. The formulations were stirred for 30 min on a hotplate at 75°C, followed by 3 min of sonification. Even the pure CAB solution was exposed to this procedure. The materials were then casted in sterile polystyrene Petri dishes and were left to evaporate 72 hr in a preheated vacuum oven (VDL 53, Binder GmbH, Germany) at 60°C and the pressure was pumped down slowly to 200 mbar. The films were then removed from the Petri dishes using water and were again placed in the vacuum oven at 70°C for 1 week to remove all remaining ethanol. The vacuum oven was pumped to 0 mbar.

Characterization

Flow birefringence

A setup containing a lamp, a magnetic stirrer, and two polarizing filters was used to investigate flow birefringence of the suspensions containing CNW. Flow birefringence is a method, which can be used to investigate if CNW are isolated in a suspension.²⁴

Microscopy

Fracture surfaces of the nanocomposite films were examined in a FESEM, Zeiss Supra 55VP. The fracture surfaces were generated in room temperature and the samples were analyzed uncoated. The accelerating voltage used was 1.0 kV. The nano structure of the composites was examined in a transmission electron microscope (TEM), Philips CM30, at an acceleration voltage of 150 kV. To examine the nanocomposites, the samples were cut and polished to rectangular sheets, embedded in epoxy and allowed to cure overnight. The final ultra microtoming was performed with a diamond knife at room temperature generating foils being 50 × 500 μm² in cross-



Figure 1 Flow birefringence of the cellulose nanowhiskers. (a) Dispersed in ethanol and (b) Dispersed in ethanol and dissolved CAB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

section and ~ 50 nm in thickness. These foils were gathered onto Cu grids. Only the CAB/CNW samples were stained by allowing the grids to float in a 2 wt % solution of uranyl acetate for 3 min.

Wide angle x-ray diffraction

Wide angle x-ray diffraction (WAXD) was carried out using a Siemens Diffractometer D5005 to investigate the degree of intercalation of the LS. The samples were exposed for a period of 11 sec for each angle of incidence (θ) using a Cu $K\alpha_{1,2}$ X-ray source with a wavelength (λ) of 1.541 Å. The angle of incidence was varied from 1.5 to 40 by steps of 0.06°. Bragg's law ($n\lambda = 2d \sin\theta$) was used to calculate the interstitial spacing of the LS.

Transparency

Transparency measurements were carried out on a Perkin Elmer UV/Vis Spectrometer Lambda 11. The

λ was varied between 700 and 200 nm and a scan rate of 240 nm/min was used. Three samples were used to characterize each material.

Dynamic mechanical thermal analysis

Dynamic mechanical properties of the nanocomposites were measured using a TA Instruments DMA 800 in tensile mode. The measurements were carried out at a constant frequency of 1 Hz, strain amplitude of 10 μm , a temperature range of 30–180°C, a heating rate of 3°C/min and gap distance of 10 mm. The samples were prepared by cutting strips from the films with a width of 3 mm. Four samples were used to characterize each material.

RESULTS AND DISCUSSION

The improvements in material properties due to the addition of nanoreinforcements depend on the dispersion of the nanoreinforcement in the polymer



Figure 2 Visual comparison of the optical clarity of the produced materials. (a) CAB, (b) CAB/CNW, and (c) CAB/LS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

matrix. A fully dispersed system where all nanoreinforcements are present as single sheets or well separated whiskers is the optimum, because this system yields the maximum available surface area of the nanoreinforcement. It is important to remember that the surface area of the LS sheets in this study is much higher than that of the cellulose nanowhiskers. This difference should have an impact on the results if both systems are fully separated.

Dispersion

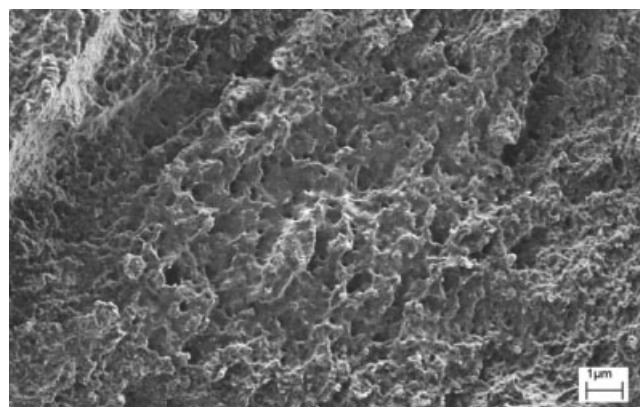
The nanocomposites in this study were produced using solution casting with ethanol as the solvent. To produce well dispersed nanocomposites, the nanoreinforcements were first isolated in ethanol before being blended with dissolved CAB. The LS was organically modified to swell in polar solvents and it was therefore added directly to ethanol forming a 3 wt % suspension. The CNW on the other hand were in a water suspension after they were produced and they therefore needed to be transferred to ethanol. A gel was produced containing 34 wt % CNW by reducing the water content of the water/CNW suspension. The gel was then diluted by ethanol forming a suspension containing 3 wt % CNW. A homogenizer was used in combination with sonification to disperse the two nanoreinforcements in the ethanol suspensions. After processing, the suspension containing CNW showed flow birefringence, see Figure 1(a). This indicated that the CNW were well isolated and dispersed in the ethanol suspension. It was also possible to see flow birefringence of the final suspension containing both CNW and dissolved CAB, see Figure 1(b). The produced composite materials were completely transparent to the naked eye, see Figure 2. This indicated that the incorporated nanoreinforcements were small enough not to scatter light.

Composite structure

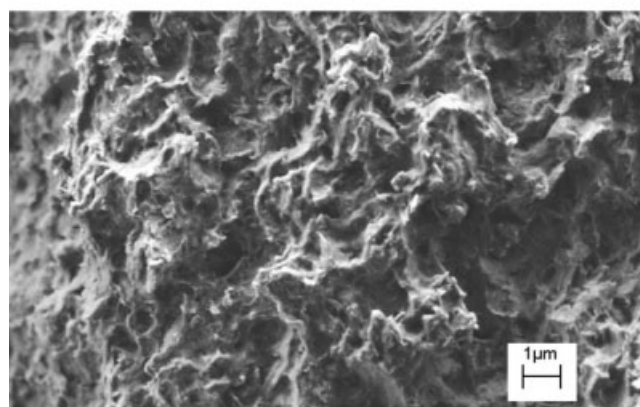
It is always important to conduct a thorough investigation of the morphology of the materials produced. In this study, both field emission scanning electron microscopy (FESEM) and TEM were performed on the produced materials. WAXD was also carried out, but only on the LS composite because cellulose whiskers do not show a similar behavior as layerate silicates showing the distance between the layers.

The FESEM images of the CAB/CNW material can be seen in Figure 3(a). There were no visible agglomerates of CNW in microscale but nanosize porosity was observed. The CAB/LS material showed totally different structure compared with the cellulose nanowhisker composite, shown in Figure 3(b). The fracture looks more brittle and no plasticity of matrix polymer can be seen. However, no agglomerates of silicates were visible.

A TEM analysis was carried out to investigate the nanostructure of the produced nanocomposites. The TEM equipment has the necessary resolution to be able to detect individual CNW and LS sheets.



(a)



(b)

Figure 3 FESEM images of the prepared nanocomposites showing an overview of (a) CAB/CNW and (b) CAB/LS microstructure.

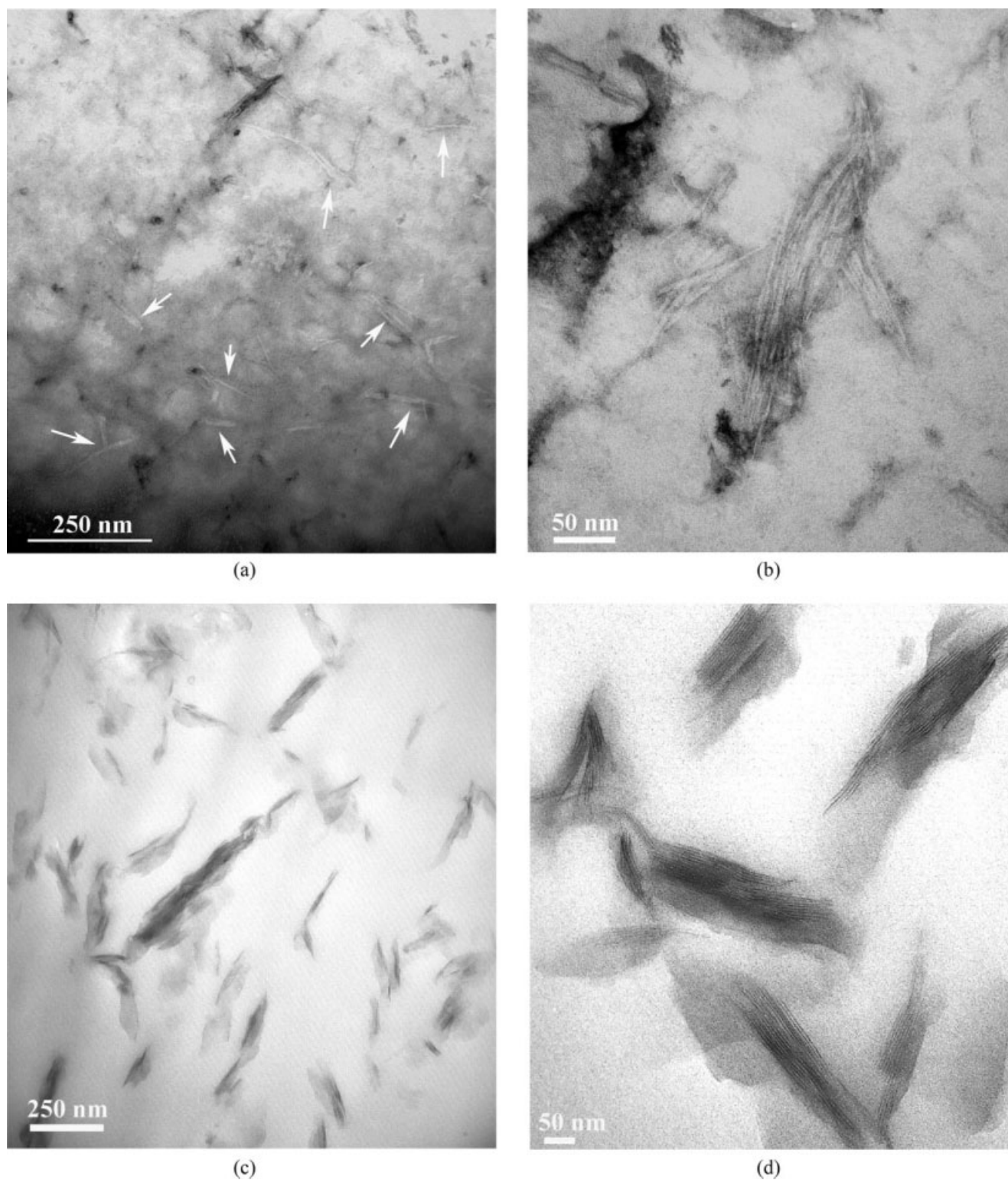


Figure 4 TEM images of the nanocomposites showing (a and b) well dispersed CNW in the CAB matrix; (c and d) well separated layers of silicates in the CAB.

The analysis of the CAB/CNW material indicated well dispersed CNW in nanoscale. However, in the images received from the TEM analysis it was difficult to identify single whiskers because of low contrast between the two phases, see Figure 4(a).

Staining was used to increase the contrast, but it did not work well on this material combination because both phases are based on cellulose. The same problem had been experienced by others.¹⁷ Figure 4(b) presents a more detailed image of the CAB/CNW

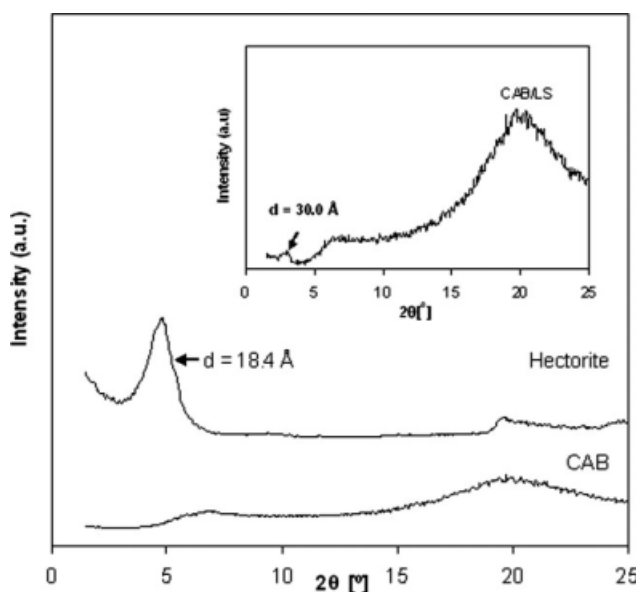


Figure 5 WAXD analysis of the CAB, LS, and CAB/LS nanocomposite material, indicating an intercalated structure.

material showing a small agglomerate of whiskers. Agglomerates received better contrast during the analysis. In Figure 4(b), it was also possible to see that the whiskers were shorter than what has been reported earlier.¹² The reason for shorter whisker length can be the low contrast received in the TEM images or that the whiskers being cut both during the homogenization process and the sample preparation before the TEM analysis. The TEM analysis of the CAB/LS indicates the presence of intercalated structures, see Figure 4(c). In a more detailed image, it is possible to see that the interstitial gap between the LS sheets has increased and that the CAB matrix has been able to penetrate this gap, see Figure 4(d). The used LS was organically modified to swell in polar solvents like ethanol and it was therefore difficult to explain why no exfoliation was achieved when a homogenizer was used during the processing. WAXD was performed to confirm the structure observed in TEM. This analysis method utilizes a larger sample size and it should therefore give a more representative analysis of the material. Figure 5 shows the results from the WAXD analysis. The results indicate that the interstitial spacing of the LS had increased from 1.8 nm to 3 nm. As the TEM analysis the WAXD indicated that the LS was present in an intercalated morphology.

Transparency

The produced nanocomposites seemed perfectly transparent to the naked eye, as seen earlier in Figure 2. This was a great improvement compared with the CAB composites produced in an earlier study.¹⁸

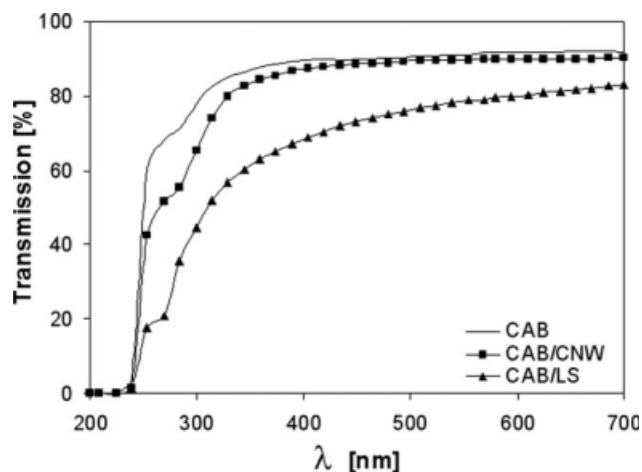


Figure 6 UV and visible light spectra comparing the transparency of nanocomposites with pure CAB.

Spectroscopy measurements were carried out to see exactly how much light the materials let through. The results from the spectroscopy can be seen in Figure 6. The results show that the nanocomposites were not as transparent as pure CAB. The CAB/CNW material was only slightly less transparent above 400 nm, whereas there was a distinct difference between the material in the wavelengths ranging from 400 nm to 250 nm. The CAB/LS nanocomposite was less transparent compared with the other two materials. This can be explained by the presence of intercalated structure and stacks. These stacks were large enough to reflect and hinder the incoming light.

Thermal properties

The thermal properties of the produced materials were investigated using a DMTA. DMTA can be used to determine how the mechanical properties of

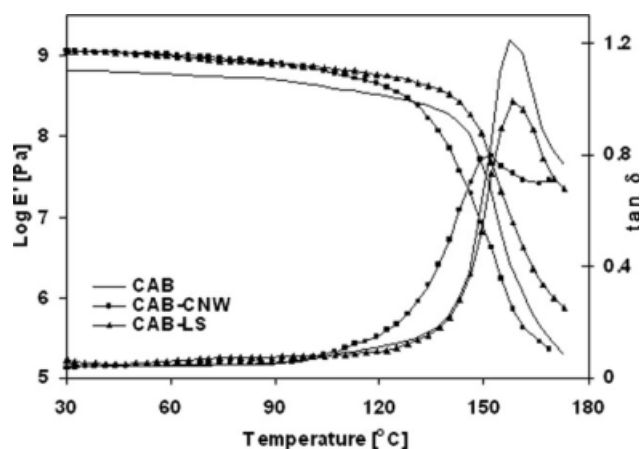


Figure 7 Storage modulus and Tan δ curves of CAB, CAB/CNW, and CAB/LS as a function of temperature.

TABLE II
Storage Modulus and Tan δ Peak Temperature from Dynamic Mechanical Thermal Analysis

Materials	Storage modulus (MPa)		Tan δ peak ($^{\circ}$ C)
	At 30 $^{\circ}$ C	At 80 $^{\circ}$ C	
CAB	664	530	158
CAB/CNW	1168	894	152
CAB/LS	1121	844	158

samples vary with temperature. Representative storage modulus and Tan δ curves from the DMTA analysis can be seen in Figure 7 and the values are shown in Table II. The results show that the two nanoreinforcements improved the storage modulus of the pure CAB over a wide range of temperatures. Because of the large specific surface area of the nanoreinforcements, they have the ability to affect the polymer chain mobility of the matrix and thereby increase the modulus even with very low reinforcement content. Figure 7 and Table II show that CNW improved the storage modulus by 76% (504 MPa) and LS by 69% (457 MPa), at 30 $^{\circ}$ C. At an elevated temperature of 80 $^{\circ}$ C, both nanocomposite showed about 60% improvements in the storage modulus, which corresponded to 364 MPa for CAB/CNW and 315 MPa for CAB/LS. Results in this study were slightly lower than what Grunert et al. reported earlier.¹³ They observed an improvement of 400 MPa at 81 $^{\circ}$ C using CNW produced from bacterial cellulose in CAB matrix. Bondeson et al. reported similar results, an improvement of 380 MPa at 80 $^{\circ}$ C on nanocomposites produced by melt compounding.¹⁷ Above 120 $^{\circ}$ C it was possible to detect a softening of the CNW composites and at 130 $^{\circ}$ C they showed a similar storage modulus to the pure CAB. The LS composites were not showing softening before 150 $^{\circ}$ C. DMTA results also showed that Tan δ peak temperature for CAB was affected by the addition of CNW. It was decreased from 158 $^{\circ}$ C for pure CAB to 152 $^{\circ}$ C for CNW composites. The reason can be the residual bound water on the whisker surfaces, which can result in a plasticizing effect for the CAB matrix. The Tan δ peak temperature of CAB/LS composites remained in the same position.

CONCLUSIONS

The aim of this study was to disperse of CNW and layerate silicates in a non aqueous low polarity medium, as well as in a non water soluble polymer (CAB). The content of nanoreinforcements was held constant, at 5% wt in both composites. The flow birefringence study showed well dispersed whiskers

in the low polarity solvent as well as in CAB solution. The morphology study on composites showed that the CNW were well dispersed in the CAB matrix. However, there was a possibility that the homogenizer used during processing could have decreased the length of the whiskers. The incorporated LS showed an intercalated structure with increased gap distance between the layers from 1.8 nm to 3 nm. CAB is known to be highly transparent and the addition of cellulose whiskers only slightly decreased the transparency. This was a great improvement compared with earlier work.¹⁸ The CAB/LS nanocomposite was less transparent compared with the other two materials. This can be explained by the presence of intercalated structure and stacks. Both nanoreinforcements increased the storage modulus of the CAB matrix over a wide range of temperatures. The CNW decreased the Tan δ peak temperature of the CAB whereas LS did not affect the Tan δ peak.

From the results it is possible to see that CNW and LSs can be dispersed in a non-aqueous low polarity solvent. Furthermore, a possible processing route for nanocomposites with non water soluble biopolymer was developed. The nanocomposites showed improved storage modulus and high transparency.

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