Polycaprolactone/Modified Bagasse Whisker Nanocomposites with Improved Moisture-Barrier and Biodegradability Properties

Mohammad L. Hassan,[1,2] **Julien Bras,**[3] **Enas A. Hassan,**[1] **Shaimaa M. Fadel,**[1] **Alain Dufresne**[3]

[1]*Cellulose and Paper Department, National Research Center, Dokki, Giza 12622, Egypt*
[2]*Center of Excellence for Advanced, Advanced Materials and Nanotechnology Group, National Research Center, Dokki, Giza 12622, Egypt*
[3]*Laboratoire de Génie des Procédés Papetiers (LGP2), Unité Mixte de Recherche (France) Centre National de la Recherche Scientifique 5518, Grenoble Institute Polytechnique de Grenoble (INP), Pagora 461, Rue de la Papeterie, 38402, Saint-Martin-d'Hères*

ABSTRACT: Bagasse whiskers isolated from bleached bagasse pulp were chemically modified with *n*-octadecyl isocyanate in the presence of dibutyltin dilaurate as a catalyst. The modified cellulose whiskers were used in ratios from 2.5 to 15% with polycaprolactone (PCL) polymer to prepare nanocomposite films by a solution/casting technique. The prepared nanocomposites were characterized with regard to their biodegradability in soil and moisture-barrier, moisture sorption, mechanical, thermal, and thermomechanical properties. The use of the modified cellulose whiskers resulted in improvements in the moisture-barrier, biodisintegration, and tensile properties of PCL. The nanocomposites containing different modified whisker loadings had very low moisture absorption (1.88–2.49%) after 4 weeks of exposure to 75% relative humidity, but these values were slightly higher than that of neat PCL (1.79%). Modified whiskers in the PCL matrix did not noticeably affect the glass-transition and melting temperatures of PCL. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: biodegradable; biopolymers; cellulose; nanocomposites

INTRODUCTION

Cellulose whiskers have attracted attention as reinforcing fillers in nanocomposites because of their low cost, renewability, and the wide availability of the starting raw materials. Their length is usually up to several hundreds of nanometers, and their diameters are up to 10 nm. Cellulose whiskers have the advantages of a very high surface area, rodlike morphology with a high aspect ratio, possibility of surface chemical modification, and low density compared to other inorganic fillers. They are promising reinforcing materials with good mechanical responses to stress and significant improvements in mechanical properties at very low volume fractions.[1–3]

One limitation of using cellulose whiskers is their noncompatibility and poor dispersion in hydrophobic polymers. This results in poor interfacial adhesion between cellulose whiskers and the polymer matrix and negatively affects nanocomposite properties. Thanks to the hydroxyl groups at the surface of cellulose, chemical modification with hydrophobic moieties makes it possible to prepare high-performance nanocomposites with hydrophobic polymer matrices. The surface modification of cellulose whiskers by acetylation, esterification with long alkyl chains, silylation, and polymer grafting have already been reported to impart the hydrophobic surface. The hydrophobic surface of modified cellulose whiskers has resulted in good dispersion in nonpolar solvents and interfacial adhesion with hydrophobic polymer matrices.[4,5]

Although most synthetic thermoplastic polymers are nonbiodegradable, polycaprolactone (PCL) is among the few synthetic biodegradable polyester polymers with a hydrophobic nature.[6] Composites of PCL with hydrophilic fillers require the use of compatibilizers or the modification of the surface properties of the hydrophilic filler to obtain high-performance composites. In the area of PCL/cellulose nanocomposites, cellulose whiskers from ramie fibers were grafted by PCL chains with various molecular weights with an isocyanate-mediated reaction. The grafting of cellulose whiskers with PCL chains induced a decrease in the modulus values and an increase in the strain at break of the prepared nanocomposites.[7] In another study, sisal whiskers and nanofibers were incorporated into the PCL matrix

Correspondence to: M. L. Hassan (mlhassan2004@yahoo.com).

after their modification with *n*-octadecyl isocyanate. No catalyst was used in the chemical modification, and the reaction was carried out only under heating at 110°C. The use of modified whiskers was found to increase the glass-transition temperature (T_g), melting temperature (T_m), and crystallinity of PCL and to enhance the mechanical properties without decreasing the elongation at break.[8]

Previous studies on the use of modified or nonmodified cellulose whiskers with PCL have not investigated the moisture-barrier properties of the PCL nanocomposites and the effect of the cellulose whiskers on the biodegradability of PCL. These two properties can be key selection parameters for packaging materials. Because of the rodlike nature of the cellulose whiskers and their high crystallinity, they are qualified to act as a barrier for the permeation of gases. However, in a previous study on the use of cellulose whiskers with natural rubber as reinforcing elements, the presence of cellulose whiskers increased the permeation of moisture across the rubber films because of their high hydrophilic character.[9] Therefore, the chemical modification of cellulose whiskers surfaces is expected to prevent such shortcomings and improve the barrier properties of nanocomposites of hydrophobic polymers in addition to improving the tensile properties.

In this study, cellulose whiskers isolated from bagasse were chemically modified with *n*-octadecyl isocyanate in the presence of dibutyltin dilaurate as a catalyst to improve the chemical modification (reaction time and extent) over the previously used method.[10] The modified cellulose whiskers were used with PCL to prepare nanocomposites by a casting/evaporation technique. The effects of the modified whiskers on the moisture-barrier, biodegradability, moisture sorption, mechanical, and thermomechanical properties of PCL were studied.

EXPERIMENTAL

Materials

Bagasse pulp was a Kraft pulp kindly supplied by Qena Co. for Pulp and Paper (Qena, Egypt). The chemical composition of bagasse was as follows: 70.6% α-cellulose, 26.8% pentosans, and 0.82% ash with a degree of polymerization of 1174.[9] PCL (number-average molecular weight = 42,500 g/mol, weight-average molecular weight = 65,000 g/mol), octadecyl isocyante (technical grade), dibutyltin dilaurate, ethyl alcohol, and toluene were obtained from Aldrich and were used as received.

Preparation of the cellulose whiskers

Cellulose whiskers were prepared by acid hydrolysis with sulfuric acid (65 wt %) at 45°C for 45 min as

described before.[9] The hydrolyzed pulp was centrifuged to remove the excess acid and dialyzed against water for several days with changing water until the pH was similar to that of distilled water. The obtained water suspension of hydrolyzed pulp was sonicated in an ice bath for 2 min with a 750-W Sonix ultrasonic processor (Sonics & Materials, Inc, Newtown, USA). The obtained cellulose whisker water suspension was kept in the refrigerator, and a drop of chloroform was added to prevent deterioration by microorganisms.

Chemical modification and characterization of the cellulose whiskers

The chemical modification of the cellulose whiskers was carried out as follows. The aqueous suspension of cellulose whiskers was solvent-exchanged to acetone and then to dry toluene by several successive centrifugations and redispersion by sonication to prevent aggregation. In a three-necked, round-bottom flask equipped with a reflux condenser, 3 g of whiskers in 100 mL of toluene was stirred and kept under a nitrogen atmosphere. An excess of *n*-octadecyl isocyanate (10 equiv = 16.9 g) was added slowly, and 2% tetrabutyltin dilaurate (on the basis of cellulose weight) was added as a catalyst. The mixture was heated to 70°C for 4 h. The modified nanoparticles were collected by centrifugation at 10,000 rpm at 10°C and washed several times with ethanol and by centrifugation to remove amines formed during the reaction and the isocyanates that did not react. Finally, the modified whiskers were put in a closed cellulose extraction thimble and purified by extraction of the residual impurities in a Soxhlet extractor with a toluene/ethanol mixture (1 : 1) for 8 h.

The modified whiskers were characterized by Fourier transform infrared (FTIR) spectroscopy with a 5000 spectrometer, (Mattson, Madison, Wisconsin, USA), by a KBr technique. Elemental analysis for nitrogen and carbon was carried by the Analysis Central Service of the Centre National de la Recherche Scientifique, Vernaison, France. Contact angle measurements were performed at room temperature on a disc of modified cellulose whiskers with an OCA20 instrument (DataPhysiscs Instruments, Filderstadt, Germany). Three different liquids (water, ethylene glycol, and diiodomethane) with different dispersive and polar surface tensions were used to determine the surface energy of both the unmodified and modified bagasse whiskers with an approach described previously.[11]

PCL/modified cellulose whisker nanocomposite preparation

Nanocomposite films were prepared by mixing of PCL solution in toluene with various percentages of

modified cellulose whiskers ranging from 0 to 15 wt %. The PCL and the cellulose whiskers were thoroughly mixed for 6 h and then poured in glass Petri dishes and left to air-dry. The obtained films were further dried *in vacuo* at 50°C for 6 h to remove residual toluene. The thickness of the obtained films was about 0.1 mm. The films were conditioned at 25°C and 50% relative humidity (RH) for 48 h before testing.

Water vapor permeability (WVP)

The static WVP of films was determined according to the 1995 ASTM standard. Film samples (60 cm^2 each) were conditioned at 25°C and 60% RH for 24 h and were then used to hermetically cover aluminum cups containing 5 g of anhydrous calcium chloride. The WVP was evaluated from the slope of the mass gain versus time curve. The WVP value of each film is reported as the average of these three values:

$$WVP(g\,m^{-1}s^{-1}Pa^{-1}) = \Delta m \times e/[A \times \Delta t \times \Delta P]$$

where Δm is the mass increase of the CaCl$_2$ sample (g), A is the area of the film, Δt is the exposure time in the chamber, e is the thickness of the film, and ΔP is the partial water vapor pressure difference across the film specimens corresponding to 0–60% RH, that is, 1875 Pa.

Water vapor sorption measurement of the PCL nanocomposites

Water vapor sorption values of the samples were determined by keeping preweighed films (three films of each sample ≈ 5 cm in diameter) in a closed desiccator above a saturated solution of sodium chloride at 25°C (RH ≈ 75%) for different lengths of time. The films were then weighed, and the percentage increase in weight due to water vapor sorption was calculated.

Biodisintegration of the nanocomposites in soil

Biodisintegration of the PCL/cellulose whisker nanocomposites in soil was carried out as previously reported.[12] Soil was taken from the surface layer. All inert materials were removed to obtain a homogeneous mass. Soil (100 g) was poured into a plastic pot up to a thickness of about 3 cm. The samples were previously dried at 50°C for 24 h. Nanocomposite samples (two films of each sample having a diameter of 10 cm) were accurately weighed and buried in the pots to a depth of 1 cm. About 30 mL of water was sprayed on the films once a day to sustain the moisture. The samples were weighed every week for 4 weeks. After each period, the samples were carefully taken out, washed with distilled water, dried at 50°C for 24 h, and then weighed.

Characterizations of the PCL nanocomposites

Tensile tests were carried out with a Lloyd instrument (Lloyd Instruments, West Sussex, United Kingdom) with a 100-N load cell. The measurements were performed at a crosshead speed of 2 mm/min at 25°C. The samples were prepared by cutting strips of the films 50 mm long and 10 mm wide. The distance between the jaws was 20 mm. Dynamic mechanical thermal analysis (DMTA) of the nanocomposites films was carried out with an Anton Paar MCR-301 rheometer (Anton Paar, Graz, Austria) working in tensile mode. The measurements were performed at a constant frequency of 1 Hz and a strain amplitude of 0.08% in the temperature range from −100 to 70°C with a heating rate of 3°C/min and a distance between the jaws of 20 mm.

Thermogravimetric analysis experiments were carried out with a hermogravimetric analyzer (Perkin Elmer Inc., Waltham, Massachusetts, USA). The heating rate was 10°C/min from 30 to 600°C a under nitrogen atmosphere; the flow rate of nitrogen was 50 mL/min. Differential scanning calorimetry (DSC) experiments were carried out with a PerkinElmer differential calorimeter (Perkin Elmer Inc., Waltham, Massachusetts, USA) fitted with a liquid nitrogen cooling system. The samples were placed in hermetically closed DSC pans. The heating rate and temperature were 10°C/min and −100 to 70°C, respectively. Environmental scanning electron microscopy was carried out with an FEI Quanta 200 scanning electron microscope (FEI Company BV, Netherlands) with an acceleration voltage of 10 kV. Optical microscopy (OM) was carried out with a Zeiss AX10 (Carl Ziess AG, Jena, Germany) AX10 optical microscope.

RESULTS AND DISCUSSION

Chemical grafting of the cellulose whiskers

Imparting cellulose whiskers hydrophobic character through surface chemical modification is important for obtaining a stable suspension of the whiskers in nonpolar solvents and better compatibility with hydrophobic polymer matrices. In this study, cellulose whiskers were isolated from bleached Kraft bagasse pulp with an average length of 96.7 ± 39 nm and an average width of 7.5 ±2.3 nm; the degree of crystallinity was 89%, as calculated from the X-ray diffraction pattern (not shown).[9] The isolated cellulose whiskers were modified with *n*-octadecyl isocyanate in the presence of a small amount of tetrabutyltin dilaurate catalyst, which is a commercial catalyst used in the preparation of polyurethane adhesives and silicones. Residual catalyst was easily removed by extraction with toluene/ethanol.

The occurrence of modification of the cellulose whiskers was proven by FTIR spectroscopy and
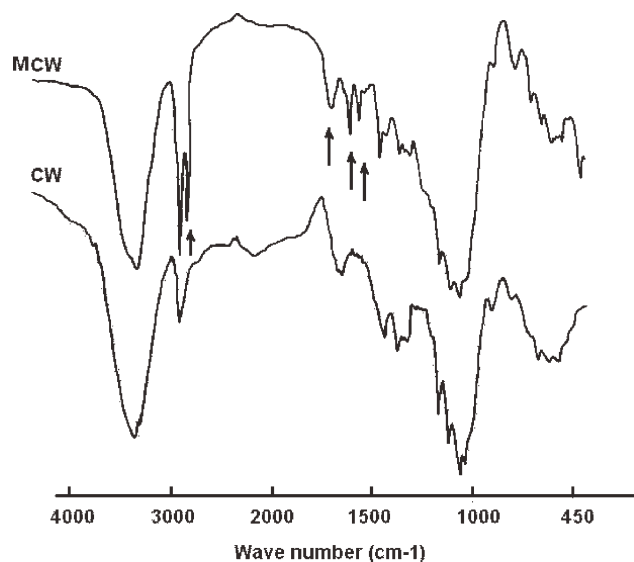
Figure 1 FTIR spectra of bagasse cellulose whiskers (CW) and octadecyl-modified cellulose whiskers (MCW).

elemental analysis of the extracted whiskers. The FTIR spectra of the modified and nonmodified cellulose whiskers are shown in Figure 1. In addition to the characteristic bands of cellulose at 3496 cm^{-1} (O—H), 1110 cm^{-1} (C—O of secondary alcohol), and 2868 and 2970 cm^{-1} (C—H from —CH$_2$), the FTIR spectra showed the appearance of new peaks at 1708, 1614, and 1572 cm^{-1} due to formation of carbamate bonds as a result of the reaction between the isocyanate groups of the octadecyl derivative and the hydroxyl groups of the cellulose whiskers. A new peak appeared at about 2850 cm^{-1} due to the introduced long alkyl chain. The absence of isocyanate or amine bands, which usually appear at about 2260, 3563, and 3472 cm^{-1}, indicated the removal of unreacted isocyanate or amine byproduct produced as a result of the reaction of isocyanate with residual moisture.

Elemental analysis showed 0.76% nitrogen in the modified bagasse whiskers; this corresponded to a degree of substitution about 0.25. Elemental analysis for carbon also showed an increase in the carbon content of the cellulose whiskers from 35.8 to 39.8% as a result of modification. The extent of modification obtained in this study was higher than that previously reported in case of the treatment of sisal whiskers, which followed a similar procedure but in the absence of dibutyltin dilaurate catalyst and at a higher reaction temperature, where the nitrogen content was 0.51%.[8]

The chemical modification of the bagasse whisker surfaces with octadecyl side chains greatly influenced the water contact angle and hydrophilicity, as it is obvious from the data shown in Figure 2 and Table I. The values of the surface energy (polar and dispersive contributions) shown in Table I confirmed the change in the surface polarity of the cellulose whiskers as a result of modification with the octadecyl side chains. As a result of modification of the
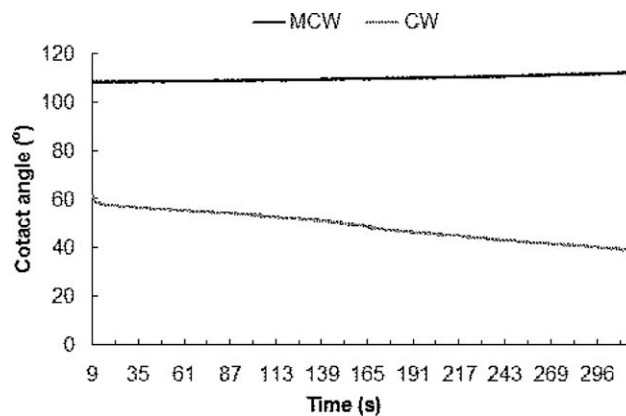
Figure 2 Water contact angle with time for bagasse cellulose whiskers (CW) and octadecyl-modified cellulose whiskers (MCW).

whiskers, homogeneous nanocomposites films were obtained at different bagasse whisker loadings, as proven by the environmental scanning electron microscopy images of the surface and cross section of the nanocomposite sample containing the highest whisker loading (Fig. 3). Because of the surface chemical modification of whiskers, no significant agglomeration of the modified cellulose whiskers took place within the film.

Water vapor sorption measurement of the PCL nanocomposites

The resistance to water vapor sorption, especially for composites used in packaging applications, is an important property because it affects the mechanical properties of composites and the shelf life of products. PCL is a hydrophobic biodegradable polymer with a good resistance toward moisture, whereas cellulose whiskers have a strong hydrophilic character. Therefore, the surface modification of cellulose whiskers was necessary to impart them with resistance to water absorption.

The effect of adding modified cellulose whiskers to PCL on its water vapor sorption was studied at 75% RH, and the results are presented in Figure 4. As shown in the figure, PCL had a very low water vapor sorption

TABLE I
Surface Energy Parameters of the Octadecyl-Modified and Nonmodified Bagasse Whiskers

	Surface energy parameters		
	γ_s^p	γ_s^d	γ_s
Modified bagasse whiskers	0.63 (0.13)	30.88 (1.97)	31.51 (2.35)
Nonmodified bagasse whiskers	18.26 (2.53)	29.05 (1.66)	47.31 (1.0)

γ_s^p, non-dispersive component; γ_s^d, dispersive component, γ_s, surface energy.

The values in parentheses are standard deviations.
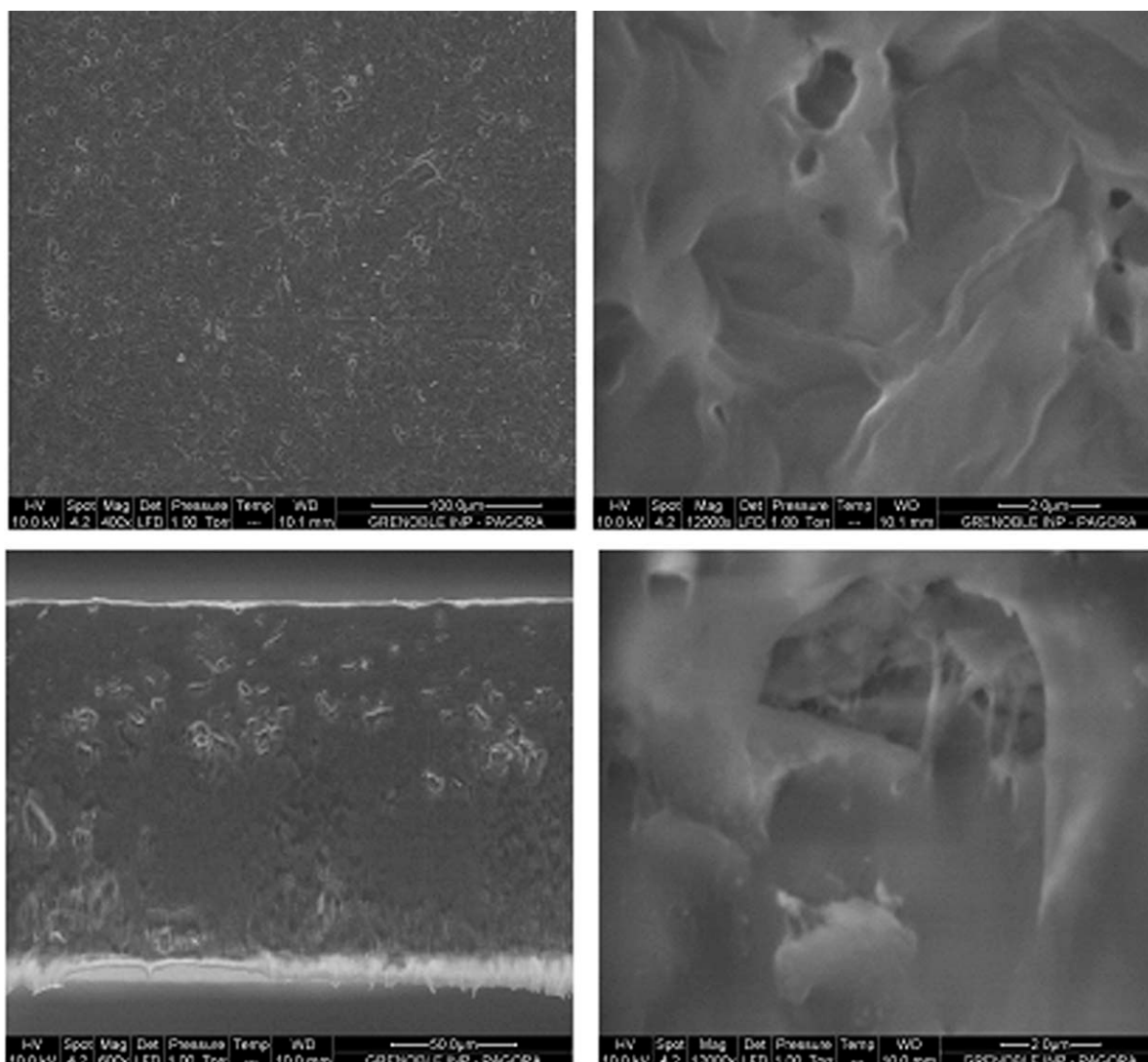
Figure 3 Scanning electron microscopy images of (top) surface and (bottom) cross section of the PCL/modified bagasse cellulose whisker sample containing 12.5% modified whiskers.

as did the nanocomposite films containing different ratios of modified cellulose whiskers. PCL had a moisture sorption of 1.8% (wt %) after 4 weeks at 75% RH, whereas the nanocomposites containing different ratios of modified cellulose whiskers had water vapor sorptions from about 1.9 to 2.5% after the same exposure time. These very low values of water vapor sorption indicated that the modification of cellulose whiskers with long alkyl chains imparted them with a high hydrophobic character. Previous use of nonmodified cellulose whiskers in rubber nanocomposites resulted in a noticeable increase in the moisture sorption,[9] which was much greater than that noticed in this study.
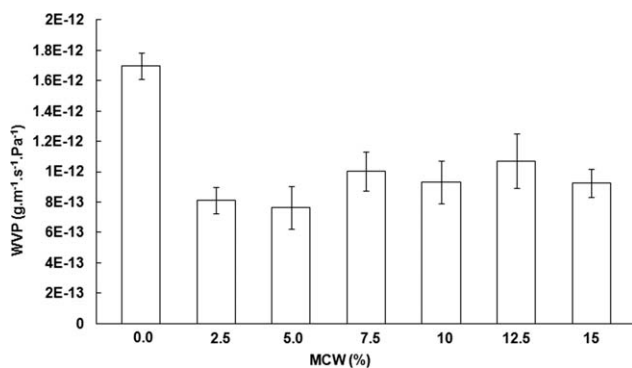
WVP of the PCL nanocomposites

WVP is an important property for evaluating materials dedicated for packaging applications.

One of the expected properties of cellulose whiskers is their barrier properties against the permeation of gases, which are due to their shape, high surface area, high crystallinity, and possible homogeneous distribution in the polymer matrix. In
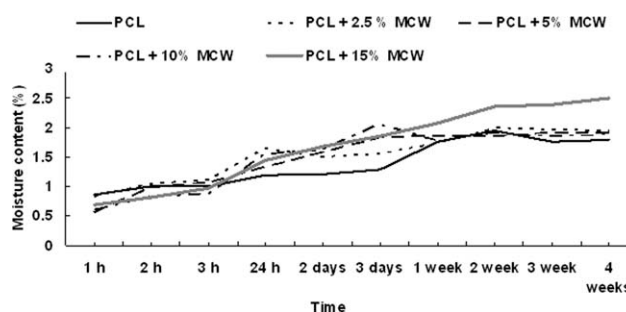
Figure 4 Moisture sorption of PCL nanocomposites containing different ratios of modified cellulose whiskers (MCW) at 75% RH.

Figure 5 WVP of PCL nanocomposites containing different ratios of modified cellulose whiskers (MCW).

a previous study on natural rubber/nonmodified cellulose whisker nanocomposites, we found that the presence of nonmodified cellulose whiskers increased WVP across the rubber films.[9] The reason for this was ascribed to the high hydrophilic nature of the cellulose whiskers, which acted as preferred avenues for moisture permeation.

In this work, the effect of the modified cellulose whiskers on WVP of PCL was studied, and the results are presented in Figure 5. PCL is a hydrophobic polymer with a low WVP. As shown in the figure, the modified cellulose whiskers successfully increased the barrier properties of PCL against moisture. WVP of the PCL films decreased by about 50% as a result of the addition of only 2.5% modified cellulose whiskers. The maximum decrease in WVP was obtained at a 5% modified cellulose whisker loading and was about 55%; this was consistent with the expected percolation threshold value for bagasse cellulose whiskers, which had an aspect ratio of 12.8.[9] No further decrease in the WVP of the PCL films was observed at higher modified whisker loadings (7.5–15%), and WVP of the prepared PCL nanocomposites was lower than that of neat PCL by about 41–45%.

The lower WVP of the PCL nanocomposites containing modified cellulose whiskers versus that of PCL was attributed to the presence of long alkyl chains on the surface of the whiskers, the homogeneous distribution of the whiskers in the PCL matrix, and as their rodlike shape and high crystallinity.

Biodisintegration of the PCL nanocomposites in soil

PCL is a degradable polymer in different biologically active environments, including rivers, soil sewage sludge, and compost.[12–15] It has a high molecular weight and crystallinity, which affect its biodegradability.[16] It has been reported that esterase and other kinds of lipase can degrade poly(ε-caprolactone) by hydrolysis.[17–19] Microbial attack occurs preferentially in the amorphous phase; this leads to chain rearrangement and an increased crystallinity index.[20] PCL biodegradation in soil has been reported to be a slow process; it started after 40 days and took more than 200 days to complete.[21,22]

On the other hand, a previous study showed that a regenerated cellulose film decomposed completely in soil into CO_2 and water after 60 days as a result of the random breakdown of bonds of cellulose macromolecules.[23]

In a previous work, it was found that the addition of cellulose whiskers or microcrystalline cellulose to slow biodegradable polymer matrices increased their rate of biodisintegration in soil, despite the low percentage of cellulose.[9,24] When exposed to a soil environment, cellulose is consumed by microorganisms; this leads to increased porosity, void formation, and the loss of integrity of the polymer matrix. The polymer matrix is broken down into smaller particles and thus becomes easier to biodegrade. In this work, the effect of the modified cellulose whiskers on the biodisintegration of PCL in soil was studied, and the results are shown in Figures 6 and 7. As shown in the OM pictures in Figure 6, the biodegradation and/or biodisintegration of PCL in soil occurred in a laminar manner, that is, the erosion of the surface of the PCL. When cellulose whiskers were present, in addition to the erosion of the PCL surface, many more tiny pits were formed, and this increased the rate of biodisintegration of PCL in soil.

Figure 7 shows the weight loss as a result of the biodisintegration of PCL nanocomposites in soil. As clearly shown in the figure, the addition of up to 7.5% modified whiskers significantly increased the rate of degradation of PCL in soil. At higher loadings of modified cellulose whiskers, the weight loss tended to decrease, but it was still higher than that of neat PCL.

The obtained results mean that presence of cellulose whiskers, even after modification, did not noticeably inhibit the attack of microorganisms on cellulose or PCL. It should be mentioned that when burring in the soil test was used and when we measured weight loss, we could be sure that the modified cellulose whiskers favored the biodisintegration of the nanocomposites in soil and, thus, may have facilitated its biodegradation. However, measurement of the CO_2 production rate was necessary to determine the effect of the modified cellulose whiskers on the rate of biodegradability.

Tensile properties of the PCL nanocomposites

The effect of the addition of modified cellulose whiskers to PCL on its tensile properties was studied, and the results are presented in Figure 8. PCL is a ductile polymer with a medium Young's modulus. The addition of the modified cellulose whiskers to
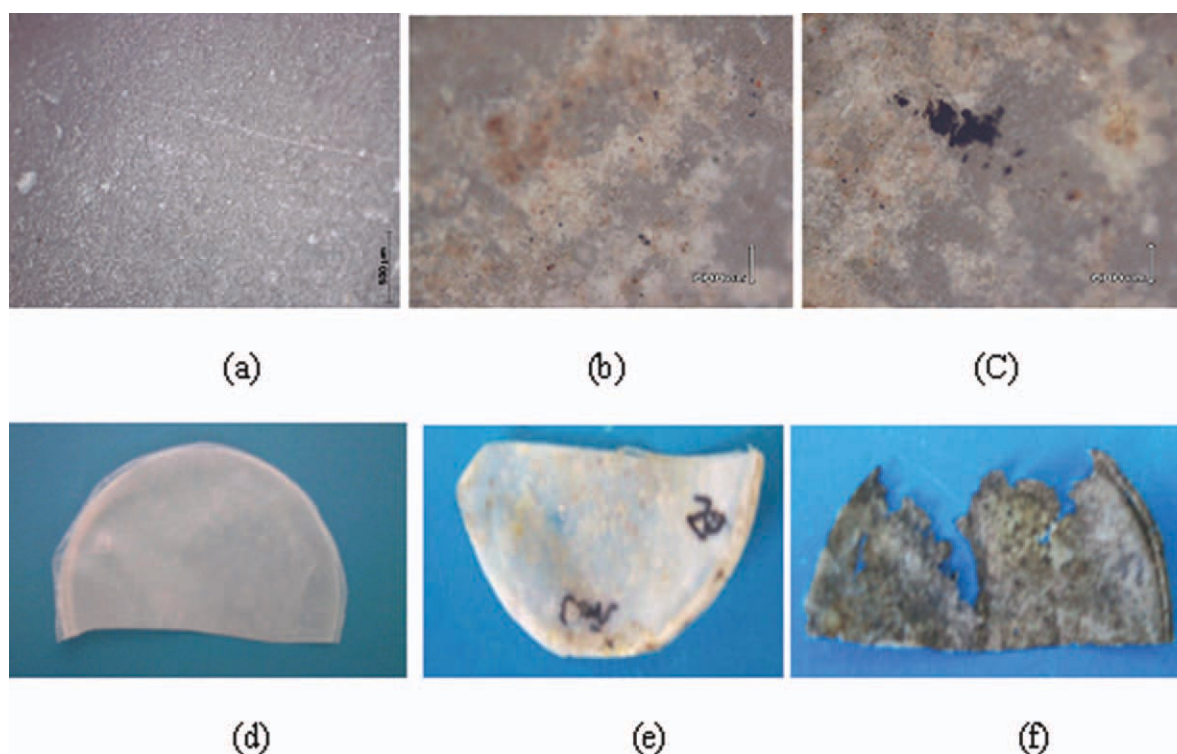
Figure 6 (Top) OM pictures of surface of (a) PCL film before the test, (b) PCL film after disintegration in soil for 8 weeks, and (c) PCL/modified cellulose whiskers (10%) nanocomposite film after disintegration in soil for 8 weeks. (Bottom, d,e,f) Corresponding photoimages of the same samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PCL resulted in a significant increase in its modulus, especially at whisker loadings of 5% or higher, that is, at and above the percolation threshold, where bagasse cellulose whiskers formed a stiff percolating network.[8,9] The maximum increase in modulus was about 77%, and it was achieved at a 12.5% whisker loading. The increase in the modulus of the prepared PCL nanocomposites indicated good dispersion of the modified cellulose whiskers in the hydro-

phobic PCL matrix and good interfacial adhesion between the modified cellulose whiskers and PCL and whisker–whisker interaction. The increase in the modulus of PCL as a result of the addition of modified cellulose whiskers could be also attributed to an increase in the crystallinity of PCL in the presence of modified whiskers.[8]
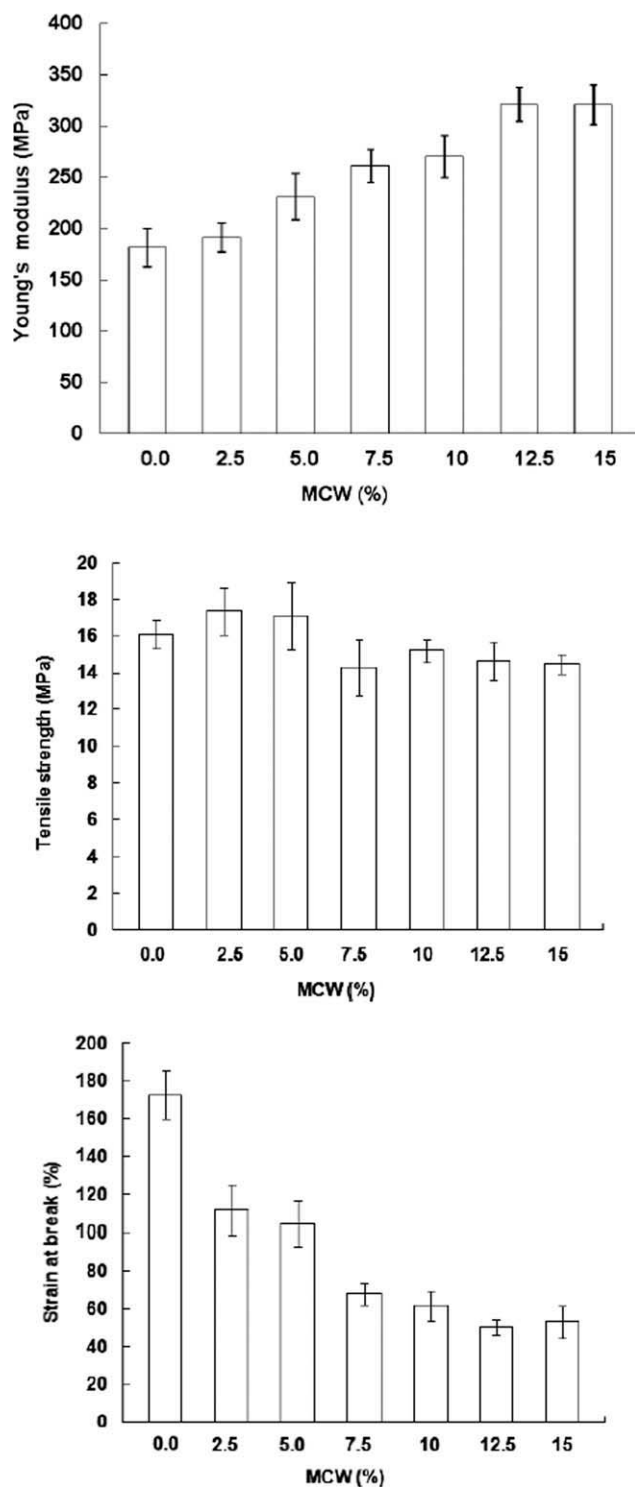
The tensile strength of nanocomposite films slightly increased with the addition of modified cellulose whiskers to PCL up to a 5% whisker loading and then slightly decreased with the addition of higher amounts of whiskers. The decrease in the tensile strength of PCL with the addition of 12.5% modified cellulose whiskers, that is, at the highest modulus obtained, was only about 9%. As expected, because of the high stiffness of the whiskers, the strain at break of the nanocomposites containing the different ratios of whiskers was greatly reduced, especially at 2.5–7.5% loadings of modified whiskers. No significant further decrease in the strain at break took place at higher loading levels of modified whiskers.
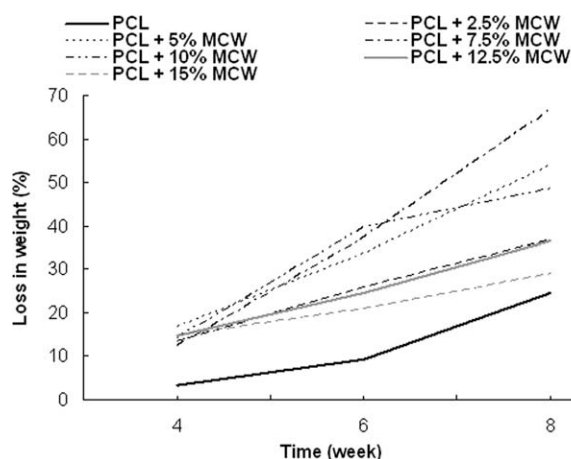
Figure 7 Loss in weight as a result of the biodegradation of PCL/modified cellulose whisker nanocomposites in soil at different whisker loadings for up to 8 weeks.
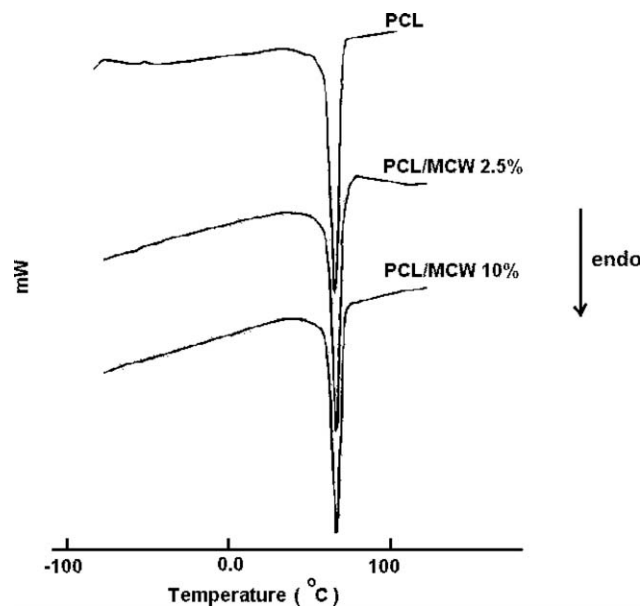
Thermal and thermomechanical properties of the PCL nanocomposites

The DSC and DMTA curves obtained for the pure PCL and PCL nanocomposites are presented in

Figure 9 DSC curves of PCL and PCL nanocomposites containing different ratios of modified cellulose whiskers (MCW).

The presence of modified cellulose whiskers in the PCL matrix resulted in the fading of the peak at −55°C in the DSC curves, which corresponds to
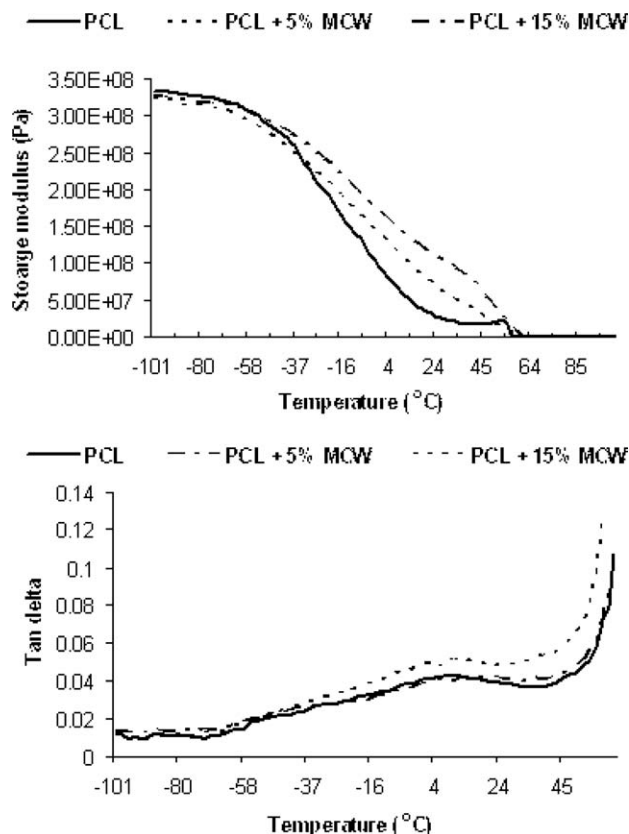

Figure 8 Tensile properties of PCL nanocomposites containing different ratios of modified cellulose whiskers (MCW).

Figures 9 and 10, respectively. The DSC thermogram of PCL showed an increase in the heat capacity at about −55°C and an endothermic peak at 64°C as a result of the transition from the glassy state to the rubbery state and the melting of PCL, respectively.

Figure 10 DMTA curves of PCL and PCL nanocomposites containing different ratios of modified cellulose whiskers (MCW).
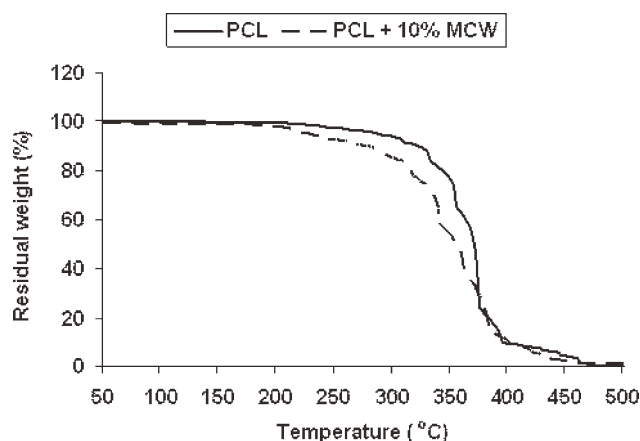
Figure 11 TG curves of PCL and PCL nanocomposites containing 10% modified cellulose whiskers (MCW).

the T_g of PCL. With regard to the melting point of the PCL matrix at about 64°C, the addition of the modified cellulose whiskers did not affect the melting of PCL.

The obtained results were in accordance with previous studies with regard to the effects of modified or nonmodified cellulose whiskers from different sources on the melting of some polymer matrices, such as plasticized starch,[25,26] poly(ethylene oxide),[27,28] and PCL.[29] The DMTA curves of PCL showed a decrease in the storage modulus associated with a change in the tan δ curve at about −55°C; this was consistent with the glass transition of PCL, as observed in the DSC curves. A second transition was observed at about 60°C as a result of the melting of PCL.

The presence of the modified cellulose whiskers in PCL resulted in an increase in the storage modulus of PCL above its T_g and at room temperature. This indicated a reinforcing effect of the modified whiskers on the PCL matrix and was also in accordance with the tensile tests results discussed previously. There was no significant change in the position of the onset temperatures of the relaxation processes at T_g and T_m of PCL as a result of presence of the modified cellulose whiskers. In accordance with the storage modulus curves, the tan δ curves showed that the onset of peaks corresponded to T_g and the melting of PCL.

Thermal stability of the PCL nanocomposites

The thermal stability of the PCL/cellulose whisker nanocomposites was tested briefly with thermogravimetric analysis. Figure 11 shows the TG curves of the PCL and PCL nanocomposite containing 10% modified cellulose whiskers. The PCL nanocomposites containing modified whiskers had a lower thermal stability than PCL. The onset degradation temperature of the PCL nanocomposite was about

200°C, whereas that of PCL was about 325°C. This could have been due to the lower thermal stability of cellulose compared to that of PCL.[30]

CONCLUSIONS

The chemical modification of bagasse cellulose whiskers with *n*-octadecyl isocyanate in the presence of dibutyltin dilaurate was achieved at a relatively lower temperature than with previous methods and with a higher degree of substitution. PCL/cellulose whisker nanocomposites with improved moisture-barrier and biodegradability properties were prepared by the chemical modification of the cellulose whiskers isolated from bagasse and their incorporation into the PCL matrix. The addition of up to 5 wt % modified cellulose increased the tensile modulus without detrimental effects on the ultimate tensile strength. At higher loadings of the modified cellulose whiskers, a slight loss (∼ 9%) in the ultimate tensile strength took place, but the tensile modulus increased. No significant effects of the modified cellulose whiskers on T_g or T_m of PCL were found.

References

1. Siqueira, G.; Bras, J.; Dufresne, A. Polymers 2010, 2, 728.
2. Bendahou, A.; Habibi, Y.; Kaddami, H.; Dufresne, A. J Bio-based Mater Bio 2009, 3, 81.
3. Bras, J.; Hassan, M. L.; Bruzzese, C.; Hassan, E. A.; El-Wakil, N. A.; Dufresne, A. Presented at the Meeting of the American Chemical Society, San Francisco, CA, March 2010.
4. Habibi, Y.; Lucia, L. A.; Rojas, O. J Chem Rev 2010, 110, 3479.
5. Lin, N.; Huang, J.; Chang, P. R.; Feng, J.; Yu, J. Carbohydr Polym 2010.
6. Puglia, D.; Tomassucci, A.; Kenny, J. M. Polym Adv Technol 2003, 14, 749.
7. Habibi, Y.; Dufresne, A. Biomacromolecules 2008, 9, 1974.
8. Siqueira, G.; Bras, J.; Dufresne, A. Biomacromolecules 2009, 10, 425.
9. Bras, J.; Hassan, M. L.; Bruzzese, C.; Hassan, E. A.; El-Wakil, N. A.; Dufresne, A. Ind Crop Prod 2010, 32, 627.
10. Siqueira, G.; Bras, J.; Dufresne, A. Langmuir 2010, 26, 402.
11. Owens, D. K.; Wendt, R. C. J Appl Polym Sci 1969, 13, 1741.
12. Dalev, P. G.; Patil, R. D.; Mark, J. E.; Vassileva, E.; Fakirov, S. J Appl Polym Sci 2000, 78, 1341.
13. Benedict, C. V.; Cameron, J. A.; Huang, J. J Appl Polym Sci 1983, 28, 335.
14. Pettigrew, C. A.; Reece, G. A.; Smith, M. C.; King, L. W. J Macromol Sci Pure Appl Chem 1995, 32, 811.
15. Albertsson, A. C.; Renstad, R.; Erlandssso, B.; Eldsater, C.; Karlsson, S. J J Appl Polym Sci 1998, 70, 61.
16. Eldsäter, C.; Erlandsson, B.; Renstad, R.; Albertsson, A.-C.; Karlsson, S. Polym J 2000, 41, 1297.
17. Ishigaki, T.; Sugano, W.; Nakanishi, A.; Tateda, M.; Ike, M.; Fujita, M. Chemosphere 2004, 54, 225.

18. Tokiwa, Y.; Suzuki, T.; Taked, K. Agric Biol Chem 1988, 52, 1937.
19. Darwis, D.; Mitomo, H.; Enjoji, T.; Yoshii, E.; Makuuchi, K. Polym Degrad Stab 1998, 62, 259.
20. Lefèvre, C.; Tidjani, A.; Wauven, C. V.; David, C. J Appl Polym Sci 2002, 83, 1334.
21. Gonçalves, S. P. C.; Martins-Franchetti, S. M. J Polym Environ 2010, 18, 714.
22. Federle, T. W.; Barlaz, M. A.; Pettigrew, C. A.; Kerr, K. M.; Kemper, J. J.; Nuck, B. A.; Schechtman, L. A. Biomacromolecules 2002, 3, 813.

23. Zhang, L.; Liu, H. Ind Eng Chem Res 1996, 35, 4682.
24. Chuayjuljit, S.; Su-Uthal, S.; Tunwattanaseree, C.; Charuchinda, S. J Reinforc Plast Compos 2010, 28, 1245.
25. Mathew, A. P.; Dufresne, A. Biomacromolecules 2002, 3, 609.
26. Angles, M. N.; Dufresne, A. Macromolecules 2000, 33, 8344.
27. Marcovich, N. E.; Auad, M. L.; Bellesi, N. E.; Nutt, S. R.; Aranguren, M. I. J Mater Res 2006, 21, 870.
28. Azizi Samir, M. A. S.; Alloin, F.; Gorecki, W.; Sanchez, J. Y.; Dufresne, A. J Phys Chem B 2004, 108, 10845.
29. Grunert, M.; Winter, W. T. J Polym Environ 2002, 10, 27.
30. Ruseckaite, R. A.; Jiménez, A. Polym Degrad Stab 2003, 81, 353.