

Mechanical Characterization of Polypropylene–Wood Flour Composites

Adrián J. Nuñez,¹ Pablo C. Sturm,¹ José M. Kenny,² M. I. Aranguren,¹ Norma E. Marcovich,¹ María M. Reboredo¹

¹INTEMA-Facultad de Ingeniería; Universidad Nacional de Mar del Plata, Juan B. Justo 4302, (7600) Mar del Plata, Argentina

²Institute of Chemical Technologies, University of Perugia, Loc. Pentima Bassa 21, Terni, Italy

Received 9 January 2002; accepted 7 June 2002

ABSTRACT: The mechanical performance of different wood flour/polypropylene (PP) composites with interface modifications was compared. Wood flour was incorporated into the matrix after esterification with maleic anhydride (MAN) or without any modification but with the addition of a compatibilizing agent [maleic anhydride–polypropylene copolymer (PPMAN)] to modify the polymer–filler interaction. Composites were prepared by injection molding with different concentrations of wood flour. Mechanical properties (except Young's modulus) were not improved either by the wood flour chemical modification or by the use of PP-

MAN. However, both compatibilization methods were successful in improving the dispersion of the wood flour in the PP matrix. Creep behavior of composite samples was improved by the addition of PPMAN, whereas the composites prepared from MAN-treated wood flour showed larger deformations than composites made with untreated particles. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1420–1428, 2003

Key words: composites; mechanical properties; compatibilization

INTRODUCTION

Composites based on thermoplastic resins are now becoming popular because of their processing advantages.¹ The mechanical properties of thermoplastics are often inadequate for specific applications, and for this reason, synthetic reinforcing fillers and more recently, natural fillers, are mixed with them to obtain composites with desired properties.

Among commodity thermoplastics, polypropylene (PP) possesses outstanding properties such as low density, good flex life, sterilizability, good surface hardness, very good abrasion resistance, and excellent electrical properties. However, the main purpose for the addition of cellulose-based fillers to thermoplastics is to reduce the cost per unit volume and to improve stiffness.² Low-price cellulose-based fibers, such as wood flour, wood fibers, and cellulose fibers, have high stiffness and low density and are recyclable and nonabrasive. Contrary to PP, wood flour is predominantly polar due the presence of polar groups on its different components, and thus, it easily absorbs mois-

ture. Thus, to improve the interaction between these otherwise incompatible surfaces, the addition of a compatibilizer or the surface modification of the fibers (or the matrix) was envisaged. Different treatments have been used to improve the adhesion and/or the compatibility between fillers and PP,^{3–6} and the use of maleic anhydride–polypropylene copolymer (PPMAN) as a compatibilizing agent has also been reported.^{2,3,7}

Despite the recent progress in processing methods and the improvement of the mechanical performance of lignocellulosic composites, limited experimental results are available on creep. Creep failure considerations are essential when lignocellulosic thermoplastic composites are used in long-term loading applications.⁸ The aim of this study was to analyze the effect of system compatibility on the mechanical and creep properties of PP–wood flour composites. To modify the compatibility, two different methods were used: (1) wood flour chemical modification and (2) the use of a compatibilizing agent added to the mixture.

THEORETICAL APPROACH

Several theoretical models have been developed for the dependence of composite properties on the filler volume fraction.⁹ The simpler model, for a two-phase particulate system, proposed by Counto, assumes perfect bonding between the particle and the matrix, and in this case, the modulus of the composite is given by

Correspondence to: M. M. Reboredo (mrebored@fi.mdp.edu.ar or marcovic@fi.mdp.edu.ar).

Contract grant sponsor: International Foundation for Sciences; contract grant number: D/2813-1 (to N.E.M.).

Contract grant sponsor: Fundación Antorchas (Argentina).
Contract grant sponsor: CNR-CONICET (Italy–Argentina).

$$\frac{1}{E_c} = \frac{1 - V_f^{1/2}}{E_m} + \frac{1}{(1 - V_f^{1/2})/V_f^{1/2} E_m + E_f} \quad (1)$$

were E is the Young's tensile modulus and V is the volumetric fraction. The subscripts c , f , and m indicate composite, fiber, and matrix, respectively.

In the approximate solution obtained by using Paul's model,⁹ the constituents are assumed to be in a state of macroscopically homogeneous stress. Perfect adhesion at the interface of a cubic inclusion embedded in a cubic matrix is proposed. With this assumption, when a uniform stress is applied at the boundary, the elastic modulus of the composite is given by

$$E_c = E_m \left[\frac{1 + (E_f/E_m - 1) V_f^{2/3}}{1 + (E_f/E_m - 1)(V_f^{2/3} - V_f)} \right] \quad (2)$$

Applying the same model but assuming a uniform displacement at the boundary, Ishai and Cohen obtained the following equation:

$$E_c = E_m \left[1 + \frac{V_f}{(E_f/E_m)/(E_f/E_m - 1) - V_f^{1/3}} \right] \quad (3)$$

Pukánszky et al.⁴ assumed that the yield stress (σ_y) of the composite is determined by the decrease of the effective load-bearing cross-section of the matrix (because of the presence of the filler) and by the polymer-filler interaction. Accordingly, they proposed the following equation:

$$\sigma_c = \sigma_m \left(\frac{1 - V_f}{1 + AV_f} \right) \exp(BV_f) \quad (4)$$

where B is a parameter characterizing the interfacial interaction and A is a shape parameter related to the packing distribution of the filler.

EXPERIMENTAL

Materials

Wood flour from *Eucalyptus saligna* (Argentina) was used as reinforcing filler. Only particles that passed through a sieve of mesh 100 (Tyler series, Buenos Aires, Argentina) were used in this study, thus, the maximum particle average diameter was 147 μm .

Wood flour was esterified with maleic anhydride (MAN) according to a procedure described in a previous article.¹⁰ The MAN content of the treated wood flour was 23.47 g of MAN/100 g of neat wood flour.

The polymeric matrix was powder PP Moplen [melt flow index (MFI) = 17.2 g/10 min, provided by Himont, Ferrara, Italy], and PPMAN (MFI = 6.6 g/10 min, provided by University of Simon Bolívar, Caracas, Venezuela) was also used as a compatibilizer

agent. The MAN content of the copolymer was 0.3 ± 0.05 MAN.¹⁰ The compatibilizer was added in the proportion of 5 g of PP-MAN for each 100 g of untreated wood flour.

Plaques made from the composite material were obtained from a Sandretto Series 8 model 60t injection-molding machine (Collegno, Turin, Italy). The barrel temperature profiles were chosen as 180, 200, and 220°C (extrusion zone) and 220°C (injection zone), and the pressure was maintained at 125 bar in the extrusion zone and at 50 bar in the injection zone.

Nomenclature

Three different types of wood flour/resin mixtures were prepared:

1. Composites where the wood flour was incorporated without treatment (WC).
2. Composites where the wood flour was pretreated with MAN (MC).
3. Composites where the wood flour was incorporated without treatment and a 5% (with respect to the wood flour weight) of PPMAN was added as a compatibilizer agent (PPMC).

In all cases, the weight percentage of filler is indicated between parentheses [e.g., WC(40) indicates a composite made with untreated wood flour in a 40:60 (filler:PP) or (filler:PP + PPMAN) proportion].

Physical and mechanical tests

The composites were fractured in liquid air, and their surfaces were observed by scanning electron microscopy (SEM) with a Philips model SEM 505 microscope (Eindhoven, Netherlands). The samples were previously coated with gold.

Tensile tests were performed according to the ASTM D 638 (sample type I, thickness = 3 mm) with an Instron 8501 universal testing machine (Buckinghamshire, UK) at a crosshead speed of 5 mm/min. The Young's tensile modulus (E), yield tensile strength (σ_y), and percentage of elongation at yield were determined from the stress-strain curves.

Flexural tests were carried out on samples cut from the injected plates, with a span of 50 mm (transversal area of $13 \times 3 \text{ mm}^2$) according to the procedure A, ASTM D 790-86, in a Shimadzu Autograph S-500-C universal testing machine (Kyoto, Japan). A crosshead speed of 1.35 mm/min was used when composites were tested (rigid samples); however, a speed of 13.5 mm/min was selected for pure PP, as recommended for semirigid materials. The flexural modulus (E) and flexural yield stress (σ_y) were calculated from the stress-strain curves.

Izod notched impact strength was measured at 18°C in a FRACTOVIS-CEAST falling weight machine (Turin, Italy). The velocity of the tests was set at 1 m/s, and the striker minimum mass (3.6 kg) was used; thus the impact energy was 1.8 J.

A PerkinElmer dynamic mechanical analyzer (DMA 7) (Norwalk, CT) was used in the creep experiments to measure deformation as a function of time. The tests were carried out with three-point bending geometry with a specimen platform 15 mm in length. The applied static stress was 1×10^7 Pa. The temperature was fixed at 20 or 50°C.

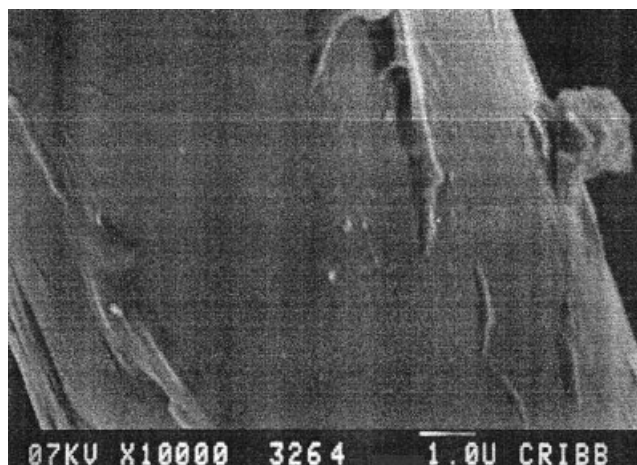
RESULTS AND DISCUSSION

The use of a chemical treatment on the wood flour particles or the addition of a compatibilizer had an obvious effect on the surface of the fibers, as was seen in the SEM micrographs of the fractured composites. Figure 1 shows the SEM micrographs of the surface of wood flour particles observed after the fracture of WC, MC, and PPMC composites. The untreated wood flour exhibited a rather smooth surface [Fig. 1(a)] with almost no matrix attachments. However, the particle surfaces showed a very similar appearance if they were treated with MAN [Fig. 1(b)] or when PPMAN [Fig. 1(c)] was added to the mixture. In the last two cases, the surface of the wood flour after the composite fracture showed a coating layer, evenly distributed on the entire surface as the result of the PP or PPMAN attachment.

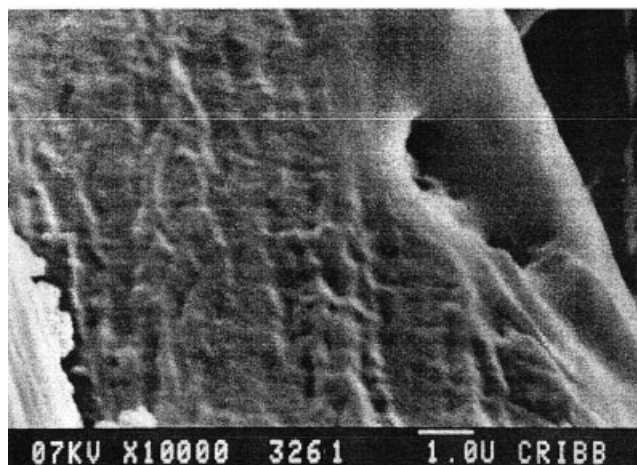
Tensile and flexural tests

Table I illustrates the effect of the wood flour concentration on the tensile properties of the composites. In all cases, the modulus increased with wood flour content, but the increment was larger for WC, except when high wood flour concentrations were considered. However, the strength of WC samples was higher than that of the MC specimens (except for samples containing 50 wt % of wood flour). In particular, PPMC(50) showed a higher modulus and strength and longer ultimate deformation than the untreated or esterified wood flour composites. As a result of filler addition, the ultimate strain decreased as the wood flour content increased because of the decreased deformability of the matrix (restricted by the rigid particles). The composition dependence of yields stress showed a similar trend.

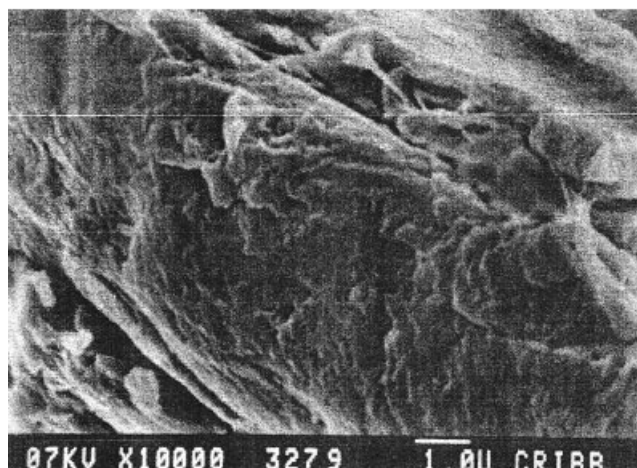
Table II shows the bending modulus (E_b) and σ_{by} of the different composites as a function of the filler content. The flexural modulus increased with the weight percentage of filler, as observed in the tensile tests, but the increment was larger for MC and even more for PPMC. Similarly, all the composites presented a flexural yield stress smaller than that of pure PP, and σ_{by} decreased as a function of the filler content.



(a)



(b)



(c)

Figure 1 SEM micrographs of the wood flour surface in (a) WC, (b) MC, and (c) PPMC.

The increment in the flexural modulus of PPMC samples with respect to that of the WC composites could be explained on the basis of the increased com-

TABLE I
Void Content and Tensile Properties of PP-Wood Flour Composites

Material	Wt %	E (GPa)	σ_y (MPa)	Ultimate deformation (%)	Void content (vol %)
PP	0	1.22 ± 0.16	36.87 ± 0.77	10.26 ± 0.97	—
	10	1.58 ± 0.01	28.98 ± 0.47	5.48 ± 0.43	0.8
WC	26	2.17 ± 0.05	23.88 ± 0.91	2.98 ± 0.33	3.2
	40	2.36 ± 0.87	18.31 ± 0.32	1.58 ± 0.15	6.2
	50	2.01 ± 0.20	11.88 ± 0.98	1.35 ± 0.09	7.8
	10	1.61 ± 0.13	26.24 ± 1.37	3.98 ± 0.25	1.7
MC	26	1.86 ± 0.09	18.98 ± 0.31	2.10 ± 0.20	7.7
	40	2.15 ± 0.03	14.57 ± 0.21	1.42 ± 0.02	8.3
	50	2.33 ± 0.28	11.33 ± 0.42	1.00 ± 0.11	4.1
PPMC	40	2.17 ± 0.07	18.57 ± 0.44	1.75 ± 0.10	8.6
	50	2.52 ± 0.04	16.82 ± 0.57	1.41 ± 0.08	7.8

NOTE E : Young modulus.

patibility between the filler and the matrix. The dispersion of the wood flour in the PP matrix was consequently improved, and thus, the reinforcing effect of the wood flour was more effective than that found for WC. It is known that strong interactions can cause a stiffening effect on the polymer matrix adjacent to the filler particles interphase.¹¹ Hence, it was expected that the improved interaction between the wood flour and PP due the addition of PPMAN would cause an increment of the composite modulus with respect to WC.

Although wood flour was MAN treated to increase its affinity for the PP matrix and improve its dispersion, previous results indicated that esterified wood flour is less thermally stable than untreated wood flour.¹⁰ Moreover, thermal degradation was evident in the color of the injected samples. The plaques obtained with untreated wood flour were light to dark brown, depending on the wood flour content, whereas the plaques obtained from MAN-treated fibers were always darker than WC or PPMC for the same wood flour contents. Degradation leads to the production of volatile compounds during processing and, thus, to porous polymer products. Thus, the thermal degradation of the esterified wood flour during injection was responsible for the lower values found in the tensile

moduli of MC samples, compared with the WC samples because the tensile tests were more sensitive to defects, pores, and voids in the sample than were flexural tests.

The improved dispersion obtained from the MAN treatment and PPMAN addition was also responsible for the increase in the Young's modulus with wood flour content up to high filler concentrations, whereas the WC tensile modulus reached a maximum at about 40 wt % and then decreased. For untreated wood flour contents higher than 40 wt %, the filler particles began to form aggregates. Direct physical bonds between filler particles are weak and, thus, easily broken during tensile loading, which explains the decrease in the Young modulus (E) at high particle contents.

Void formation during MC injection could explain the decrease of flexural and tensile strength of MC samples compared with those of the WC samples. Furthermore, the contribution of a loose interphase formed between esterified wood flour and PP should also be considered because MAN moieties in the wood flour surface cannot supply entanglements with the PP matrix. Felix and Gatenholm,¹² who worked with different molecular-weight modifiers, indicated that the longer the modifier chain is, the stronger the achieved interface is. Esterification with MAN improved the compatibility (wettability) between the filler and the matrix but did not improve the interfacial strength.

Most of the published works on the use of PPMAN compatibilizers in lignocellulosic PP systems report the improvement of the mechanical response^{7,13} because the PP chains of PPMAN are compatible with the matrix and long enough to get entangled with the matrix chains. In this case, no improvement in flexural stress and only a marginal improvement in tensile strength were found up to 40% filler, probably because the selected PPMAN contained a small amount of MAN segments (0.3% grafted MAN) to interact effectively with the wood flour. However, the benefits of using the compatibilizer were more visible at the highest filler content, where the good compatibility led to

TABLE II
Flexural Properties of PP-Wood Flour Composites

Material	wt %	E_b (GPa)	σ_{by} (MPa)
PP	0	1.22 ± 0.08	54.43 ± 0.8
	10	1.28 ± 0.09	45.32 ± 1.7
WC	26	1.60 ± 0.11	43.63 ± 1.5
	40	2.16 ± 0.31	42.47 ± 3.6
	50	2.43 ± 0.07	37.20 ± 0.4
	10	1.55 ± 0.03	48.92 ± 0.7
MC	26	2.13 ± 0.40	42.55 ± 0.6
	40	2.43 ± 0.12	35.48 ± 2.5
	50	2.72 ± 0.20	31.44 ± 1.0
PPMC	40	2.71 ± 0.11	41.21 ± 1.1
	50	3.04 ± 0.13	35.04 ± 1.1

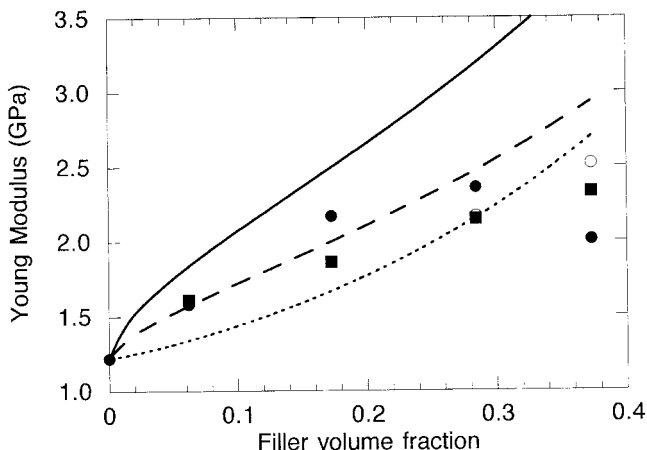


Figure 2 Young's modulus versus volume fraction. Theoretical predictions: (—) Counto, (---) Ishai-Cohen, and (·) Paul. Experimental values: (●) WC, (■) MC, and (○) PPMC.

higher tensile strength and modulus. The untreated fiber composite at 50 wt % was beyond the wetting possibilities of the matrix, and the modulus dropped below the maximum value.

Fillers with larger stiffnesses than the matrix can increase the modulus of the composites but generally cause a dramatic decrease in the elongation at break. Almost all of the elongation occurs in the matrix if the filler is rigid. This effect was observed for all of the wood flour composites (Table I).

To improve our understanding of the mechanical behavior of the composites, the experimental tensile response was compared to simple theoretical or empirical expressions. Woodhams et al.¹⁴ suggested that the Young's modulus of the wood fibers varies between 10 and 80 GPa, Rohatgi et al.¹⁵ selected 40 GPa as the Young's modulus of the Kraft wood fiber, and Buttrey¹⁶ suggested 4.9 to 14 GPa for wood flour. The lower bond proposed by Buttrey¹⁶ seems to be very low because the Paul upper bond predicts lower values than the experimental ones; thus, for the following discussion, the modulus of wood flour particles was taken as the average value proposed by Woodhams, $E_f = 45$ GPa, whereas the modulus of the matrix ($E_m = 1.22$ GPa) was experimentally determined.

In Figure 2, the experimental Young's modulus values of WC, MC, and PPMC are compared to the predictions of the Counto, Ishai-Cohen, and Paul models. Paul's upper bound overestimated the data, whereas Ishai-Cohen estimations gave lower values than the experimental ones for lower wood flour concentrations. The data fell mainly on the curve predicted by the Counto equation, although this model was unable to account for the decrease of the modulus because of incomplete wetting (at higher wood flour concentrations) or voids. None of the selected models was able to consider the first effect, but the second could be taken into account by recalculation of the "effective"

matrix modulus. In this case, the matrix modulus was calculated as if it were a PP matrix with voids. The void content of the samples was calculated with a simple rule of mixtures for the density of the composites ($\rho_{\text{matrix}} = 0.91$ g/cm³, experimental value and $\rho_{\text{cell wall}} = 1.53$ g/cm³ where ρ is density; see ref. 17). Then, the effective matrix modulus was used to predict the composite modulus with the Counto, Paul, and Ishai-Cohen expressions. These results are shown in Figure 3, compared with the experimental MC values. Figure 3 shows that in this case, the experimental data fell mainly between the Paul's upper bond and the Counto model, whereas the Ishai-Cohen lower bond underestimated the data. These corrected models were now capable of predicting the change in the slope of the curve E versus V_f because of the increasing void content. At the highest concentration, the incomplete wetting of the particles further decreased the composite modulus. The same conclusions were obtained when WC experimental data were compared with theoretical predictions, although the agreement was not as good as in the shown case because the void content was lower for WC composites and incomplete wetting was the main reason for the reduction of modulus at high wood flour concentrations.

Tensile strength is much dependent on interfacial adhesion than the Young's modulus. For instance, tensile σ_y proved to be an excellent property to correlate with interfacial interactions in heterogeneous polymer systems.¹⁸ In general, tensile σ_y of particulate filled composites is determined by two main factors: (1) the decrease in the effective load-bearing cross-section of the matrix, because of filling, and (2) the polymer filler interactions.⁴

The experimental results were fitted with eq. (4), with B allowed to be the fitting parameter (Table III). Both the morphology and the size distribution of the particles are important for the determination of the

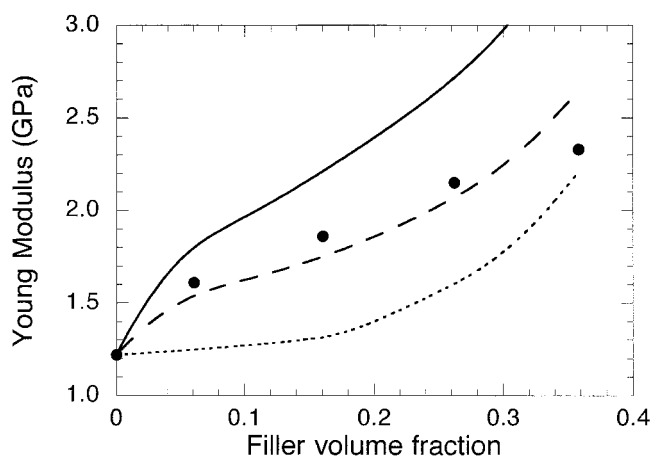


Figure 3 Experimental Young's modulus of MC versus volume fraction. Theoretical predictions corrected due to void content: (---) Counto, (---) Ishai-Cohen, and (—) Paul.

TABLE III
Calculated *B* Parameters [Corresponding to eq. (4)]

Sample	<i>B</i>
WC	1.8
MC	1.1
PPMC	2.1

shape parameter; thus, *A* was taken as 5.56, which corresponds to the case of a bigranulometric distribution where the smaller particles totally occupy the interstitial holes located at the center-face position of a simple cubic arrangement.¹⁹ Hence, values of *A* higher of 2.5 (which corresponds to spherical particles in hexagonal closed-packed or face-centered arrangements) indicate that a nonmonodispersed distribution of particles is used.²⁰ This assumption seems applicable to this case where a distribution of particle size is being used. The results reported in Table III show that the *B* parameter was similar for WC and PPMC samples, but it was quite low for MC composites, indicating that the interaction between the filler and matrix was reduced after esterification and was improved when PPMAN was added as a compatibilizer.

Impact behavior

The notched Izod impact energy of composites is plotted against the weight percentage of wood flour in Figure 4. The Izod strength initially exceeded that of the neat PP because of the additional mechanisms of energy absorption effective during fracture in the filled systems. However, the impact strength of reinforced PP decreased with increasing wood flour content, whereas stiffness simultaneously increased. Although impact resistance usually decreases with increasing amount of filler, quite frequently a maximum is observed at a low or intermediate (< 15% volume)

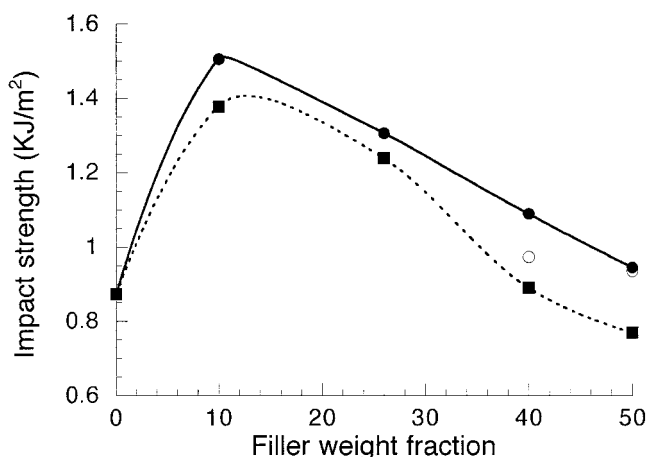
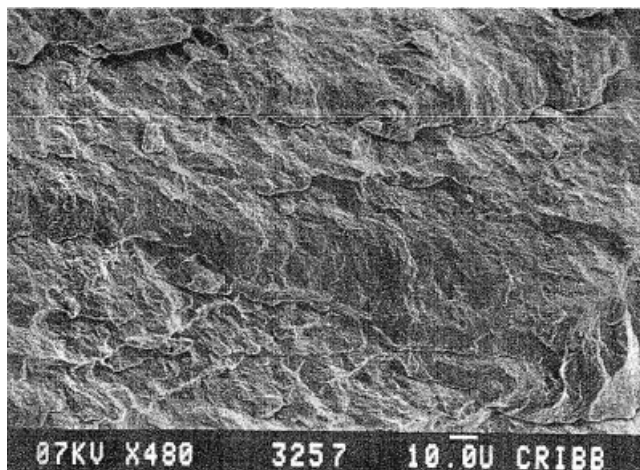
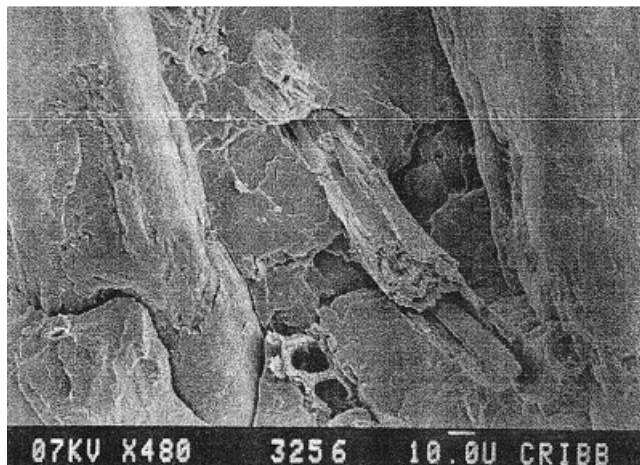


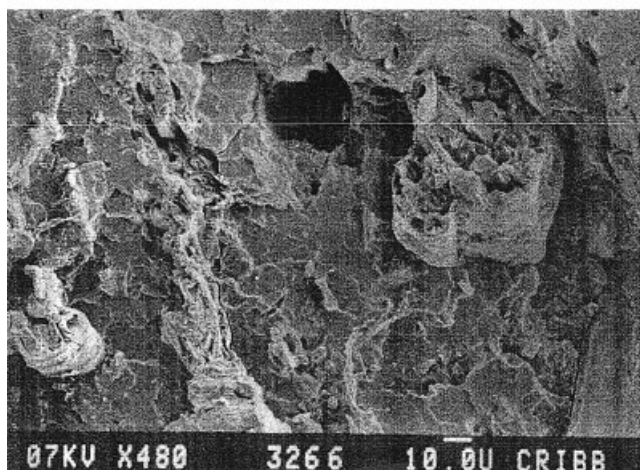
Figure 4 Notched Izod impact strength of (—●—) WC, (---■---) MC, and (○) PPMC.



(a)



(b)



(c)

Figure 5 Fracture surface of (a) neat PP, (b) WC(26) and (c) WC(40).

filler content. The maximum is most probably the combined result of different competitive micromechanical deformation processes influenced by poly-

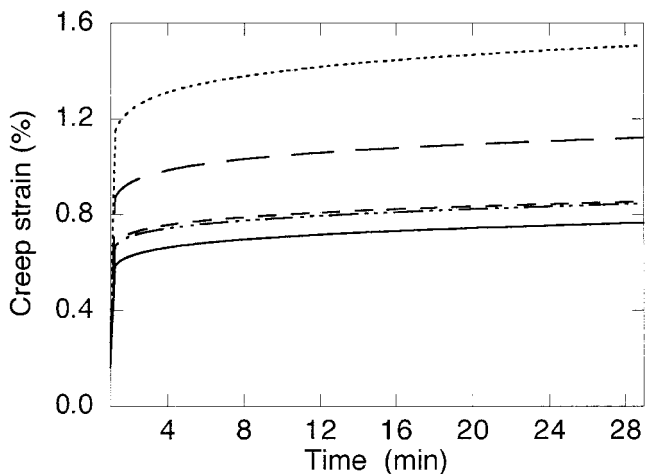


Figure 6 Short-term creep behavior of WC samples at 20°C: (· · ·) PP and (— —) 10, (— · —) 26, (—) 40, and (— · · ·) 50%.

mer–filler interactions and particle–particle interactions.²¹ As the concentration of wood flour increased, the material became more rigid, and the impact strength was reduced. Figure 5 shows the fracture surface of neat PP, WC(26), and WC(40) samples. As the wood flour content increased, there was a change from ductile to more brittle fracture behavior because of the restrictive presence of the rigid particles.

The PPMAN compatibilizer had little or no effect on the notched impact strength, whereas the energy values of MC samples were always lower than the corresponding WC, which was in agreement with the higher void volume fraction of these composites. Notched impact behavior is controlled to a greater extent by factors affecting the propagation of fracture initiated at the predominant stress concentration at the notch tip. Fracture propagation absorbs less energy as it finds voids in front of the tip crack.

Although the addition of rigid particles to a polymer matrix tends to cause a reduction in the strength of the filled material, it is well established that crack propagation becomes more difficult in such materials.²² However, the decrease in the impact strength with wood flour content could be attributed to the increment in fiber ends within the body composites, which could cause crack initiation and, hence, potential composite fracture.²³ Also, at high filler content, the probability for fiber agglomeration²⁴ also increases, creating regions of stress concentration that require less energy to initiate or propagate a crack.

However, the addition of PPMAN had little or no effect on the notched impact strength with respect to that of WC composites. Different results were reported in literature. Myers et al.⁷ reported that PPMAN did not improve the impact strength but instead reduced it with increasing PPMAN content. Järvelä et al.²⁵ indicated that PPMAN located at the interlayer between the matrix and the filler played the role of a

crosslinking agent because MAN groups of PPMAN chains may have reacted with —OH groups of wood flour, resulting in hardening of the interlayer. In addition, a PP segment of PPMAN was the same as the one of PP; thus, PPMAN increased the interactions between the matrix and the filler. Such interactions could also inhibit polymer mobility and, thereby, lower the ability of the system to absorb energy during fracture propagation. The hardening of the interlayer led to an increase in modulus, but reduced the impact strength of the composites. Other authors have reported the opposite behavior.^{1,13} In this case, there was no improvement in impact properties due to the addition of PPMAN compatibilizer.

Short-term creep

Short-term creep tests of the composites were also carried out. The effect of the wood fiber concentration on the short-term creep response is shown in Figure 6 for untreated WC samples tested at 20°C. The neat polymer showed the highest creep in the range of time analyzed. When a small amount of wood flour (10 wt %) was added, the creep decreased, and it continued to decrease with increasing wood flour content up to approximately 40 wt %. Samples prepared with 50 wt % showed a larger deformation than those prepared with 40 wt % wood flour. At this high concentration, the amount of polymer was not enough to completely wet the reinforcement, and thus, particle agglomerates were formed, which reduced the mechanical properties of the composite. However, the MC and PPMC composites showed lower creep deformation at 50% wood flour than at 40% filler, in agreement with the observed improved dispersion obtained by the esterification of the wood flour or by the addition of PPMAN. This behavior is shown in Figure 7, where creep

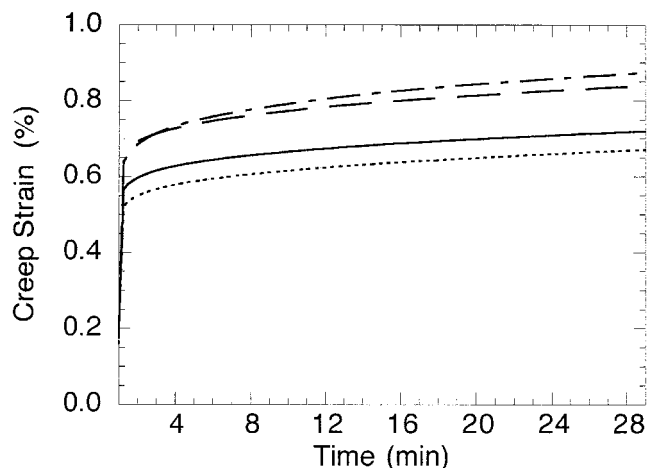


Figure 7 Short-term creep behavior of MC and PPMC containing 40 and 50 wt % wood flour at 20°C: (— · —) MC(40), (— · —) MC(50), (—) PPMC(40), and (· · ·) PPMC(50).

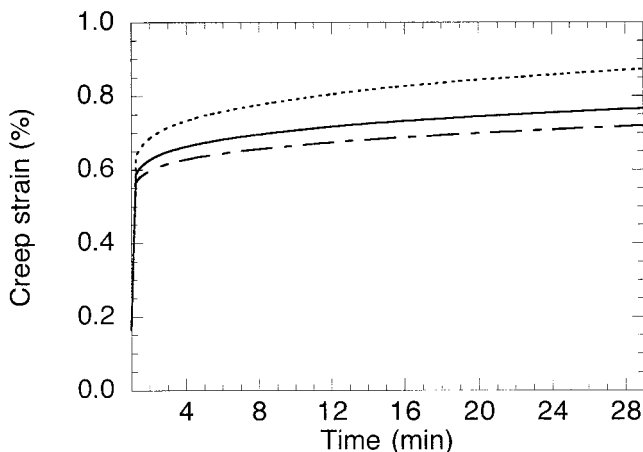


Figure 8 Short-term creep behavior for composites with 40 wt % wood flour at 20°C: (—) WC, (- - -) MC, and (- · -) PPMC.

curves for MC and PPMC containing 40 and 50% of wood flour are compared. The stronger interface obtained with the addition of PPMAN was responsible for the better creep behavior of these composites with respect to the MC samples.

Figure 8 shows the behavior of WC, MC, and PPMC composites with 40 wt % wood flour at 20°C. The deformation of the MC samples was higher than that of the untreated composite, and this trend was also verified for different wood flour concentrations and temperatures. This behavior was in agreement with the improved dispersion and filler-matrix interaction of the PPMC samples and the high void content in the MC samples. Figure 9 shows the behavior of WC(50), MC(50), and PPMC(50) samples at 50°C. The deformation of the samples at this higher temperature was larger than that at room temperature. Thermoplastic materials are typically softened at elevated temperatures, and as a result, their composites show reduced creep resistance. Although the trend was the same as that was found at 20°C, the differences between WC, MC, and PPMC curves were more important at 50°C.

As previously indicated, the esterification of wood flour particles did not enhance the creep response. The loose interface between treated particles and the PP matrix may have been responsible for the reduced response in creep tests. Moreover, esterification produces some plastification²⁶ of the wood flour particles that might undergo larger deformations than untreated wood flour. The hydrogen bonding present in wood, which provides a significant portion of the strength of the fibers, was reduced because of the esterification with MAN, adversely affecting the wood flour mechanical properties.

CONCLUSIONS

The tensile, flexural, creep, and impact properties of PP composites made with untreated wood flour and

MAN-treated wood flour and with the addition of PPMAN compatibilizer were studied.

The tensile (E) and (E_b) moduli increased with the addition of filler. This increment was more important in the flexural moduli if treated wood flour was used or if PPMAN was added to the composite. Tensile σ_y of MC samples was more affected by the incipient thermal degradation of the wood flour during processing and, consequently, showed lower values.

Simple models were utilized to fit the experimental tensile modulus, finding that correction by the presence of voids allowed good fitting of the experimental results with Counto's model. Tensile strength results were also analyzed with the Pukánszky et al. model. In that case, the data indicated a poorer interface in the MC samples. The addition of PPMAN did not produce significant differences with respect to the untreated wood flour composites. However, the experimental results show advantages in its use at high concentrations (with higher modulus, yield strength, and ultimate deformation than WC).

The addition of wood flour to PP initially increased the impact strength of the material because new deformation mechanisms are active during fracture. However, as filler concentration increased, the material became more rigid, and the impact energy dropped. Moreover, the absorbed energy was lower for MC composites.

The deteriorated properties observed in highly concentrated WC samples were attributed to the incomplete wetting of the fibers by the matrix and to the agglomeration of the fiber. The thermal degradation that occurred in MAN-treated samples during processing was responsible for the poor mechanical response of the corresponding composites.

MAN treatment was not effective for reducing the strain level in creep tests (with respect to that of the

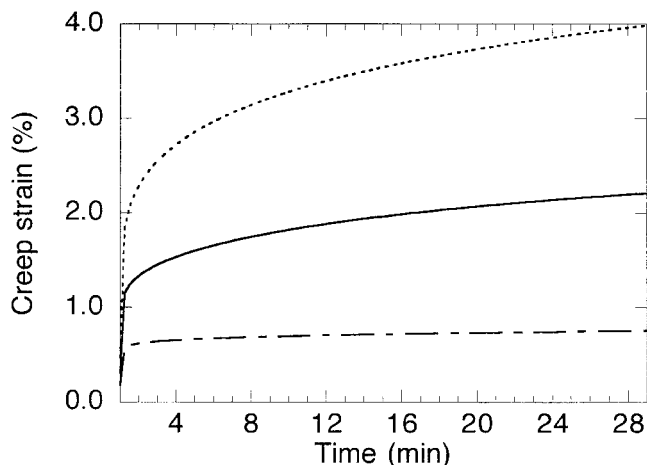


Figure 9 Short-term creep behavior for composites with 50 wt % wood flour at 50°C: (—) WC, (- - -) MC, and (- · -) PPMC.

WC composites) because of the presence of voids, the incipient thermal degradation of the fibers, and possible plastification of the esterified wood flour. However, the use of PPMC compatibilizer reduced the creep deformation of these materials because of the improved filler dispersion and the stronger filler-matrix interactions that were obtained.

References

1. Rana, A. K.; Mandal, A.; Mitra, B. C.; Jacobson, R.; Rowell, R.; Banerjee, A. N. *J Appl Polym Sci* 1998, 69, 329.
2. Oksman, K.; Clemons, C. *J Appl Polym Sci* 1998, 67, 1503.
3. Avella, M.; Casale, L.; Dell'erba, R.; Focher, B.; Martuscelli, E.; Marzetti, A. *J Appl Polym Sci* 1998, 68, 1077.
4. Pukánszky, B.; Tudos, F.; Jancar, J.; Kolarik, J. *J Mater Sci Lett* 1989, 8, 1040.
5. Gauthier, R.; Joly, C.; Coupas, A. C.; Gauthier, H.; Escoubes, M. *Polym Compos* 1998, 19, 287.
6. Coutinho, F. M. B.; Costa, T. H. S.; Carvalho, D. L. *J Appl Polym Sci* 1997, 65, 1227.
7. Myers, G. E.; Chahyadi, I. S.; Coberly, C. A.; Ermer, D. S. *Int J Polym Mater* 1991, 15, 21.
8. Park, B.-D.; Balantinecz, J. J. *Polym Comp* 1998, 19, 377.
9. Ahmed, S.; Jones, F. R. *J Mater Sci* 1990, 25, 4933.
10. Nuñez, A. J.; Kenny, J. M.; Reboredo, M. M.; Aranguren, M. I.; Marcovich, N. E. *Polym Eng Sci* 2002, 42, 733.
11. Stricker, F.; Bruch, M.; Mülhaupt, R. *Polymer* 1997, 38, 5347.
12. Felix, M.; Gatenholm, P. *J Appl Polym Sci* 1993, 50, 699.
13. Dalvåg, H.; Klason, C.; Strömval, H. E. *Int J Polym Mater* 1985, 11, 9.
14. Woodhams, R. T.; Thomas, G.; Rodgers, D. K. *Polym Eng Sci* 1984, 24, 1166.
15. Rohatgi, P. K.; Satyanarayana, K. G.; Chand, N. In *International Encyclopedia of Composites*; Lee, S. M., Ed.; VCH: New York, 1991; Vol. 4 p 8-16.
16. Buttrey, D. N. In *Polymer Engineering Composites*; Richardson, M. O. W., Ed.; Applied Science: London, 1977; Chapter 12.
17. Browning, B. L. In *Encyclopedia of Polymer Science and Technology*; Bikales, N. M.; Gaylord, N. G.; Mark, H. F., Eds.; Wiley: New York, 1971; Vol. 15 p 1-40.
18. Pukánszky, B. *Composites* 1990, 21, 255.
19. Turcsánsky, B.; Pukánszky, B.; Tudos, F. *J Mater Sci Lett* 1988, 7, 160.
20. D'almeida, J. R. M.; Carvalho, L. H. *J Mater Sci* 1998, 33, 2215.
21. Pukánszky, B. In *Polypropylene: Structure, Blends and Composites*; Karger-Kocsis, J., Ed.; Chapman & Hall: Cambridge, England, 1995; Vol. 3.
22. Kinloch, A. J.; Young, R. J. *Fracture Behavior of Polymers*; Applied Science: London, 1983.
23. Folkes, M. J. In *Short Fibre Reinforced Thermoplastics*; Devis, M. J., Ed.; Wiley: Herts, England, 1982.
24. Mascia, L. *The Role of Additives in Plastics*; Edwar Arnold: London, 1974; Chapter 3.
25. Järvelä, P. A.; Shuca, L.; Järvelä, P. K. *J Appl Polym Sci* 1997, 65, 2003.
26. Marcovich, N. E.; Aranguren, M. I.; Reboredo, M. M. *Polymer* 2001, 42, 815.