

SURFACE MODIFICATION OF SUGARCANE BAGASSE CELLULOSE AND ITS EFFECT ON MECHANICAL AND WATER ABSORPTION PROPERTIES OF SUGARCANE BAGASSE CELLULOSE/ HDPE COMPOSITES

Daniella Regina Mulinari,^{a*} Herman J. C. Voorwald,^a Maria Odila H. Cioffi,^a George J. Rocha,^b and Maria Lúcia C. Pinto Da Silva^c

Cellulose fibres from sugarcane bagasse were bleached and modified by zirconium oxychloride in order to improve the mechanical properties of composites with high density polyethylene (HDPE). The mechanical properties of the composites prepared from chemically modified cellulose fibres were found to increase compared to those of bleached fibres. Tensile strengths of the composites showed a decreasing trend with increasing filler content. However, the values for the chemically modified cellulose fibres/HDPE composites at all mixing ratios were found to be higher than that of neat HDPE. Results of water immersion tests showed that the water absorption affected the mechanical properties. The fracture surfaces of the composites were recorded using scanning electron microscopy (SEM). The SEM micrographs revealed that interfacial bonding between the modified filler and the matrix was significantly improved by the fibre modification.

Keywords: Polymer-matrix composites (PMCs); Fibre/matrix bond; Injection moulding; Mechanical properties

Contact information: a: Department of Materials and Technology, UNESP/FEG, Guaratinguetá/SP, Brazil, b: Department of Biochemical, USP/EEL, Lorena/SP, Brazil, c: Department of Chemical Engineering, USP/EEL, Lorena/SP, Brazil; * Corresponding author: dmulinari@hotmail.com

INTRODUCTION

Recently, interest in composite materials reinforced with natural fibres has increased considerably. These materials present low cost, low density, high specific properties, and also are biodegradable and nonabrasive (Habibi et al. 2008; Luz et al. 2007; Mulinari et al. 2009a). Brazil has a large range of natural resources, including natural fibres from several sources, curaua, banana, coconuts, sisal, cotton, and sugarcane bagasse (Satyanarayana et al. 2007). Sugarcane bagasse fibre-reinforced composites, compared with those reinforced by glass fibres, exhibit better specific mechanical properties, such as stiffness, impact resistance, flexibility, and modulus (Mulinari et al. 2009b). Other desirable properties, related to processing, include lower equipment abrasion and lower energy consumption (Saheb and Jog 1999). For these reasons, natural fibre composites have been used in many applications such as furniture, architectural materials, and, more recently, in the automotive industry (Gerrard and Kandlikar 2007; Zah et al. 2007; Zampaloni et al. 2007).

However, natural fibres also have an undesirable property, namely, hygroscopicity, which can be attributed to their chemical constituents (John and Thomas 2008). The moisture absorption by composites that contain natural fibres has several adverse effects on their properties and thus affects their long-term performance (Dhakal et al. 2007). Moisture absorption leads to degradation of the fibre–matrix interfacial region, creating poor stress transfer efficiencies and resulting in a reduction of mechanical and dimensional properties (Dhakal et al 2007). One of the main concerns for the use of natural fibre-reinforced composite materials is susceptibility to moisture absorption and the resulting harm to physical, mechanical, and thermal properties (Chow et al. 2007).

Moisture absorption also increases with increasing loading of fibres in a composite. George et al. (1998) investigated the relationship between the moisture absorption of pineapple-leaf fibre-reinforced low density polyethylene (LDPE) composites and the fibre loadings (10%, 20%, and 30% by weight). They found that moisture absorption increased almost linearly with fibre loading. Stark (2001) found that wood flour-polypropylene (PP) composites with 20 wt% wood flour reached equilibrium after 1500 h in a water bath and absorbed only 1.4% moisture, while composites with 40 wt% loading reached equilibrium after 1200 h water submersion and absorbed approximately 9.0% moisture. After the analysis, she concluded that the wood flour is inhibited from absorbing moisture due to encapsulation of the wood flour by the PP matrix and that the degree of encapsulation is greater for a 20% wood flour composite than that for a 40% wood flour composite.

Several studies in the use of natural fibres reinforced polymeric composites have shown that the sensitivity of certain mechanical and thermal properties to moisture uptake can be reduced by the use of coupling agents and fibre surface treatments (Luz et al. 2008; Pasquini et al. 2008).

Because of this, the objective of the present work was to study the surface modification of sugarcane bagasse cellulose and its effect on mechanical and water absorption properties of sugarcane bagasse cellulose/HDPE composites.

EXPERIMENTAL

Materials

Non-modified cellulose

Natural sugarcane bagasse was first pretreated with 10% sulfuric acid solution (reactor of 350 L at 120°C, 10 min), followed by centrifugation for the purpose of separating a solution rich in pentosans from the solid material. The extracted lignocellulosic fraction was delignified with 1% NaOH solution (reactor with 350L volume at 100°C, 1 h). The crude pulp (50 g) obtained was bleached with 1 mL acetic acid PA and 3 g sodium chlorite under stirring during 1 hour at 70 °C, followed by filtration under vacuum. It was then exhaustively washed with distilled water. This technique was used to remove residual lignin. Finally the bleached cellulose was dried at 50 °C for 12 h (Mulinari and Da Silva 2008).

Modified cellulose

Cellulose fibres were modified by dissolution of 2 g of zirconium oxychloride in 100 mL of hydrochloric acid solution (0.5 mol L^{-1}) at room temperature; then 5 g of cellulose fibres were immersed in this solution. Solids were precipitated with ammonium solution (1:3) at pH 10.0, under stirring during 5 hours, filtered under vacuum, exhaustively washed with distilled water for the complete removal of chloride ions (negative silver nitrate test), and dried at $50 \text{ }^\circ\text{C}$ for 24 h. The resulting material was designated as Cell/ $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ (Mulinari and Da Silva 2008).

High density polyethylene (EI60070) used as matrix was kindly provided by Riopol.

X-Ray Diffraction

Crystallinity of the cellulose fibres was evaluated by X-ray diffraction, using a Shimadzu diffractometer model XRD6000. The measurement conditions were: $\text{CuK}\alpha$ radiation with graphite monochromator, 30 kV voltage, and 40 mA electric current. The patterns were obtained within a 10 to 40° 2θ angular interval with 0.05° step and 1s of counting time. The degree of crystallinity (CI) was calculated as the ratio of the intensity differences in the peak positions at 18° and 22° according to equation 1 (Rodrigues Filho et al. 2007),

$$CI = \frac{I_{(22)} - I_{(18)}}{I_{(22)}} \times 100 \quad (1)$$

where I_{22} is the maximum intensity of the 002 lattice reflection of the cellulose I , and I_{18} is the maximum intensity of X-ray scattering broad band due to the amorphous part of the sample.

Scanning Electron Microscopy

A JEOL JSM5310 model scanning electron microscope (SEM) was used to observe the modification on cellulose fibres. Samples to be observed under the SEM were mounted on conductive adhesive tape, sputter coated with gold, and observed in the SEM using a voltage of 15 kV.

Composites Preparation

High density polyethylene (HDPE) composites reinforced with 5 to 20 wt% of non-modified and modified cellulose fibres from sugarcane bagasse were prepared in a thermokinetic mixer at 5250 rpm for 1 min; the same procedure was made for HDPE. After mixing, the composites and HDPE were cooled with water, and after that, ground to 13 mm. The composites were dried in an oven at $80 \text{ }^\circ\text{C}$ for 3 h and thereafter injected directly in a mold with specific dimensions for tensile specimens, where fibres were dispersed in the matrix. This method makes it possible to obtain a homogenous distribution of the natural fibres in the matrix.

Mechanical Tests

For tensile tests, composites and high density polyethylene were analyzed with an Istron universal-testing machine (model 8801). In the tensile tests, five specimens of composites and high density polyethylene were analyzed before and after water absorption during 7 days, with dimensions in agreement with the ASTM D 638 standard: 19 mm width, 165 mm length, and 3.2 mm thickness, with a 10 mm min⁻¹ crosshead speed.

Water Absorption Tests

Effects of water absorption on cellulose fibres from sugarcane bagasse reinforced HDPE composites were investigated in accordance to ASTM standard D570. The percentage of water absorption in the composites was calculated by the weight difference between the samples immersed in water and the dry samples, using the following equation (2),

$$\Delta M(\%) = \frac{M_f - M_i}{M_i} \times 100 \quad (2)$$

where $\Delta M(\%)$ is moisture uptake, and M_f and M_i are the mass of the specimen after and before immersion, respectively. Samples for tensile tests containing different fibre volume fractions of reinforcement were made after water absorption to evaluate the effect on mechanical properties.

RESULTS AND DISCUSSION

The incorporation of hydrous zirconium oxide on to cellulose fibres surface can be described by the following reaction (3):

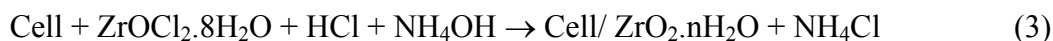


Figure 1 shows a schematic representation of the reaction of a Lewis acid with cellulose (Gushikem and Toledo 1999). The reaction is carried out under anhydrous conditions in the first step because it is supposed that primarily a donor-acceptor bond is formed between $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and the oxygen of the $\text{C}^1\text{-O-C}^5$ and $\text{C}^1\text{-O-C}^4$ bonds. The attack to the former oxide bond leads to a ring opening and provides a molecule rupture process in order to form micro-fibres. Ammonium solution is a required means to promote the chemical link of the metallic oxide with fibres surfaces.

X-Ray Diffraction

Figure 2 shows diffractograms obtained for cellulose fibres from non-modified and modified sugarcane bagasse. A major diffraction peak was observed for 2θ ranging between 22° and 23° , which corresponds to the cellulose (0 0 2) crystallographic planes.

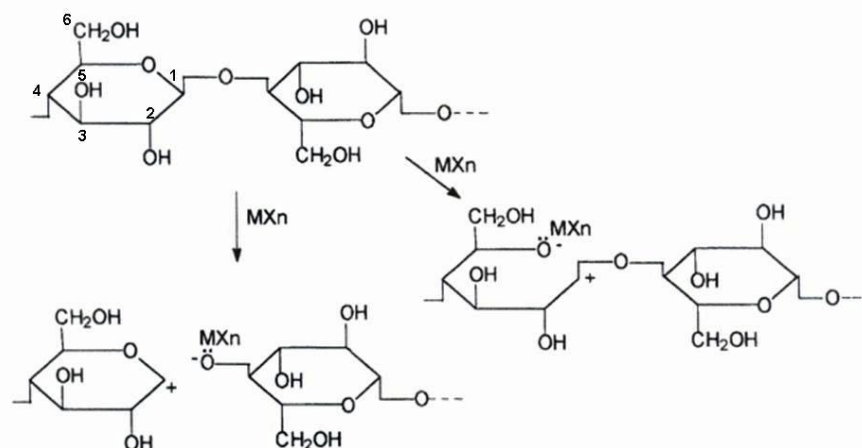


Fig. 1. Reaction of the Lewis acid with cellulose and formation of the donor-acceptor bond

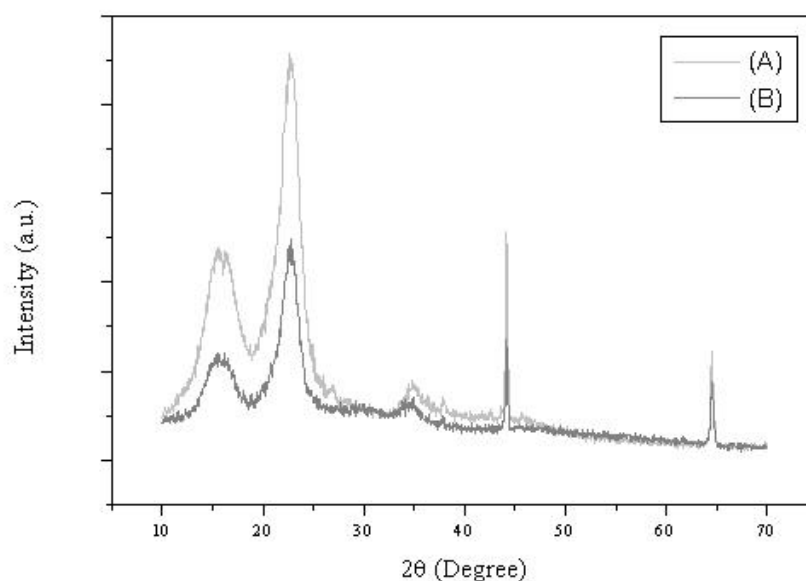


Fig. 2. X-ray: (A) cellulose fibres; (B) Cell/ZrO₂.nH₂O

X-ray diffraction peaks for both materials can be attributed to crystallinity scattering, whereas the diffuse background can be attributed to disordered regions. Thus the tested materials are semicrystalline.

The spectrum corresponding to the non-modified cellulose fibres shows diffraction peaks at the following 2θ angles: 15.7° and 22.82° . In the case of modified cellulose fibres, the same peaks can be observed at 15.9° and 22.82° . The presence of the peaks at 15° and 22° provides evidence of fibre modification. The position of these peaks indicates an increase of the interplanar distance in comparison to the modified fibres. This behavior occurs due to the generation of disorder when fibres are modified (Rodrigues Filho et al. 2007). Patterns for both materials were similar, however non-modified cellulose fibres were less crystalline compared to the modified fibres. According to this method, non-modified cellulose fibres and modified fibers showed 47% and 53% of crystallinity, respectively. These values can be attributed to modification of

the fibres caused by hydrous zirconium oxide, so that the modified fibers exhibit amorphous characteristics due presence of oxide (Mulinari et al. 2006).

Scanning Electron Microscopy

Micrographs of non-modified cellulose fibres reveal flattened forms and different sizes (Fig. 3). On the other hand, micrographs of modified cellulose fibres show hydrous zirconium oxide dispersed on the cellulose fibres (Fig. 4), yielding a chemically and morphologically heterogeneous surface. The presence of hydrous zirconium oxide chemically attached to the fibre surfaces was verified by Mulinari et al. (2006) using by the X-ray diffraction spectroscopy (EDS) technique.

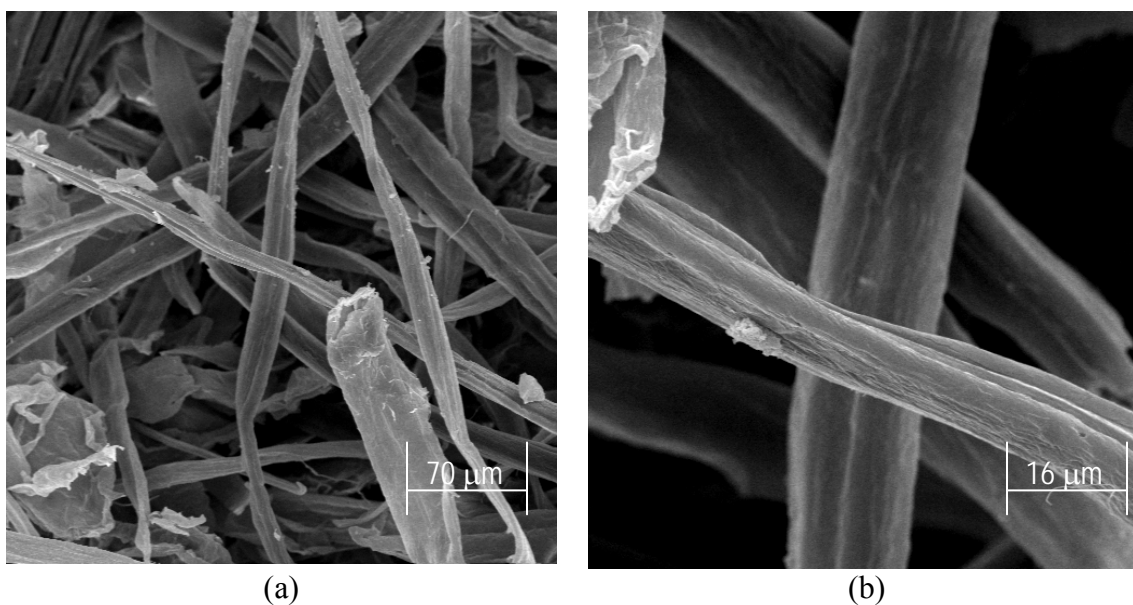


Fig. 3. Morphology of non-modified cellulose fibres: (A) 500X; (B) 2000X

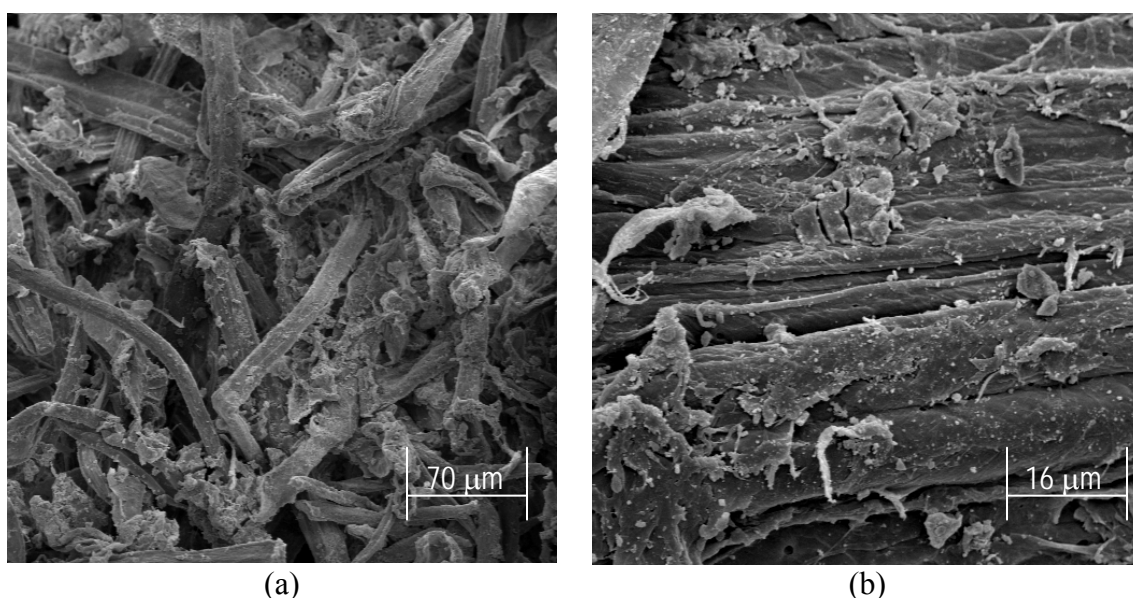


Fig. 4. Morphology of cellulose/ $ZrO_2 \cdot nH_2O$ fibres: (A) 500X; (B) 2000X

Water Absorption

Figure 5A shows the percentage of water absorbed in non-modified cellulose fibres from sugarcane bagasse-reinforced HDPE composites, designated as CB. Five specimens of each sample were submerged in distilled water at room temperature during 7 days.

It was observed that the composites exhibited higher water absorption compared to pure HDPE. This is attributed to the fact that the lignocellulosic materials change their dimensions when they absorb humidity. Therefore the composite (CB20%) showed higher water absorption compared to the others.

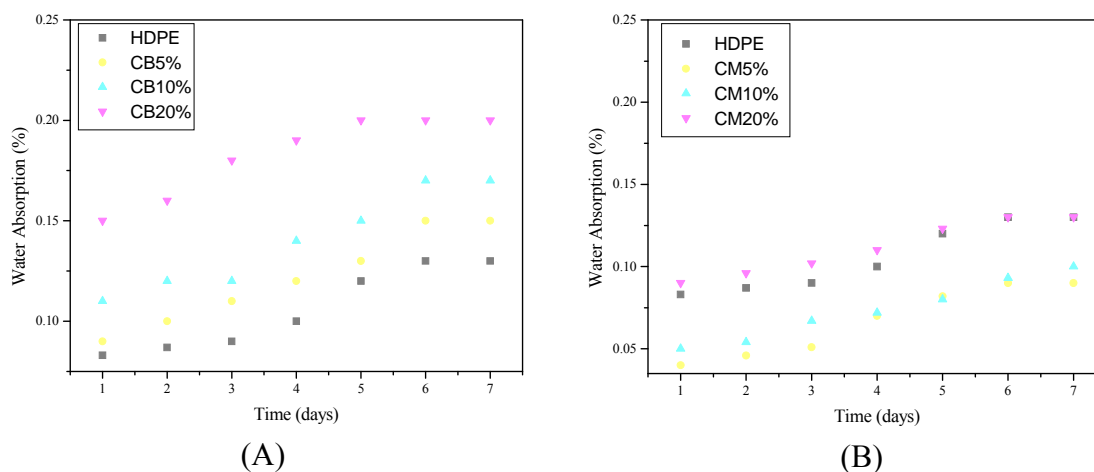


Fig. 5. Water absorption curves for composites: (A) CB; (B) CM

On the other hand, it was confirmed that the modification of cellulose fibres with hydrous zirconium oxide decreased the water absorption in composites (Fig. 5B). This effect was attributed to the hydrophilic character of the fibres, which it was reduced by modification with oxide on cellulose surface. Figure 5B shows the percentage of water absorbed in modified cellulose fibre reinforced HDPE composites designated as CM.

Based on these results, it is expected that modified cellulose fibre-reinforced HDPE composites should achieve higher tensile strength in comparison to the non-modified cellulose fibre-reinforced HDPE composites independent fibres volume.

Effect of Water Absorption on Mechanical Properties

Mechanical properties of composites are summarized in Table 1. Modified cellulose fibres reinforced HDPE composites exhibited higher tensile strength in comparison to the non-modified cellulose fibre-reinforced HDPE composites.

The amount of added reinforcement contributed to variation of the tensile modulus, as indicated in Table 1, but CM10% composites achieved higher tensile strength. Fibres insertion can contribute to an increase of modulus because the Young's modulus of the fibres is higher compared to the modulus of the thermoplastic matrix. However, to obtain a significant increase, a good interfacial bond between fibres and matrix is necessary.

Table 1. Mechanical Properties of the Composites Before Water Absorption at Room Temperature during 7 Days

Materials	Properties		
	Elongation at break (%)	Tensile strength (MPa)	Tensile modulus (MPa)
HDPE	8.9 ± 0.8	15.7 ± 1.1	732.45 ± 90.6
CB5%	5.4 ± 0.4	16.2 ± 0.7	942.5 ± 98.6
CB10%	5.5 ± 0.2	15.6 ± 0.3	897.4 ± 27.5
CB20%	5.7 ± 0.3	15.8 ± 0.3	1140.7 ± 62.5
CM5%	7.2 ± 0.1	20.8 ± 0.4	1177.7 ± 25.0
CM10%	7.4 ± 0.4	21.9 ± 0.6	1238.5 ± 41.0
CM20%	6.5 ± 0.2	20.9 ± 0.4	1306.4 ± 26.9

Reinforcement in wt%.

Experimental results in Table 1 may be explained by the interaction observed between fibres and matrix during the mixing process. The modified cellulose fibres exhibited better tensile strength and adhesion between fibres and matrix compared to the non-modified cellulose, confirming that cellulose modification with zirconium oxychloride improves the adhesion between fibres and matrix.

Therefore the mechanical properties obtained after water absorption in both composites (CB and CM) were affected (Table 2).

Table 2. Mechanical Properties of the Composites After Water Absorption

Materials	Properties		
	Elongation at break (%)	Tensile strength (MPa)	Tensile modulus (MPa)
HDPE	8.5 ± 0.3	14.9 ± 1.4	728.5 ± 85.1
CB5%	4.9 ± 0.6	15.5 ± 0.8	919.4 ± 88.3
CB10%	5.1 ± 0.7	14.8 ± 0.6	867.1 ± 31.3
CB20%	5.3 ± 1.1	15.1 ± 0.9	1129.5 ± 63.8
CM5%	6.8 ± 0.1	18.4 ± 1.3	1143.4 ± 25,0
CM10%	6.4 ± 0.4	20.6 ± 1.8	1219.8 ± 40,3
CM20%	6.1 ± 0.8	19.3 ± 0.6	1299.1 ± 66,4

Reinforcement in wt%.

The decrease in mechanical properties with increase in moisture content may be caused by formation of hydrogen bonding between the water molecules and cellulose fibres. CM5% and CM10% composites exhibited lower water absorption compared to CB5% and CB10% composites but influenced tensile strength. In general, the mechanical properties of these materials can decrease after the moisture uptake, due to the effect of the water molecules, which change the structure and properties of the fibres, matrix, and the interface between them. Once the moisture penetrates inside the composite materials, the fibres tend to swell. The matrix structure can also be affected by the water uptake.

Natural fibres are hydrophilic, with many hydroxyl groups (–OH) in the fibre structure forming a large number of hydrogen bonds between the macromolecules of the cellulose and polymer (Sombastsompop and Chaochanchaikul 2004). With the presence of a high –OH group percentage, natural fibres such as sugarcane bagasse tend to show low moisture resistance. This leads to dimensional variation of composites, a poor interfacial bonding between the fibres and matrix, and a decrease in the mechanical

properties (Diamant et al. 1981). The characteristics of water-immersed specimens are influenced not only by the nature of the fibres and matrix materials but also by the relative humidity and manufacturing technique, which determines factors such as porosity and volume fraction of fibres.

Figure 6 shows SEM micrographs of the fractured specimens, which correspond to the composites with higher amount water absorption (CB20% and CM20%) at room temperature for 7 days.

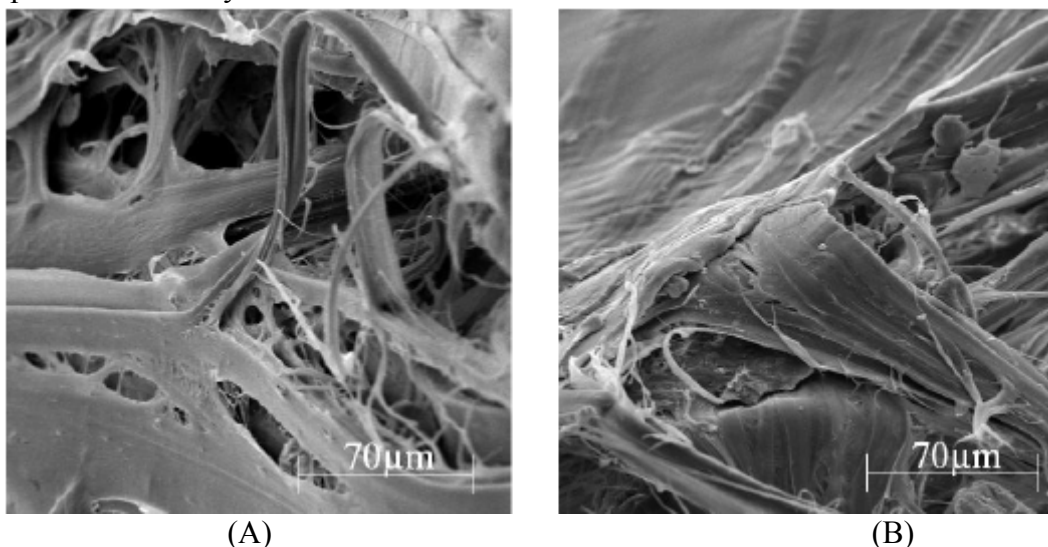


Fig. 6. SEM fracture surface of composites for 7 days: (A) CB20%; (B) CM20%

As shown in Fig. 6A, there was obvious separation of the HDPE and non-modified cellulose fibres, due to incompatibility between the hydrophobic matrix and the hydrophilic fibres. However, with the addition of modified cellulose fibres in the matrix (Fig. 6B) this incompatibility was reduced, confirming an interfacial bonding improvement between the fibres and matrix.

CONCLUSIONS

1. The present results reveal that cellulose fibres from sugarcane bagasse can be used as reinforcing filler in high density polyethylene composites.
2. Cellulose fibres were chemically modified with zirconium oxychloride in acid solution with a view to reducing the hydrophilicity of the fibres, and the modification was confirmed spectrophotometrically. Both bleached and modified cellulose fibres were utilized for the composites preparation.
3. The tensile strengths of the composites of both bleached and modified were found to increase with increasing filler content. For modified cellulose fibres composites, a 10% cellulose filled composite showed the highest tensile strength. This may be attributed to the better distribution of the filler in the matrix and stronger filler-matrix interaction, compared to non-modified cellulose. The improved mechanical properties of the modified cellulose fibres/HDPE composites were further supported

by SEM images of the fracture surface, showing better matrix-filler interaction compared to those prepared from bleached cellulose fibres.

4. The water absorption tendency of the composites increased with an increase in filler content; however, the modified cellulose/HDPE composites showed lower water absorption capacity compared to those prepared from bleached cellulose fibres, indicating that cellulose modification reduced the hydrophilicity of cellulose fibres.

ACKNOWLEDGMENTS

The authors are grateful for the research support by CAPES.

REFERENCES CITED

- Chow, C. P. L., Xing, X. S., and Li, R. K. Y. (2007). "Moisture absorption studies of sisal fibre reinforced polypropylene composites," *Compos. Sci. Technol.* 67 (2), 306-313.
- Dhakal, H. N., Zhang, Z. Y., and Richardson, M. O. W. (2007). "Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites," *Compos. Sci. Technol.* 67(7-8), 1674-1683.
- Diamant, Y., Marom, G., and Broutman, L. J. (1981). "The effect of network structure on moisture absorption of epoxy resins," *J. Appl. Polym. Sci.* 26 (9), 3015-3025.
- George, J., Bhagawan, S. S., and Thomas, S. (1998). "Effects of environment on the properties of low-density polyethylene composites reinforced with pineapple-leaf fiber," *Compos. Sci. Technol.* 58(9), 1471-1485.
- Gerrard, J., and Kandlikar, M. (2007). "Is European end-of-life vehicle legislation living up to expectations? Assessing the impact of the ELV Directive on 'green' innovation and vehicle recovery," *J. Cleaner Prod.* 15(1), 17-27.
- Gushikem, Y., and Toledo, E. A. (1999). *Preparation of Coated Cellulosic Fiber*. K. Esumi (ed.), Marcel Dekker, USA.
- Habibi, Y., El-Zawawy, W. K., Ibrahim, M. M., and Dufresne, A. (2008). "Processing and characterization of reinforcement polyethylene composites made with lignocellulosic fibers from Egyptian agro-industrial residues," *Compos. Sci. Technol.* 68(7-8), 1877-1885.
- John, M. J., and Thomas, S. (2008). "Biofibres and biocomposites," *Carbohydr. Polym.* 71(3), 343-364.
- Luz, S. M., Del Tio, J., Rocha, G. J. R., Gonçalves, A. R., and Del'Arco, A. P. (2008). "Cellulose and cellulignin from sugarcane bagasse reinforced polypropylene composites: Effect of acetylation on mechanical and thermal properties," *Compos. Part A* 39(9), 1362-1369.
- Luz, S. M., Gonçalves, A. R., and Del'Arco Jr, A. P. (2007). "Mechanical behavior and microstructural analysis of sugarcane bagasse fibers reinforced polypropylene composites," *Compos. Part A* 38(6), 1455-1461.

- Mulinari, D. R., Da Silva, G. L. J. P., and Da Silva, M. L. C. P. (2006). "Adsorção de íons dicromato nos compósitos celulose/ZrO₂.nH₂O preparados pelos métodos da precipitação convencional e em solução homogênea," *Quim. Nova.* 29(3), 496-500.
- Mulinari, D. R., and Da Silva, M. L. C. P. (2008). "Adsorption of sulphate ions by modification of sugarcane bagasse cellulose," *Carbohydr. Polym.* 74 (3), 617-620.
- Mulinari, D. R., Voorwald, H. J. C., Cioffi, M. O. H., Da Silva, M. L. C. P., and Luz, S. M. (2009). "Preparation and properties of HDPE/sugarcane bagasse cellulose composites," *Carbohydr Polym* 75(2), 317-321.
- Mulinari, D. R., Voorwald, H. J. C., Cioffi, M. O. H., Da Silva, M. L. C. P., Cruz, T. G., and Saron, C. (2009). "Sugarcane bagasse cellulose/HDPE composites obtained by extrusion," *Compos. Sci. Technol.* 69(2), 214-219.
- Pasquini, D., Teixeira, E. M., Curvelo, A. A. S., Belgacem, M. N., and Dufresne, A. (2008). "Surface esterification of cellulose fibres: Processing and characterization of low-density polyethylene/cellulose fibres composites," *Compos Sci Technol* 68(1), 193-201.
- Rodrigues Filho, G., Assunção, R. M. N., Vieira, J. G., Meireles, C. S., Cerqueira, D. A., Barud, H. S., Ribeiro, S. J. L., and Messaddeq, Y. (2007). "Characterization of methylcellulose produced from sugar cane bagasse cellulose: Crystallinity and thermal properties," *Polym. Degrad. Stab.* 92(2), 205-210.
- Saheb, D. N., and Jog, J. P. (1999). "Natural fiber polymer composites: A review," *Advances Polym. Technol.* 18, 351-363.
- Satyanarayana, K. G., Guimaraes, J. L., and Wypych, F. (2007). "Studies on lignocellulosics fibers of Brazil. Part I: Source, production, morphology, properties and applications," *Compos. Part A* 38(7), 1694-1709.
- Sombastsompop, N., and Chaochanchaikul, K. (2004). "Effect of moisture content on mechanical properties, thermal and structural stability and extruded texture of poly (vinyl chloride)/wood sawdust composites," *Polym. Int.* 53(9), 1210-1218.
- Stark, N. (2001). "Influence of moisture absorption on mechanical properties of wood flour-polypropylene composites," *J. Thermoplastic Compos. Mater.* 14(5), 421-432.
- Zah, R., Hischier, R., Leão, A. L., and Braun, I. (2007). "Curauá fibers in the automobile industry - A sustainability assessment," *J. Cleaner Prod.* 15(11-12), 1032-1040.
- Zampaloni, M., Pourboghra, F., Yankovich, S. A., Rodgers, B. N., Moore, J., Drzal, L. T., Mohanty, A. K., and Misra, M. (2007). "Kenaf natural fiber reinforced polypropylene composites: A discussion on manufacturing problems and solutions," *Compos Part A* 38(6), 1569-1580.

Article submitted: January 8, 2009; Peer review completed: February 11, 2010; Revised version received, accepted and published: February 22, 2010.