

Preparation and Properties of Bio-Nanoreinforced Composites from Biodegradable Polymer Matrix and Cellulose Whiskers

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ABSTRACT: Crystalline cellulose was extracted from one of the cheapest source; grass by alkali, acid, and mechanical treatments. To evaluate the reinforcing effect of this filler, biodegradable polymer matrix, polylactic acid (PLA) was used and samples were prepared at different concentrations. The modified whiskers were also used as filler to examine the effect on mechanical properties. Crystallinity, thermal behavior, surface morphology and functional group variation was monitored through, XRD, TGA, SEM, and FTIR respectively. The properties were largely depending on the concentration of filler whereas; modification of hydroxyl groups did not exhibit remarkable change in mechanical properties. Thermal resistance was decreased in comparison of neat matrix and reduction in crystallinity

was also observed for composites, regardless of filler nature. It was thought that the hydrophilicity of cellulose could be altered by modifying its hydroxyl groups, thereby promoting dispersion. However, the possibility of phase separation was increased, and the thermal stability of the composites gradually decreased with increasing filler load in the matrix. In the examined systems, it was observed that improvement of reinforcing capacity may not only depend on the chemical compatibility between matrixes but also some compositional and physical parameters may be responsible for variation in properties. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2493–2501, 2010

Key words: cellulose; Biocomposites; biodegradable polymer

INTRODUCTION

There is increasing interest in the nanoreinforcement of polymers, because it may not only tremendously alter the mechanical properties of the resultant composite but also reduce its weight. Several nanofillers and their effects on polymer properties have been studied to optimize the cost-performance ratio. Recently, a renaissance in the use of fillers from natural resources has occurred, mainly for the purpose of introducing an eco-friendly character to the resultant composites.¹ Biofiber-based composites can contribute significantly to an automotive manufacturer's final goal by providing 30% weight and 20% cost reductions.²

The major challenges in replacing conventional glass-reinforced plastics with cellulose fiber-based

products are stability during storage and use, and complete environmental degradation upon disposal.³ Unfortunately, natural fiber composites do not reach the same level of strength as glass fiber composites, primarily because of the poor compatibility of natural fibers with the generally hydrophobic host polymer matrix. Apart from incompatibility and dispersion considerations, there are compositional parameters such as filler content, particle size, and use of coupling agents that also determine the fate of the resultant hybrids. Furthermore, there have been reports of selective consumption of the biological part of composites by microbes, leaving behind intact, harmful, nonbiodegradable polymer fragments.^{4,5} Therefore, cellulose fiber-reinforced composites made of biodegradable polymer matrices such as polylactic acid (PLA) are considered to be the most environmentally friendly option, owing to their complete conversion to water and carbon dioxide during microbial attack, without leaving harmful residue.

Cellulose fibers can be blended with PLA either by melt compounding in the presence of adequate compatibilizer or by graft polymerization of the monomer on a cellulose surface. Both processes may be associated with incompatibility, thermal chain

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scission of the matrix, and nonhomogenous and costly grafting reactions. Additionally, the concentrations and orientations of the microfibers and compatibilizer are critical to achieving the desired mechanical properties. Recently, it has been observed that highly crystalline cellulose has a unique and outstanding potential to increase the material properties of a composite, compared with those of unfilled polymer matrix or their microcomposite counterparts, at lower filler concentrations.^{6–8} The extended chain conformation and fibril morphology of cellulose result in significant load-carrying capability. Depending on their origin, microfibrils have diameters ranging from 2–30 nm and lengths that can reach several tens of microns.⁹ Each microfibril can be considered as a string of cellulose crystals linked with amorphous domains. The amorphous regions are oriented randomly in a spaghetti-like arrangement, leading to lower density, and are susceptible to acid attack. Hydronium ions can penetrate the cellulose chains at these amorphous domains, promoting the hydrolytic cleavage of glycosidic bonds and releasing individual crystallites.^{10,11} Mechanical treatments such as ultrasonification of these charged microcrystallites (broadly referred to as whiskers) disperse the aggregates, producing colloidal suspensions.

The high aspect ratio and modulus of whiskers (density, 1.5 gm/cm³; tensile strength, ~ 1 GPa; Young modulus, ~ 150 GPa⁶) are expected to improve the mechanical properties of the resultant hybrids without unbalancing their environmentally friendly nature. Cellulose whiskers have been employed for reinforcing silk fibroin,⁷ cellulose acetate butyrate,⁸ starch,¹⁰ poly(lactic acid),¹¹ polyvinyl alcohol,^{12,13} and other plastics.¹⁴ They have been extracted from many resources such as algal (valonia), wood, tunicate, sugar beet, brown algae (Oomycota), and bacteria.^{9,25} Nevertheless, for cellulose whiskers to be useful as nanofillers for industrial applications, several disadvantages must be overcome, including their time consuming preparation procedures with very low yield, highly hydrophilic surface, lack of commercial availability, poor dispersion due to a tendency for agglomeration, low thermal stability, and most importantly, comparatively higher cost related to their sources.

The dispersion of cellulose whiskers in organic solvent is very important and may be increased by the surface modification of cellulose crystals to enhance the reaction between surface hydroxyl groups and different reagents.^{18,19} In the present work, cellulose whiskers were obtained from common lawn grass and used, after modification, to prepare composites with PLA, using a solution method. The main objective of this extended¹⁷ work was to elucidate in detail the effects of cellulose

modification on the thermal and mechanical characteristics of the resultant hybrids and to analyze the potential practical application of whisker-reinforced materials.

EXPERIMENTAL

Materials

Chloroform, maleic anhydride (MA), diisopropylamine, acetone, and polyethylene glycol were obtained from Dae Jung Chemicals and Metals (Gyeonggi-go, Korea) and were used after drying and purification as required. PLA (specific gravity, 1.24 g cm⁻³; melting density at 230°C was 1.08–1.12, weight-average molecular weight (M_w) of 195×10^5 g mol⁻¹ and polydispersity of 1.88 as determined by gel permeation chromatography (GPC) was kindly donated by Natureworks LLC and was reprecipitated after dissolving in the appropriate solvent.

Characterization fourier transforms infrared spectroscopy (FTIR)

Attenuated total reflectance infrared (ATR-IR) spectra of samples were recorded using a FTIR 300E (Jasco) spectrometer. The incident beam angle was 45°. For each measurement, 60 scans were acquired, with a spectral resolution of 4 cm⁻¹. WinFirst software version 3.57 (Mattson Instruments) was used for the acquisition and elaboration of IR spectra. For the measurement of intensity at a particular wave number, two samples of each specimen were tested and the results were averaged.

X-ray diffraction (XRD)

Wide-angle X-ray diffraction (XRD) was used to measure crystallinity characteristics. XRD patterns were obtained using a Rigaku (Japan) diffractometer with Cu-K α radiation at 50 kV and a scan rate of 1°/min. The samples were exposed for a period of 14 s for a specific range. The wavelength of the source was 1.54 Å.

Scanning electron microscopy (SEM)

SEM microscopy (DS-130C, Topcon) of gold-coated samples was used to study the morphological changes at various stages of treatment.

Transmission electron microscopy (TEM)

The effects of modification or treatment on the shape and size of the fibers were monitored by TEM (JEOL 2010), operating at an accelerating voltage of 100 kV. Samples were prepared by placing one drop of

TABLE I
Composition of Different Samples (NCM and NC
Represent Modified and Unmodified Filler Respectively
Whereas, Number Exhibited the Concentration (%) Used
to Fill the Matrix)

| No. | Sample name | PLA (%) | Filler (%) |
|-----|-------------|---------|------------|
| 1 | PLA | 100 | 0 |
| 2 | NCM 5 | 95 | 5 |
| 3 | NCM 7 | 93 | 7 |
| 4 | NCM 10 | 90 | 10 |
| 5 | NC 5 | 95 | 5 |
| 6 | NC 7 | 93 | 7 |
| 7 | NC 10 | 90 | 10 |

cellulose suspension on a carbon grid and keeping this under vacuum overnight, at 50°C.

Mechanical properties

Samples of ~ 2.3 mm thickness were obtained in a greased Petri dish. Specimen strips (5 mm wide with 20-mm lengths between grips) were tested by Instron for comparative mechanical properties, after cleaning in an ultrasonic cleaner for 10 min to remove any physically bonded entity. At least six specimen strips were tested for each composition, and the comparative results are presented as an average.

Thermo gravimetric analysis (TGA)

TGA was conducted with a model TG/DTA 32 (Seiko, Torrance, CA) thermal analysis system. The TGA scans were recorded from 50 to 500°C at 10°C/min, under nitrogen.

Preparation of composites

After physical cleaning and alkali soaking, the grass powder was treated for 1 h in 2% alkali solution. A mixture of acetate buffer and chlorite solution was used to bleach the grass until the colored substances were removed. The obtained suspension, after centrifugation and sonication, contained microfibers and nanofibers of approximately 10–60 nm width and 200–700 nm length, abbreviated as cellulose whiskers.^{15,16} The obtained nanodimension cellulose crystals were modified with MA. The processing of cellulose is restricted by its limited solubility in common solvents and an inability to melt due to its numerous inter- and intramolecular hydrogen bonds. The appropriately modified reaction was carried out in the presence of a catalyst after neutralization and solvent exchange.^{18,19} MA solution (10%, w/w) was added to a two-necked flask, equipped with an inlet and outlet for nitrogen, that contained cellulose (50 μmol/mg) and diisopropylamine. The mixture was kept at room temperature for 5 h and

then heated until 70% of the solvent was removed. The samples were washed many times with distilled water, and the solvent was exchanged again. PLA was mixed in a chloroform suspension of whiskers, keeping the required concentrations, and polyethylene glycol (5% w/w, M_w 1000) was added by sonication for 15 min (5 × 3 min) at 45% power output and 5 × 10% cycles. The compatibilized solvent-cast specimens of filler, ~ 2.3 mm thick, were obtained in a greased Petri dish. The specimen specifications are listed in Table I.

RESULTS AND DISCUSSION

Characterization

Broadly, plant cell walls may contain semicrystalline cellulose fibrils, a few nanometers thick, embedded in an amorphous matrix of natural polymers such as hemicelluloses and lignin. The presence of cellulose microfibrils provides extraordinary strength to plant cell walls. Traditionally, the extraction of cellulose fibrils has been followed by FTIR to monitor changes in functional groups such as the carboxyl and hydroxyl regions (1800 and 1600 cm^{-1} for C=O and 3600–3000 cm^{-1} for OH vibrations), as these groups may undergo significant changes during the conversion of macro- to nanofibers (Table II).^{19–21} The peak assigned to methyl ester groups (1245 cm^{-1}) vanished, establishing the removal of hemicelluloses,²⁰ and the peak for lignin (1510 cm^{-1}) was minimized, supporting the elimination of lignin from the treated material. Acid treatment breaks the linkages in the interfibrillar region, and cellulose then undergoes extensive degradation, which may cause defects in its structure. The peak at 1427 cm^{-1} , which is related to the crystalline nature of the fibrils, increased in size in agreement with the XRD measurements, strongly supporting the assumption of an increased crystalline nature of cellulose after extraction. The increase in C=O bands near 1730 cm^{-1} was interpreted as a result of carbohydrate degradation.²²

TABLE II
Different Characteristic Peaks in FTIR During
Extraction of Cellulose Whiskers

| Component | Wave number (cm^{-1}) | Band assignment |
|---------------|----------------------------------|-----------------------------------------|
| Lignin | 1510 | Aromatic skeletal vibrations |
| | 1423 | Aromatic skeletal vibrations |
| | 1221 | C–C, C–O stretch |
| | 1140 | Aromatic C–H in plane deformation |
| Hemicellulose | 1730 | C=O stretch side groups |
| | 1600 | C=O stretch side groups |
| | 1245 | C=O side groups |
| Cellulose | 1160 and 1107 | Antisymmetric C–O–C and ring stretching |

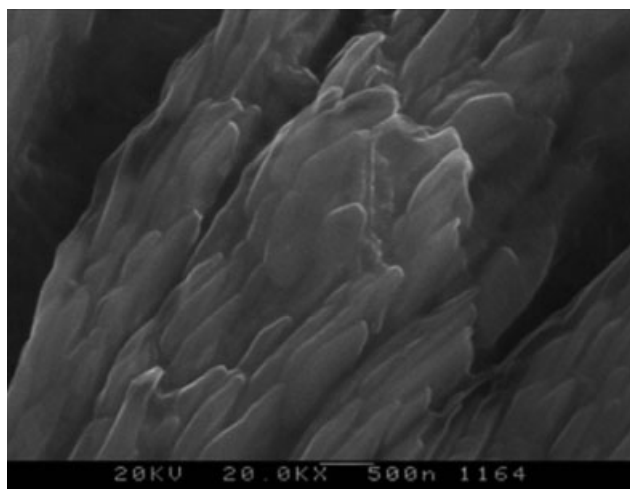


Figure 1 SEM micrograph of acid treated samples.

The bundles of fibers were constituted by small “packets” of microfibrils (Fig. 1), which were not separated perfectly but were arranged one above each other with reduced thickness. The nanocrystals were well separated after mechanical treatment by sonication, as depicted in Figure 2. Typical XRD data for cellulose crystals and vacuum-dried grass, after passing through sieves and refluxing in ethanol and water solution, indicated changes in crystallinity, as evidenced by the pattern and shapes of the diffraction peaks. It has been observed that a broader reflection profile may result from a smaller crystal size, which is explained by the merging of two peaks as a shoulder.^{21–24} Two additional peaks originated at $2\theta = 15.5$ and 16.2° , indicating the presence of higher crystallinity. Thermal analysis suggested the occurrence of two pyrolysis patterns,²³ in which degradation took place over a temperature range of 220–500°C and was associated with an initial moisture loss at around 120°C. The untreated fibers exhibited many steps of degradation, including water loss at 110°C and hemicellulose decomposition at 280°C. Decomposition beyond 280°C was not observed in the case of extracted whiskers, further supporting the removal of hemicellulose during alkali treatment. It has been found that cellulose crystals may begin to decompose at temperatures lower than those for larger microcrystals, mainly because of the increasing numbers of free-end chains at the surface.²³ The increased initial degradation temperature corresponds to moisture in cellulose crystals and could be attributable to the strong adhesion of moisture molecules to highly exposed fibers of greater surface area.

The FTIR spectrum of modified cellulose is shown in Figure 3. The appearance of a peak at around 1737 cm^{-1} may reflect C=O stretching of the ester bond, generated by the reaction between MA and

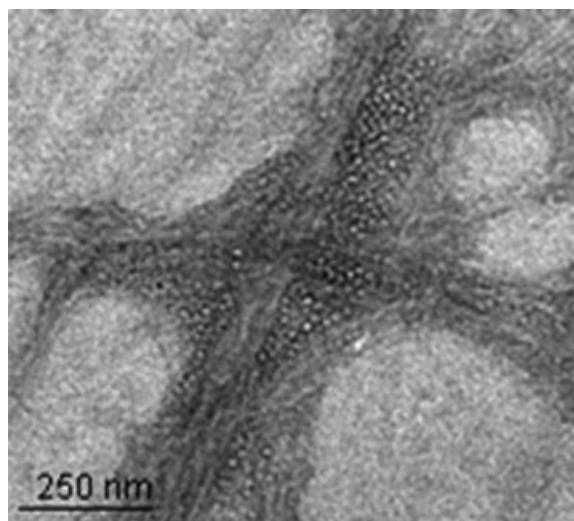


Figure 2 TEM of cellulose water suspension (1 drop on carbon grid).

the fiber. As this region also represents the presence of ester moieties found in the natural matrix of cellulose, it complicates the estimation of esterification reactions. In the present system, the intensity of this peak was greater for the modified cellulose than for the untreated fibers,¹⁵ and this was attributed to the insertion of ester groups. The increase in C—O—C ester stretching at 1162 cm^{-1} further supports the formation of ester bonds.

Scanning electron microscopy

SEM was employed to examine the surface characteristics of cellulose-reinforced composites. Although the examined specimens were too small for evaluate of the whole composite, SEM was very useful for a

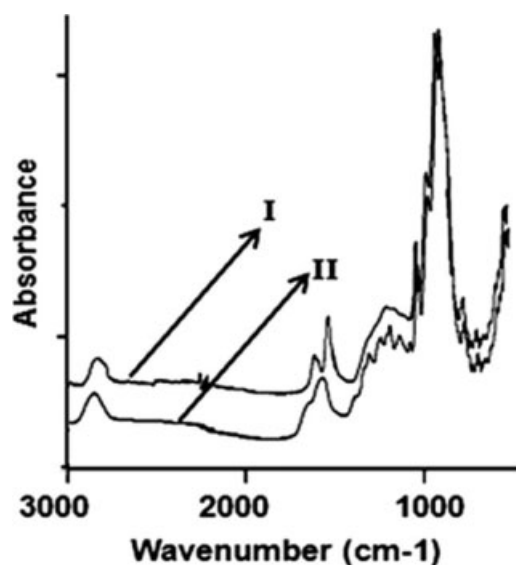


Figure 3 FT-IR spectra of samples (I, II after and before modification respectively).

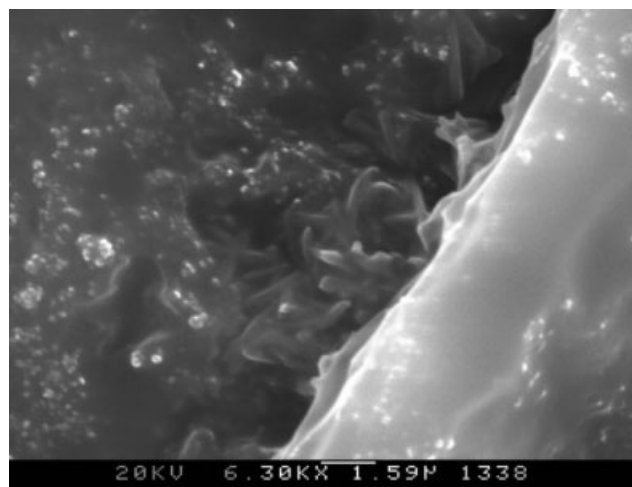


Figure 4 SEM of NC 7 samples exhibiting the distribution of cellulose whiskers in the form of shiny dots.

qualitative analysis of compatibility by monitoring the extent of filler dispersion. A typical SEM micrograph of NC 7 is presented in Figure 4. The many white dots on the surface represent cellulose whiskers, possibly corresponding to transversal sections of cellulose whiskers, and their concentration may be considered as a direct function of the composition of cellulose in composites.²⁵ Visible examination (Fig. 5) revealed the flexible films of the composites, where all NCMs, in general appeared similar by SEM analysis before surface fracture (Figs. 6 and 7). Fine cellulose whiskers tended to combine to form strongly bonded aggregates, with further joining to produce even larger structures termed agglomerates. Morphological examination of the treated and untreated fibers showed a significant difference in surface smoothness, where the fractured surface showed traditional splitting of two portions. Fiber pull out has been clearly observed in composites of PLA and cellulose, and it was suggested that interfacial failure was responsible for the fatal failure of the composites.²⁶ SEM micrographs of NC 5, 7, and 10 are displayed in Figures 7(a–c). The NC 5 specimen exhibited small kinks on the surface, whereas the filler distribution was not conclusive. The surface of unmodified filler composites exhibited round domains of small clusters, which may represent the aggregation of cellulose crystals. The surface was rough and nonhomogenous, and the large gap between fiber clusters and the matrix indicated poor filler dispersion in the NCM specimens. The fracture surfaces of NCMs, shown at different magnifications in Figure 8(a, b), further support the weaker adhesion of the two phases in the composites. The uneven distribution of the highly hydrophilic cellulose phase apparent in the current study is indicative of fewer matrix chain interactions and less reinforcement at the interphase, which are gen-

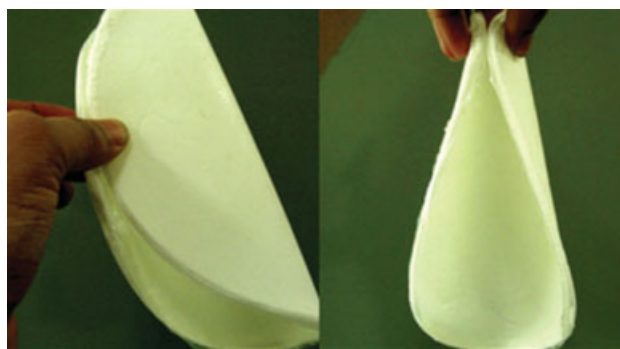


Figure 5 The solvent cast samples of NCM 5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

erally associated with a poor load transfer capacity from one phase to the other and results in comparatively poorer mechanical properties of the composites.

XRD analysis

To qualitatively analyze the crystalline nature of the composites, XRD was performed. PLA exhibited a well-established XRD peak at around $2\theta = 16.5^\circ$; this was diffuse in the composites, indicating the presence of lower crystallinity compared with neat PLA. It was concluded that the crystallinity of the composites had decreased, because the two peaks present in cellulose crystals ($2\theta = 15.5$ and 16.2°) were not distinct in any sample, but overlapped with the PLA diffraction pattern. This trend was the same for all hybrids, including the composites of unmodified cellulose crystals, and no significant difference was measured between the NCM 5 and NCM 7 specimens (Fig. 9). The peak at around $2\theta = 22.3^\circ$, reflecting the crystalline state of the cellulose filler, was roughly similar for all samples. However, a broad,

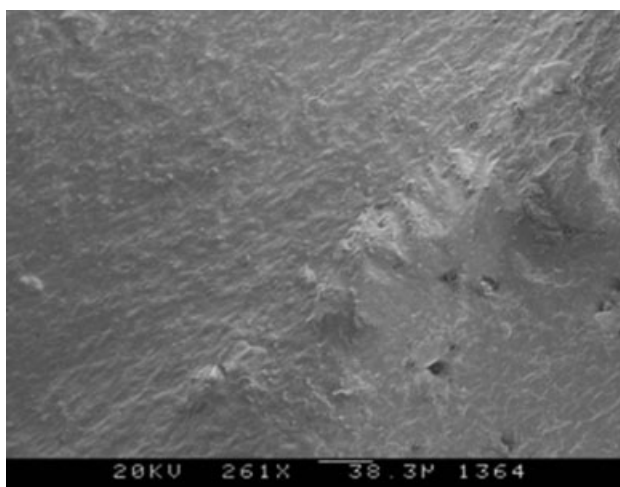


Figure 6 SEM of NC 5 with voids on the surface.

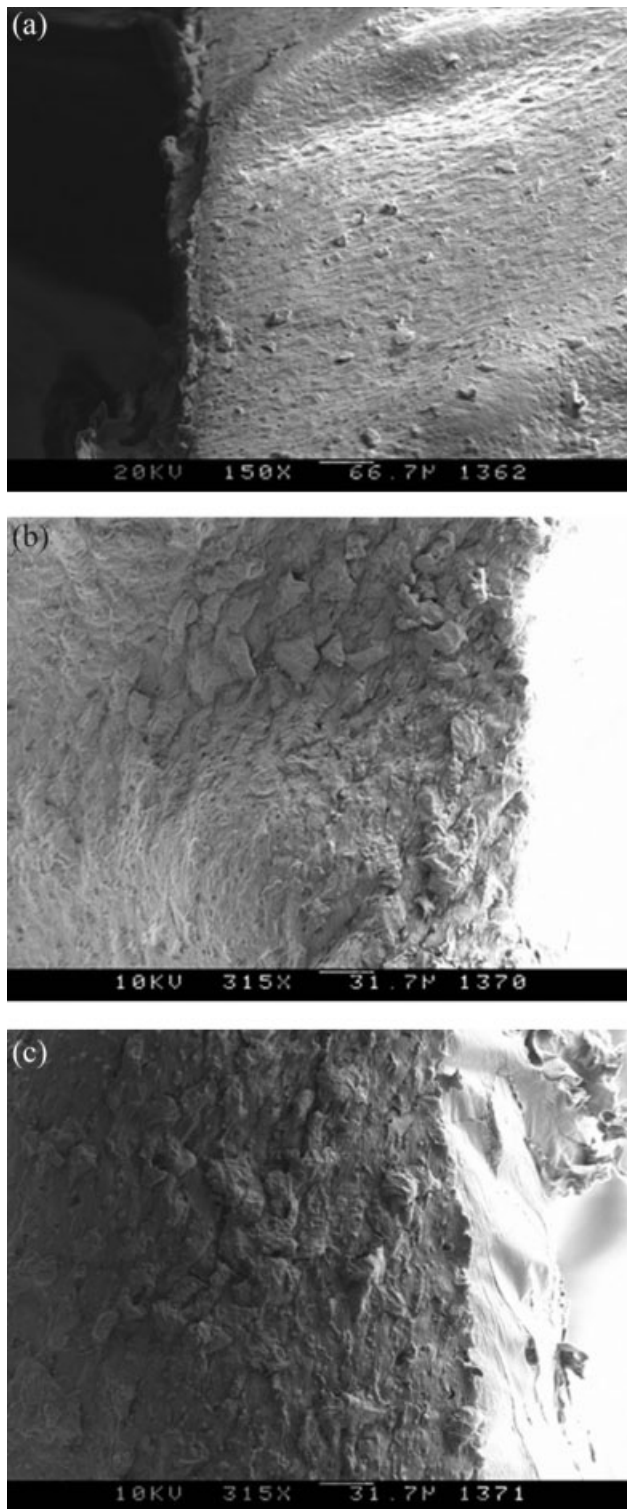


Figure 7 (a) SEM micrograph of NC 5 showing the edge of sample; (b) SEM micrograph of NC 10 showing the edge of sample; (c) SEM micrograph of NC 7 showing the edge of sample.

hump-like peak formed with the NCM 10 sample, indicating a greater reduction in the crystallinity of the matrix with filler content above 7%. There are reports of changes in the crystallinity of composites

upon addition of cellulose nanofillers. A significant increase in crystallinity of sorbitol plasticized starch was observed when the tunicate whisker content was increased in composites; this was ascribed to the anchoring effect of cellulose fillers acting as a nucleating agent, and the same effect was reported for polyoxyethylene filled with nanowhiskers.²⁷ On the contrary, cellulose nanofiller showed no nucleating effect in an isotactic polypropylene matrix, either untreated or grafted with MA.²⁵ Thus, the nucleating effect may be governed by surface chemical considerations. The modification of hydroxyl groups may have an adverse effect on the crystallinity. After modification with MA, a decrease in the crystallinity of cellulose chains has been observed and diffuse peaks resulted. Studies of the esterification of cellulose with different chemical reagents^{22,24} concluded that the reagent first reacted with disordered chains on the surface of crystals, because the highly ordered crystalline structure prevents penetration by reagents. This process may reopen the

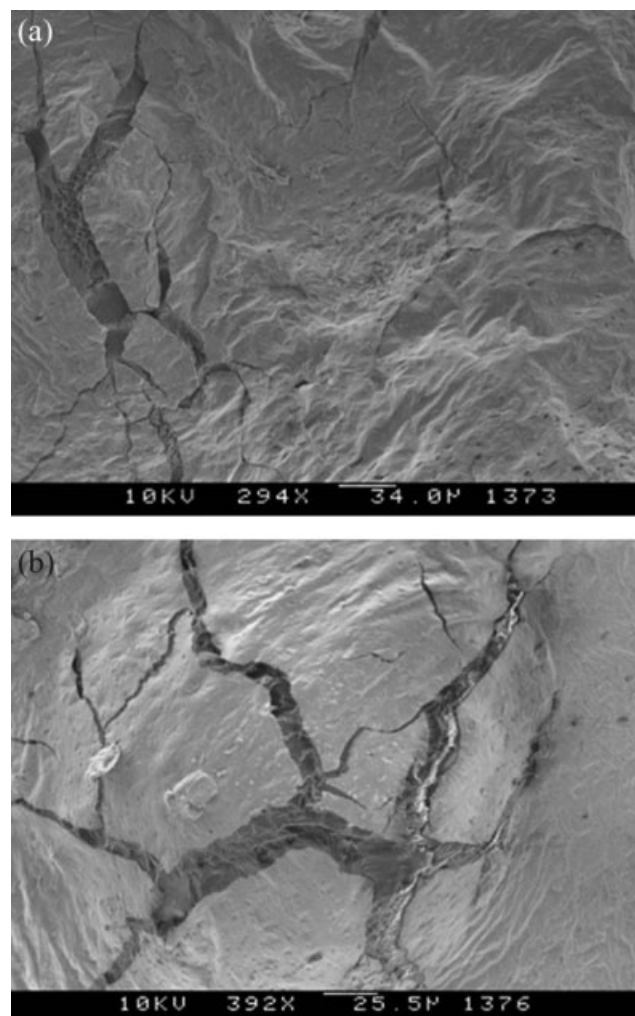


Figure 8 (a) Cracked surface of NCM 7; (b) cracked surface of NCM 7 at higher magnification.

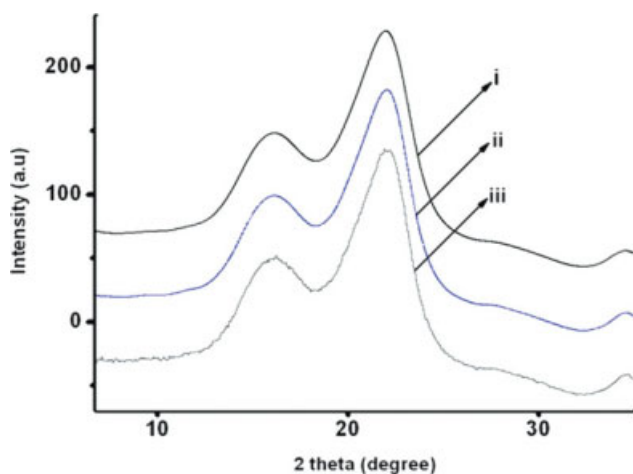


Figure 9 XRD graphs of NCMs. i, ii, and iii are for 5, 7 and 10% filler content respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydrogen-bonded cellulose chains that contribute to crystallinity and finally reduce the crystallinity of the remaining portion.

Mechanical properties

The mechanical properties of composites may be associated mainly with the geometrical ratio of filler, processing methods, compatibility of filler with matrix, and filler-to-filler interactions. The comparative mechanical properties revealed that the modulus increased with the filler, regardless of chemical treatment (Table III). The elongation of samples decreased for NCM 7 and 10, indicating that the brittleness of PLA increased with the addition of cellulose reinforcements. NCM 5 exhibited no significant difference in elongation compared with the matrix; this was attributed to less agglomeration and the optimum number of modified fibers, compared with NCM 7 and 10. The unmodified filler had a more adverse effect on composite strength, and a drastic decrease occurred at 7 and 10% filler content. This observation was further associated with the aggregation and rough dispersion of filler within the matrix. A decrease in the mechanical properties of

TABLE III
Mechanical Properties of Different Composites

| Sample | E-modulus (GPa) | Tensile strength (MPa) | Elongation at break (%) |
|--------|-----------------|------------------------|-------------------------|
| PLA | 4.5 | 50.9 | 2.3 |
| NCM 5 | 4.8 | 51.7 | 2.1 |
| NCM 7 | 4.9 | 40.2 | 1.4 |
| NCM 10 | 6.2 | 37.6 | 1.2 |
| NC 5 | 4.7 | 50.9 | 1.6 |
| NC 7 | 4.8 | 37.2 | 1.2 |
| NC 10 | 5.9 | 35.4 | 1.1 |

the sonicated neat PLA was observed, due to the degradation of matrix chains. The composites possessed higher or equivalent properties compared with the sonicated sample for a similar time, further supporting a reinforcing effect of cellulose; this may be attributed to increased compatibility between the matrix and the filler with modified hydroxyl groups. SEM of specimens, particularly NCM 7 and NC 10, revealed the formation of large domains surrounded by polymer matrix, and these were responsible for the poor mechanical characteristics of these hybrids (Figs. 7 and 8). For NCM 7, NCM 10, NC 7, and NC 10, the strength of the composite decreased with increased filler concentration. With SEM, the edges of samples clearly showed lump-like structures in NC 10; whereas, a comparatively more interconnected distribution was seen in NCM 7. The modulus was similar between NCM 5 and NC 5, and their tensile strengths were not substantially different. The data obtained in the present system indicate that at up to 5% filler content, the modification has no significant effect; at 7 and 10% filler content, the modulus increased as has been observed in macro fiber reinforced composites.^{2,3,7} The composites of modified cellulose whiskers showed remarkable differences in mechanical properties compared with the composites of unmodified fillers in all of the specimens examined; this was likely due to the increased compatibility between phases, as has been observed classically in different natural fiber-reinforced composites. These results indicate presence of some other factors during reinforcement by cellulose whiskers to decide the final properties of composites. In fact, the properties of cellulose whisker-reinforced composites depended mainly on the processing technique, which depends generally

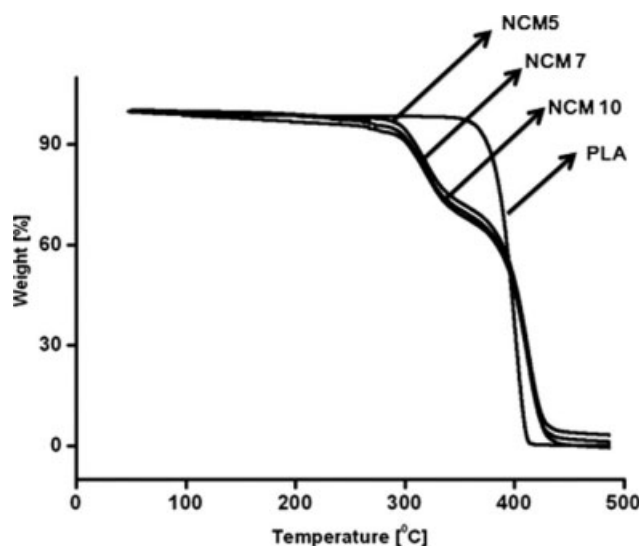


Figure 10 Thermal resistance of different samples prepared from modified cellulose whiskers.

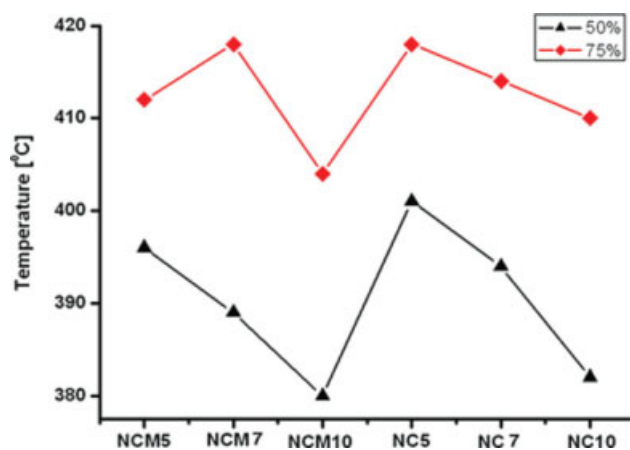


Figure 11 Temperature of 50 and 75% weight loss in the cellulose whisker reinforced composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

on the composition, morphology, and interfacial properties. As cellulose whiskers have a high affinity for water, the best reinforcing effect was observed when water was used as the medium for preparing composites.¹⁰ Cellulose nanowhiskers generate a rigid network owing to strong interactions via hydrogen bonding between adjacent whiskers. The percolated network may cause the effective reinforcement of the matrix, with filler-to-filler interactions being critical to the final mechanical properties.¹³ The agglomerated moieties may be responsible for further increasing the strength of the filler-to-filler interconnected network generated through electrostatic hydrogen bonding between two atoms of different electronegativity.²⁵

Thermal analysis

The degradation of polysaccharides and hemicellulose/cellulose have been observed to start at temperatures of 220 and 290°C, respectively.²⁴ The modification of hydroxyl groups may alter the thermal stability of fibers. The composites showed lower thermal stability and faster degradation in comparison with commercial PLA. The changes in degradation temperatures reported with the modification of cellulose fibers depended on the type of modification agent applied; maleic and succinic anhydride treatments caused a decrease in thermal stability, and fatty acids, acrylonitrile, and methyl methacrylate increased thermal resistance.²⁶ The weight variations of the composites at different temperatures are shown in Figure 10. NCM 5, NCM 7, and NCM 10 displayed a linear decrease in the temperature at 50% weight loss (Fig. 11). Neat PLA exhibited 50% weight loss at around 403°C and 75% loss at 420°C. In contrast, for NC 5, NC 7, and NC 10, 50% weight loss occurred at around 396, 394, and 380°C, respectively. Thus,

higher filler content was associated with lower thermal stability. A similar trend was observed for composite samples with unmodified cellulose, which were degraded at slightly higher temperatures than the NCMs. The alkaline and acid treatment is believed to degrade amorphous regions of a composite and increase the degree of crystallinity, which consequently should lead to higher heat resistance and increased temperature of thermal degradation. The lowering of thermal resistance in the present study might have been caused by the possible generation of defects along the longitudinal cellulose chains during acid treatment or the unfolding of ordered cellulose chains due to the esterification reactions.

CONCLUSION

The initial aim of the present research was to reduce the cost of composite polymers by using an inexpensive source of cellulose whiskers (i.e., grass) and to reduce the aggregation of the filler by modifying the cellulose. Cellulose whiskers extracted from grass were used to reinforce PLA. Chemical de-lignification altered the orientation of the cellulose chains, resulting in microcrystals consisting of cellulose whiskers. Owing to a very high aspect ratio and the presence of hydroxyl groups on the surface, the unmodified whiskers tended to agglomerate inside the matrix, producing heterogeneous filler-reinforced composites with numerous locally oriented domains of cellulose crystals. It was thought that the hydrophilicity of cellulose could be altered by modifying its hydroxyl groups, thereby promoting dispersion. However, the possibility of phase separation was increased, and the thermal stability of the composites gradually decreased with increasing filler load in the matrix. In general, modified cellulose whiskers may be useful for overcoming dispersion problems in some cases and for reinforcing phase for different polymer matrices.

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