

The Effect of Plasticizer and Cellulose Nanowhisker Content on the Dispersion and Properties of Cellulose Acetate Butyrate Nanocomposites

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ABSTRACT: We studied the effects of plasticizer and cellulose nanowhisker content on the dispersion and properties of cellulose acetate butyrate (CAB)-based bionanocomposites. The cellulose nanowhiskers in an aqueous medium were solvent-exchanged to nonaqueous polar solvent (acetone) and used for nanocomposite processing by solution casting. The plasticized and unplasticized nanocomposites with 5 and 10 wt % cellulose nanowhisker content were prepared. Atomic force microscopy indicated nanoscale dispersion of whiskers in the CAB matrix. The dynamic mechanical analysis showed an increase in storage modulus with addition of cellulose nanowhiskers, especially above the glassy-rubbery transition region.

Thermogravimetric analysis showed an improvement in thermal stability with increased whisker content for both unplasticized and plasticized nanocomposites. The plasticized nanocomposites showed better transparency than the unplasticized composites, indicating a better dispersion of cellulose nanowhiskers in CAB, in the presence of a plasticizer. The dynamic mechanical properties and thermal stability increased, whereas transparency decreased with increased CNW content. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2723–2730, 2009

Key words: nanocomposites; plasticizer; dispersion; cellulose nanowhiskers; thermal properties

INTRODUCTION

Cellulose is the most common organic polymer and is considered to be a renewable raw material resource for the increasing demand for environmentally friendly and biocompatible products.¹ Cellulose-based products have a long industrial significance, and cellulose nitrate has been produced since 1878.² Thermoplastic cellulose ester was discovered in 1865 and developed further and commercialized by Bayer AG.³ The esterification of cellulose using inorganic and organic acids was the pioneering process in cellulose chemistry and is still the most important technical derivative of cellulose.^{4,5} The cellulose-based biopolymers such as cellulose acetate (CA), cellulose acetate butyrate (CAB), and cellulose acetate propionate (CAP) are being used for several engineering applications.^{4–6} In addition to this, owing to the interest in replacing petroleum-based polymers with biobased ones, cellulose-based polymers are also being used as thermoplastic matrix component in composites to produce high-performance materials based on renewable resources.^{6,7}

The use of cellulose reinforcements in polymers has been studied for several years. Cellulose-based composites were developed as early as 1950, in which cotton fibers were used as reinforcement in polyesters.⁸ In recent years, the use of two different kinds of cellulose reinforcements in nanoscale, namely microfibrils and nanowhiskers, are very much in focus, and researchers all over the world are looking at cellulose and cellulose-based materials with renewed interest. Cellulose is found in plants in the form of microfibrils, which form the structurally strong framework in cell walls. Microfibrils are bundles of cellulose (C₆H₁₀O₅) molecules that are elongated and stabilized laterally by hydrogen bonds. A single microfibril contains multiple elementary fibrils constituting many cellulose chains. The elementary fibrils have a diameter of approximately 2 to 20 nm, depending on the source.⁹ The elementary fibrils are composed of amorphous and crystalline regions and by the removal of the amorphous region using acid hydrolysis, crystalline cellulose entities called cellulose whiskers can be obtained. It is also expected that the removal of the defective areas in a cellulose chain, viz, amorphous regions, will result in the well-ordered defect-free structures in nanometre scale and having an enormous surface area. As early as 50 years ago, Rånby reported a process using acid hydrolysis that could

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isolate cellulose nanowhiskers from the fibrils.¹⁰ It has been researched that the cellulose nanowhiskers have mechanical strength equated to the binding force of neighboring atoms.⁹ As such, cellulose nanowhiskers have better mechanical properties than most of the commonly used reinforcement materials. Research in this direction was accelerated in the early 1990s by a group at CERMAV-CNRS in France. It is now possible to isolate cellulose nanowhiskers from different sources such as tunicates, wood, and wheat straw.^{11,12} Cellulose nanowhiskers have been incorporated into matrices such as starch, cellulose acetate butyrate, polyether, poly(hydroxyalkanoates), poly(lactic acid), poly(polyethylene oxide), polyurethanes, and polyvinyl chloride, etc.^{13–19}

Biopolymer nanocomposites can be produced by incorporating materials that have one or more dimensions on the nanoscale ≤ 100 nm into a biopolymer matrix. Because of their small size and large surface area, only a small percentage (1–10%) of the nanomaterials is needed to be incorporated into the polymer matrix to induce vast improvement. Using nanoreinforcements to improve the biopolymer's water vapor permeability, mechanical properties and thermal stability can be done without affecting the transparency of the biopolymers to a great extent.^{20,21} During nanocomposite production with a biodegradable polymer as the matrix, it is very important to use nanoreinforcements that are equally biodegradable in nature.

This study deals with the morphology and properties of a bionanocomposite in which the matrix (CAB) and the reinforcement (CNW) are based on cellulose. There are earlier reports on CAB-based cellulose nanocomposites produced by solution casting as well as melt compounding.^{13,22–24} Grunert and Winter reported studies on cellulose acetate butyrate reinforced with cellulose nanowhiskers isolated from bacterial cellulose microfibrils by sulfuric acid hydrolysis. They used both surface-treated (trimethylsilylated nanowhiskers) and native nanowhiskers to make the nanocomposites.¹³ Petersson and Oksman investigated how swollen microcrystalline cellulose (MCC) affects the properties of CAB.²² The results of the nanocomposite properties showed an improvement of 30 and 135% in the tensile strength and elongation to break, respectively, compared with CAB. Petersson also used sulfuric acid-hydrolyzed whiskers to reinforce CAB.²³ The study on CAB nanocomposites by the twin-screw extrusion process was reported by Bondeson et al., with whiskers isolated from MCC using hydrochloric acid.²⁴ The nanocomposite was obtained successfully by feeding a combined solution of 5% whiskers and 15% plasticizer in ethanol into the melt CAB in an extruder and showed very promising results in terms of mechanical properties and thermal stability.²

The main aim of this study was to obtain well-dispersed cellulose whiskers in CAB matrix using a plasticizer. Films used to investigate the mechanical properties of polymers are usually made by solution casting because polymeric thin films are easily obtained by this method. The general expectation is that the structure of polymer membranes is remarkably dependent on the solvent evaporation rate during film formation.²⁵ In the current system, acetone is used as the medium for solution casting. The plasticizer is expected to increase the polymer chain flexibility and thereby facilitate more uniform mixing between the matrix and the reinforcement.

EXPERIMENTAL PROCEDURES

Materials

Matrix

Cellulose acetate butyrate (CAB-553-0.4) was purchased from Eastman Chemicals (USA). CAB has a butyryl content of 46 wt %, acetyl content of 2 wt %, and a hydroxyl content of 4.8%. CAB is soluble in low-molecular-weight alcohols (methanol, ethanol, isopropanol, and *n*-propanol) as well as other common organic solvents. Its high hydroxyl content contributes to its alcohol solubility. CAB has a density of 1.2 kg/m³, molecular mass of 70,000 g/mol, and glass transition temperature (T_g) of 136°C. The melting temperature is between 150 and 160°C, and films of CAB are transparent and have good ultraviolet stability. CAB is supplied as a dry and free-flowing powder.

Nanoreinforcements

The nanoreinforcements in this study, cellulose nanowhiskers (CNW), were obtained by acid hydrolysis as described by Araki et al.²⁶ of commercially available microcrystalline cellulose. The microcrystalline cellulose (MCC), commercially available as VIVAPUR[®] Type 105, was obtained from JRS PHARMA, Weissenborn, Germany. During the hydrochloric acid hydrolysis of MCC, the amorphous region of the cellulose is destroyed, leaving only the crystalline regions, which are called cellulose nanowhiskers. Solvent exchange was done in a process whereby the whiskers were concentrated to a gel by removing almost 90% of the water through centrifugation. The whiskers in the gel state are redispersed at satisfactory concentration in acetone and sonified to obtain uniform dispersion in acetone medium.

Plasticizer

Cellulose acetate butyrate is a very brittle polymer, so a plasticizer was added to attain toughness.

Triethyl citrate (TEC) $C_{12}H_{20}O_7$ was chosen as plasticizer for the cellulose acetate butyrate and was provided by Fluka Chemie GmbH (Buchs, Switzerland). Triethyl citrate is an environmentally friendly plasticizer and is compatible with all cellulose esters.

Chemicals

Acetone 99.5% pure, purchased from VWR international (Stockholm, Sweden), was the solvent in all processes from solvent exchange to film formation. Hydrochloric acid (HCl) 32%, purchased from Merck KGaA 64271, Darmstadt, Germany, was used in the hydrolysis of the microcrystalline cellulose.

Nanocomposite processing by solution casting

The CAB and CAB nanocomposite films were prepared by solution casting. A mixture of CAB, TEC, and different weight percentages of cellulose nanowhiskers in acetone were prepared by stirring on a hot magnetic plate at 50°C for 3 h until a homogeneous mixture was obtained. The prepared formulations were sonified for 5 min before casting on well-dried glass Petri dishes. The formulations were left to evaporate in the vacuum oven at 45°C for 48 h. The prepared films had a thickness of ≈ 0.15 mm and a total dry weight of 3 g. Formulations of prepared materials are shown in Table I.

Characterization

Birefringence

Flow birefringence was used as a method to confirm the presence of isolated whiskers in a suspension. A setup containing a lamp and two crossed polarizing filters with one rotated at 90° were used to investigate flow birefringence of the cellulose nanowhisker suspensions in water medium and CAB/acetone medium.

Atomic force microscopy

The cellulose whiskers as well as the nanocomposites were characterized using a Veeco MultiMode scanning probe microscope with a Nanoscope V controller (Veeco Instruments BV, Breda, Netherlands). For the analysis of CNWs, a droplet of the aqueous whisker suspension (0.5% by weight) was dried on a mica surface before atomic force microscopy (AFM) examination. The nanocomposite films were embedded in epoxy resin and ultramicrotomed to expose the cross section and were analyzed directly. Overview images and detailed images for the nanocomposites were collected using a tapping mode etched silicon tip, with a nominal spring constant of 5 N/m and a nominal frequency of 270 kHz.

TABLE I
Prepared CAB and CAB Nanocomposite Formulations

Sample code	CAB (wt %)	CNW (wt %)	TEC (wt %)
CAB	100	–	–
CAB/CNW5	95	5	–
CAB/CNW10	90	10	–
CAB/TEC	95	–	5
CAB/TEC/CNW5	90	5	5
CAB/TEC/CNW10	85	10	5

Dynamic mechanical thermal analysis

The dynamic mechanical and thermal properties were studied using Dynamic Mechanical Thermal Analysis (DMTA) Q800 TA instruments (USA), in tensile mode. The temperature range of the studies was between 30 and 180°C in air. The rectangular samples were tested in tensile mode with a heating rate of 3°C/min using a frequency of 1 Hz. The samples were measured by cutting strips from the films with length of 12 mm, width of 5.6 mm, and thickness of ~ 0.15 mm. The results presented are the averages of three tests; the graphs are representative curves.

UV-spectroscopy

The transparency of CAB and CAB nanocomposite films were examined on a Hitachi U-1500 UV spectrometer (Hitachi High Technologies Inc., USA). The wavelength of transmission was between 800 and 200 nm; 1 spectral bandwidth scan rate, 50 nm/min.

Thermogravimetric analysis

The thermal stability of CAB and CAB nanocomposites were studied using thermogravimetric analysis (TGA) Q500 TA instruments, at temperature range of 30–600°C in air with a heating rate of 5°C/min; the samples weights were between 5 and 10 mg. Three samples were tested for each material, and the tests gave reproducible results.

RESULTS AND DISCUSSION

Cellulose nanowhisker characterization

It has been reported that whiskers form liquid crystalline phases of either chiral nematic (cholesteric) ordering or a flow-induced nematic ordering.^{26,27} The whiskers used in this study were produced by hydrolysis using hydrochloric acid. Unlike sulfuric acid, hydrochloric acid does not introduce negative surface charges on the whiskers during hydrolysis. Figure 1 shows the flow birefringence of whiskers when viewed under cross-polarized light; this is



Figure 1 Photographs showing the flow birefringence of whiskers in (a) water and (b) acetone. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

supporting evidence for the existence of cellulose whiskers. Figure 1(a) confirms the presence of liquid crystalline phases in the aqueous cellulose suspension obtained after hydrolyzing microcrystalline cellulose. Figure 1(b) shows birefringence after dispersing in acetone medium, which confirmed that the whiskers were well isolated in the nonaqueous medium used.¹

The structure and size distribution of the prepared suspension of CNWs were analyzed by AFM, as shown in Figure 2. The height, amplitude, and phase images show the presence of well-isolated and dispersed whiskers in the nanometer scale. The diameter of the whiskers determined based on AFM height images were about 17–19 nm. The measurements are made using the software in which the height of the whiskers is determined and is expected to be more accurate than measuring the width,

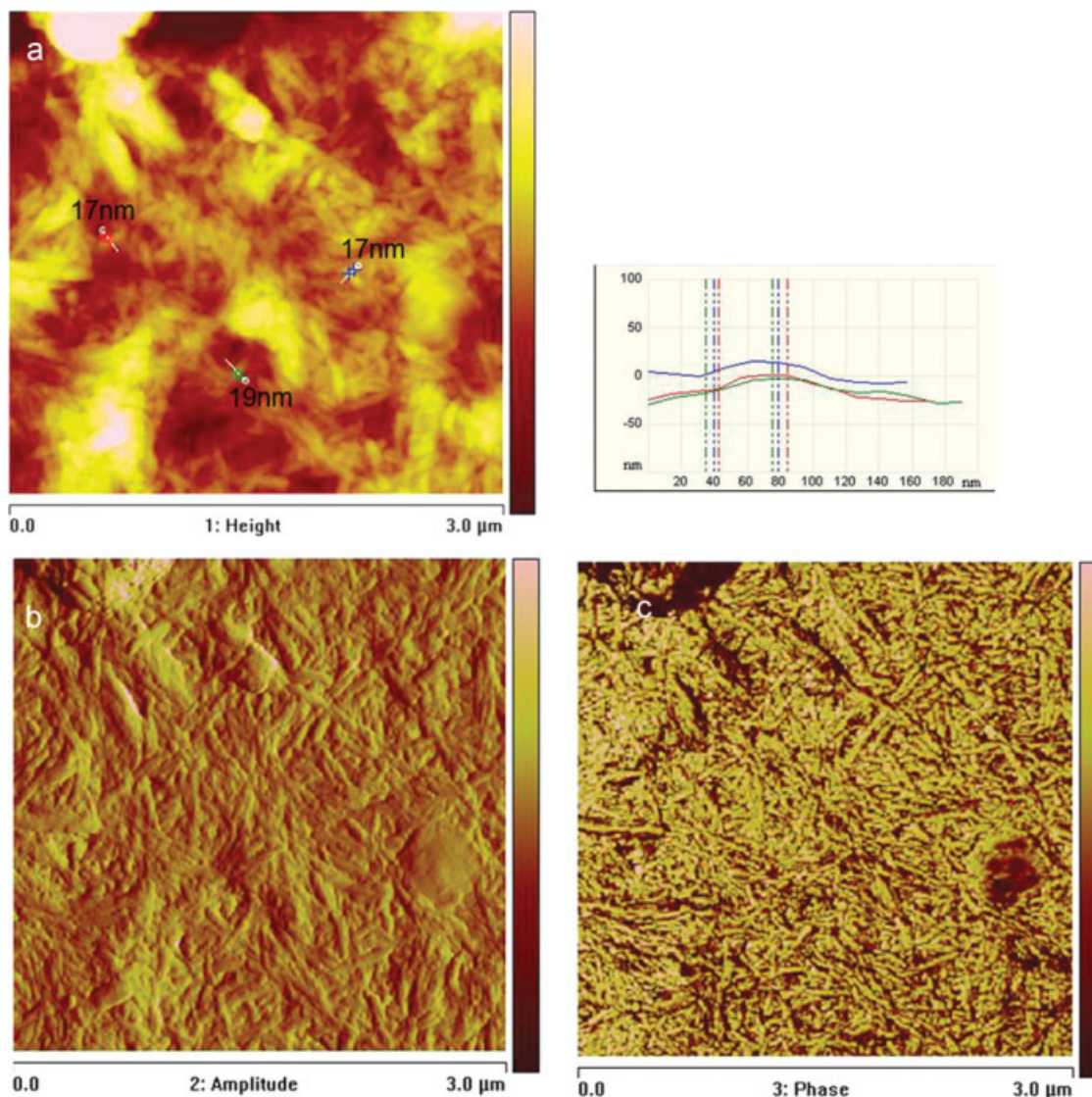


Figure 2 AFM images of cellulose nanowhiskers: (a) height and diameter measurement, (b) amplitude, and (c) phase. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

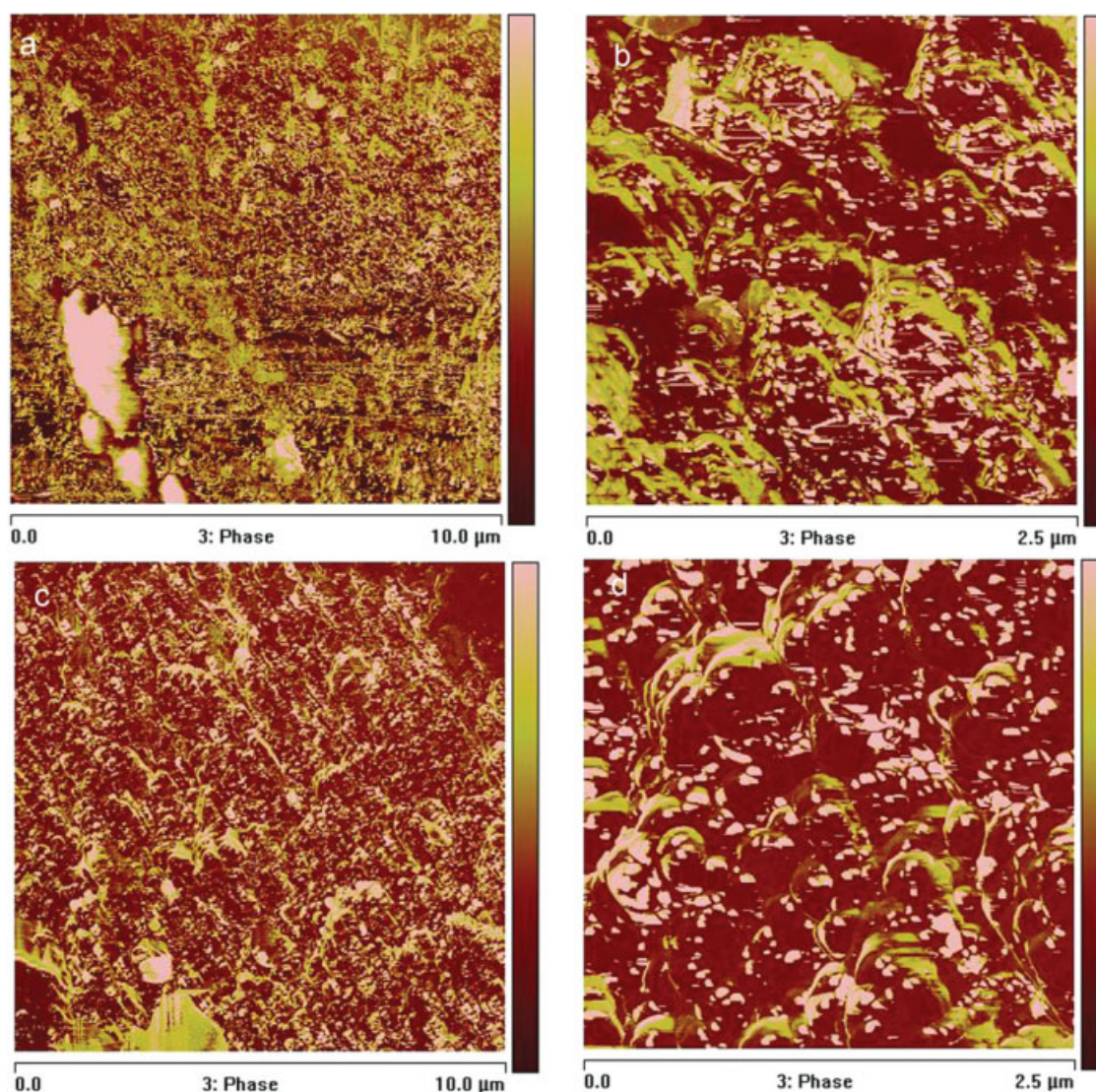


Figure 3 AFM images of cellulose nanocomposites without plasticizer CAB/CNW10: (a) overview, (b) detailed view; and with plasticizer CAB/TEC/CNW10: (c) overview, (d) detailed view. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which may cause a broadening effect based on the tip geometry during scanning.²⁸

CAB nanocomposites

AFM studies were done to investigate the dispersion of whiskers in the matrix phase. The AFM images of the unplasticized and plasticized CAB nanocomposites with 10% CNWs are shown in Figure 3, as representative cases. Figure 3(a,b) shows the overview and detailed view of CAB/CNW10; Figure 3(c,d) shows the overview and detailed view of CAB/TEC/CNW10 system, respectively. All the images show a homogeneous two-phased system without any microscaled agglomerates. It is possible to see a second phase embedded in the continuous phase and having various sizes and shapes that may be

cellulose nanowhiskers embedded in the matrix. The white-colored spots in the phase image of CAB/CNW10 and CAB/TEC/CNW10 samples are considered to be CNWs embedded in the matrix phase. The sizes and shapes of the white-colored spots were found to vary considerably, which indicates that cellulose nanowhiskers exist mostly as nano-scaled aggregates and/or are oriented in different directions in the matrix, which is an expected behavior of nanocomposites prepared by solution casting. If we compare the sizes of the whiskers (white dots) in the composites with the AFM images of the cellulose nanowhiskers in Figure 2, it can be seen that the sizes are comparable. The dispersion and distribution of CNWs in the matrix were very uniform in the plasticized and unplasticized composites even at CNW concentration of 10 wt %.

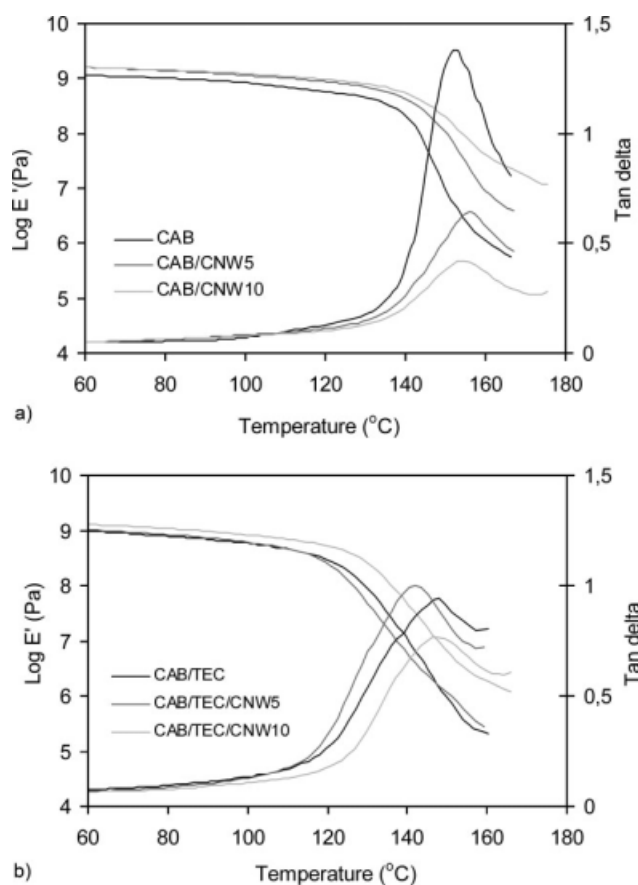


Figure 4 Storage modulus and $\tan \delta$ of CAB and nanocomposites reinforced with cellulose nanowhiskers: (a) unplasticized, (b) plasticized.

Dynamic mechanical thermal properties

The values for the storage modulus (E') and the $\tan \delta$ peak of the nanocomposites as a function of temperature are seen in Figure 4. In the whole range of tested temperatures, CAB/CNW nanocomposites showed higher storage modulus compared with CAB. The storage modulus values at 30, 80, and 155°C are given in Table II for comparison. At 30°C, CAB/CNW5 nanocomposite showed an increase of 8%, whereas at the same temperature CAB/CNW10 nanocomposite showed an increase of 32% in the storage modulus. At 80°C, CAB/CNW5 nanocomposite showed an improvement of 19% storage modulus, which corresponded to 189 MPa. This is lower than the improvement of 364 MPa reported by Petersson using cellulose nanowhiskers hydrolyzed with sulfuric acid and dispersed in ethanol into CAB matrix.²³ Bondeson et al. also reported a better result with an improvement of 380 MPa at 80°C using HCl-hydrolyzed whiskers to reinforce plasticized CAB in an extrusion process.²⁴ However, an improvement of 380 MPa was observed for CAB/CNW10 nanocomposite at 80°C for the storage modulus. At a temperature of 155°C (Table II), CAB/

CNW5 and CAB/CNW10 showed an increase of 788 and 2865%, respectively, in the storage modulus. In Figure 3(a), the $\tan \delta$ peak temperature shows a very slight shift toward higher temperatures for both CAB/CNW nanocomposites compared with CAB.

For plasticized CAB, the values of storage modulus and $\tan \delta$ are presented in Figure 3(b) and Table II. The storage modulus increased at 30°C with 3 and 17% for CAB/TEC/CNW5 and CAB/TEC/CNW10, whereas at 80°C, the increase was 10% and 31%, respectively. However, at a higher temperature of 155°C, in which the matrix polymer chains undergo chain relaxation, the plasticized CAB/CNW5 nanocomposite showed no improvement, but CAB/CNW10 nanocomposite showed improvement of 393% in storage modulus. The $\tan \delta$ peak for the plasticized nanocomposites shows no tendency to shift to higher temperatures, compared with plasticized CAB. Comparing the unplasticized and plasticized nanocomposites, it can be seen that the improvement in modulus is more prominent in unplasticized nanocomposites. This was contrary to the expectation that the plasticizer will ultimately give rise to better performance of the nanoreinforcements by facilitating the dispersion of the nanowhiskers in the matrix. We believe in this case that the plasticizer was functioning as a lubricant between CAB and the whiskers and thereby weakened the interface to some extent, even with the better dispersion.

Transparency

The spectroscopic results of the transparency of CAB and the CAB nanocomposites are shown in Figure 5. It can be seen that the transparency was slightly reduced for CAB nanocomposites and decreased with increasing amount of whiskers. Below 400 nm, the transmittance is low and the UV-light is effectively blocked by the whiskers where as the visible light is transmitted. The values of percent transmission at 400 and 540 nm are given for comparison in Figure 5. The percent transmission at 540 nm

TABLE II
Storage Modulus and $\tan \delta$ of CAB and CAB Nanocomposites

Sample code	Storage modulus E' (GPa)			$\tan \delta$ peak (°C)
	30°C	80°C	155°C	
CAB	1.3 ± 0.1	1.0 ± 0.1	2.9 ± 0.8	154 ± 0
CAB/CNW5	1.4 ± 0.4	1.2 ± 0.2	25.6 ± 0.4	157 ± 0
CAB/CNW10	1.8 ± 0.1	1.4 ± 0.6	85.4 ± 0.0	155 ± 0
CAB/TEC	1.2 ± 0.0	0.8 ± 0.0	0.4 ± 0.1	147 ± 1
CAB/TEC/CNW5	1.3 ± 0.0	0.8 ± 0.0	0.4 ± 0.2	142 ± 1
CAB/TEC/CNW10	1.4 ± 0.1	1.0 ± 0.1	2.1 ± 0.9	147 ± 1

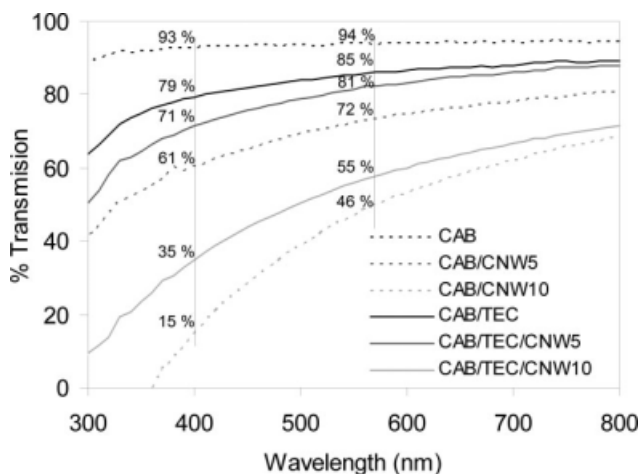


Figure 5 Percent transmission of UV visual light through plasticized and unplasticized CAB and CAB cellulose nanocomposites.

decreases with the addition of 5 and 10 wt % of CNW for unplasticized CAB as well as plasticized CAB. The decrease in transparency with the addition of nanoreinforcements is less in the plasticized nanocomposites compared with the unplasticized ones. The transmission of light is lowest for CAB/CNW nanocomposite with 10% whisker content.

It was found in our earlier study on CAB matrix that the transparency was reduced drastically from 74.5% to 6.5% with addition of 5 wt % microcrystalline cellulose as reinforcement.²² Studies on polylactic acid nanocomposites containing 5 wt % well-dispersed nanoclays also showed lower transparency compared with pure PLA.²⁹ The data on the transparency from the present study indicate very good nanoscale dispersion of CNWs in the CAB matrix. The plasticized CAB/CNW composites were more transparent than the corresponding unplasticized ones, which indicates that the plasticizer helps the uniform dispersion of whiskers.

Thermal degradation

The TGA results of the thermal stability of CAB and the CAB/CNW nanocomposites are graphically represented in Figure 6. In Figure 6(a), which represents unplasticized CAB and nanocomposites, it can be clearly seen that there is a shift in curves of CAB containing 5 and 10 wt % cellulose nanowhiskers compared with CAB, indicating that the whiskers had actually enhanced the properties of CAB, making it more thermally stable. The TGA results of plasticized CAB/CNW nanocomposites shown in Figure 6(b) indicate that the onset of degradation is delayed substantially with the addition of CNWs and the thermal stability increased as a function of increase in CNWs. The positive shift in the thermal

degradation temperatures for the unplasticized and plasticized nanocomposites can be attributed to the delay in the escape of degradation products from the bulk materials by diffusion, in the presence of CNWs. This improvement in thermal degradation temperatures even at high whisker content is considered to be an indication for efficient dispersion of whiskers in the matrix, which in turn hinders the diffusion and escape of the degradation products.

CONCLUSIONS

The cellulose acetate butyrate nanocomposite films were successfully produced by dispersing cellulose nanowhiskers in the CAB matrix with and without plasticizer in a nonaqueous polar solvent as the dispersing and casting medium. The whiskers produced by HCl hydrolysis were well dispersed in the nonaqueous medium. The AFM results showed that the whiskers with a diameter of ~ 17 to 19 nm were homogeneously dispersed in the CAB matrix in the case of both plasticized and unplasticized nanocomposites.

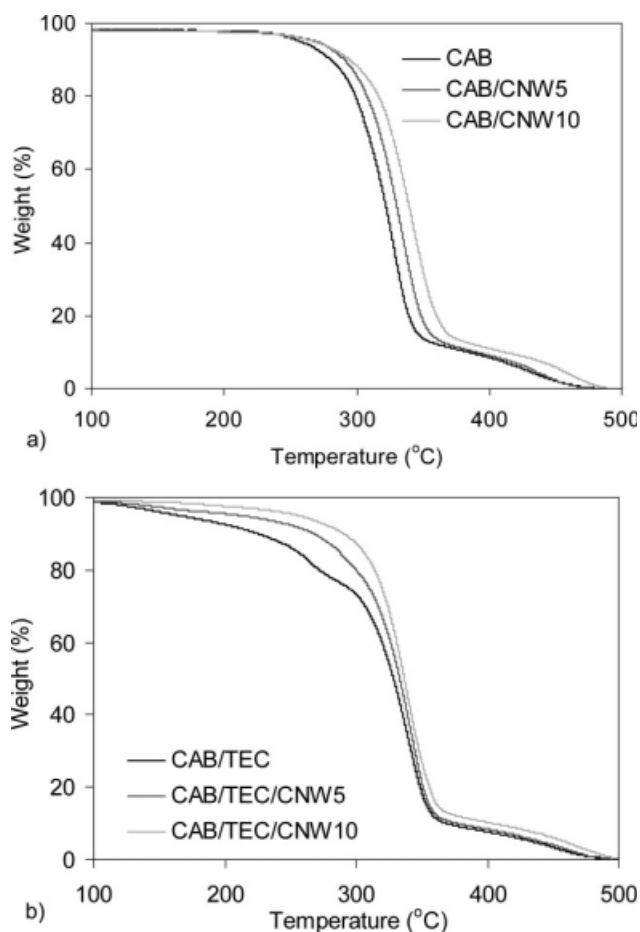


Figure 6 Thermograms comparing the thermal stability of CAB and its nanocomposites: (a) unplasticized, (b) plasticized.

The DMTA results showed an increase in the storage modulus of CAB reinforced with 5 and 10 wt % CNW for both unplasticized and plasticized nanocomposites. The increase in storage modulus is more remarkable in the temperature range of polymer relaxation and above. The $\tan \delta$ peak temperature showed a slight positive shift compared with that of CAB in the case of unplasticized nanocomposites only.

The UV visual spectroscopy data showed that the transparency of a material was not affected drastically when cellulose nanowhiskers were introduced into the transparent matrix. The plasticized nanocomposites had better optical clarity than unplasticized nanocomposite, possibly indicating a better dispersion of whiskers in the plasticized system.

The TGA results of both unplasticized and plasticized nanocomposites showed a substantial improvement in the thermal stability of the CAB when reinforced with cellulose nanowhiskers. The thermal stability increased with increase in CNW content, indicating efficient dispersion of whiskers in the matrix even at higher CNW content.

The current study leads to the conclusion that plasticizers have a positive effect on the dispersion of nanowhiskers in the matrix, transparency, and thermal stability. On the other hand, the DMTA data indicate that despite better dispersion, the plasticizer might weaken the interface and gives a lower percentage of improvement in properties compared with the unplasticized system.

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