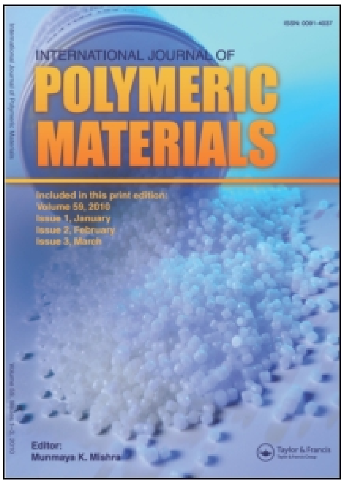

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

INFLUENCE OF COMPATIBILIZATION TREATMENTS ON THE MECHANICAL PROPERTIES OF FIQUE FIBER REINFORCED POLYPROPYLENE COMPOSITES

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To cite this Article Gañán, Piedad and Mondragon, Iñaki(2004) 'INFLUENCE OF COMPATIBILIZATION TREATMENTS ON THE MECHANICAL PROPERTIES OF FIQUE FIBER REINFORCED POLYPROPYLENE COMPOSITES', International Journal of Polymeric Materials, 53: 11, 997 — 1013

To link to this Article: DOI: 10.1080/00914030490516648

URL: http://dx.doi.org/10.1080/00914030490516648

International Journal of Polymeric Materials, 53:997–1013, 2004
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ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490516648

INFLUENCE OF COMPATIBILIZATION TREATMENTS ON THE MECHANICAL PROPERTIES OF FIQUE FIBER REINFORCED POLYPROPYLENE COMPOSITES

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Fique fibers reinforced polypropylene (PP) composites have been investigated for different fiber lengths and contents. Fiber/matrix interfacial adhesion has been modified by fiber treatments such as mercerization, esterification with maleic anhydride, and adding of an isocyanate compound. A copolymer of polypropylene with maleic anhydride has been employed as compatibilizer agent, by previous mixing with PP matrix. Both compatibilization ways improve fiber/matrix adhesion, as shown by changes of the free surface energy of fibers and also by SEM analysis. Addition of the compatibilizer agent leads to higher flexural properties than those obtained for composites where the fibers were treated. Dynamical mechanical properties of composites seem to indicate that movement in the crystalline PP phase, possibly occurring on the fiber/matrix interphase, takes place in between the glass transition and the melting temperatures of PP matrix.

Keywords: fique fibers, polypropylene, mechanical, compatibilization, viscoelastic behavior

Abbreviations: PP: Polypropylene; M: Mercerization fiber treatment; MA: Maleic acid fiber treatment; I: Isocyanate fiber treatment; MAPP: Copolymer of polypropylene with maleic anhydride; SEM: Scanning electron microscopy

Received 12 February 2003; in final form 18 February 2003.

The authors thank compañía de Empaques in Medellin (Colombia), Universidad del País Vasco/Eukal Herriko Unibertsitatea and Universidad Pontificia Bolivariana for the financial and logistics support that has made this research work possible.

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INTRODUCTION

Natural fibers present a medium mechanical behavior when compared to glass or carbon fibers. However, they present other important advantages, such as high availability, low cost, low abrasion, low density, and also recyclability and biodegradability. Different works have been performed to investigate the mechanical, physical, and thermal behavior of composites developed with different plant fibers such as cellulose [1], sisal [2], jute [3], or wood [4].

Fique fibers are cultivated in Colombia and other tropical regions, such as Ecuador or Mauritius Islands. They are hard fibers similar to sisal [5]. Due to their low density (0.87 g/cm^3) and appropriate tensile properties, the use of fique fibers as reinforcement for thermoplastic matrices can be of interest.

Natural fiber composite properties depend on several variables, including type of fiber, length, orientation, loading, and dispersion of the fibers. As a consequence, their evaluation for each new material to be developed becomes rather important. Another important factor that affects the behavior of natural fiber composites is the fiber/matrix adhesion. To enhance the fiber/matrix interactions, it is possible to employ different alternatives, such as addition of coupling agents to the matrix or modification of the fiber surface. Different surface treatments of natural fibers as mercerization [6], silanization [7], acetylation [8], or steam explosion [9] have been studied to enhance the interfacial behavior.

This article deals with the influence of fiber length, content, and surface treatments on mechanical and physical behavior of fique fibers reinforced polypropylene matrix composites. Surface treatments as mercerization (M), esterification with maleic acid (MA), and adding of an isocyanate compound (I) have been employed. On the other hand, the MAPP has also been used as compatibilizer agent, by previous mixing with the PP matrix. Compression molded plates have been manufactured with untreated and treated fique fibers.

EXPERIMENTAL

Materials

Fique fibers were kindly supplied by Compañía de Empaques S.A. (Medellín, Colombia). Polypropylene (PP) was purchased from Targor (Novolen 2300K, density: 0.91 g/cm^3, MFI: 4 g/10 min at 190°C). The fibers were cleaned and chopped at different mesh sizes: 4, 6, and 8 mm.

Fiber Surface Modification

Mercerization Treatment (M)

Fique fibers were immersed at room temperature in a 20 wt% sodium hydroxide solution for 1 h. Then, the fibers were soaked repeatedly in distilled water with a few drops of glacial acetic acid until neutralization of the solution occured.

Isocyanate Treatment (I)

This treatment was carried out according to the process proposed by Joseph et al. for treatment of sisal fiber with a compound derived from isocyanate and propyleneglycol [10]. In this case, the isocyanate employed was methylenediphenyl diisocyanate, supplied by Quimidroga. The reaction temperature was 70 ± 10°C.

Esterification Process

Maleic anhydride (MA), supplied by Cepsa, was employed for esterification. Fique fibers were dipped in 2.5 wt% solution of maleic anhydride in acetone. The treatment was carried out at 55 ± 5°C for 25 h. Then the fibers were washed with acetone and distilled water to remove the unreacted maleic anhydride.

All treated fibers were dried at 105 ± 5°C for 24 h and stored into a dessicator until final application.

Coupling Agent

The compatibilizer agent employed to enhance the fiber/matrix compatibility was Epolene 43 (Eastman), a copolymer of polypropylene with maleic anhydride (MAPP). Prior to composite processing, neat PP was mixed with the compatibilizer agent in a twin-screw extruder (Haake Rheomex CTW 100) using the method suggested by Felix et al. [11]. A screw speed of 25 rpm and a mixing temperature of 180°C were used. After cooling, the bulk was granulated for further processing.

Composite Processing

Untreated and treated fibers were compounded with polypropylene matrix by melt mixing, using a twin-screw extruder (Haake Rheomex CTW 100) with four heating zones operating at 180°C and 15 rpm screw speed. The residence time was 15 min, approximately. The compound so obtained was molded into plaques for mechanical analysis with a compression press (Satim) by heating the material to 180°C for 7 min to allow total melting, thereafter subjecting it to a different pressure of 10 MPa during the last 3 min. The plaques were then cooled to room temperature at a rate of 4°C/min.

Test Methods

To evaluate the effect of different treatments on the surface of fique fibers, contact angle measurements were carried out by dynamic angle method using the Wilhelmy plate technique [12]. The liquids used were water, ethyleneglycol, and α-bromonaphtalene at 24°C. Ten fibers were investigated for each type of treatment. The surface energy was calculated using the method of Owens and Wendt [13].

Flexural testing was performed according to ASTM D-790M by employing a Instron universal testing machine, model 4026. At least five samples were tested for each treatment. The average values are reported.

The composite densities were calculated by means of weight and volume measurements. The volumes were evaluated accurately from sample dimensions. This method is possible to employ due to the regular shape of specimens in accordance to the procedure proposed in the ASTM D2734 standard test method. Five flexural samples of each material were employed to calculate the average values.

Fracture surfaces of different samples were examined using a scanning electron microscope (SEM), Jeol 6400. An optical microscope was employed to analyze the fiber length distribution for the different mesh sizes used.

Dynamic mechanical properties of neat matrix and untreated composites were measured as a function of temperature using a Metravib viscoanalyzer with a flexural device of 44 mm span and sample dimensions were $60 \times 12 \times 3\,\mathrm{mm}^3$. The heating rate and frequency employed were 3°C/min and 10 Hz, respectively.

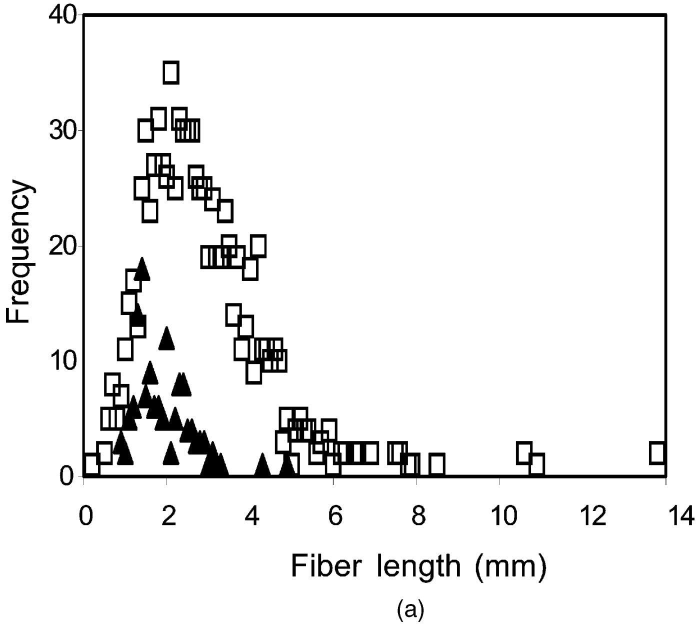
RESULTS AND DISCUSSION

The presence of natural fibers affects the behavior of their composites. In this study the main aspects considered are associated with fiber length, fiber content, and the use of different surface treatments to modify the behavior of the fiber/matrix interface.

Mechanical Behavior

Fiber Length

The length distribution curves for chopped fibers and for those extracted from composites with a 20 wt% fiber content are shown in Figure 1. Table 1 presents the average fiber lengths for the different



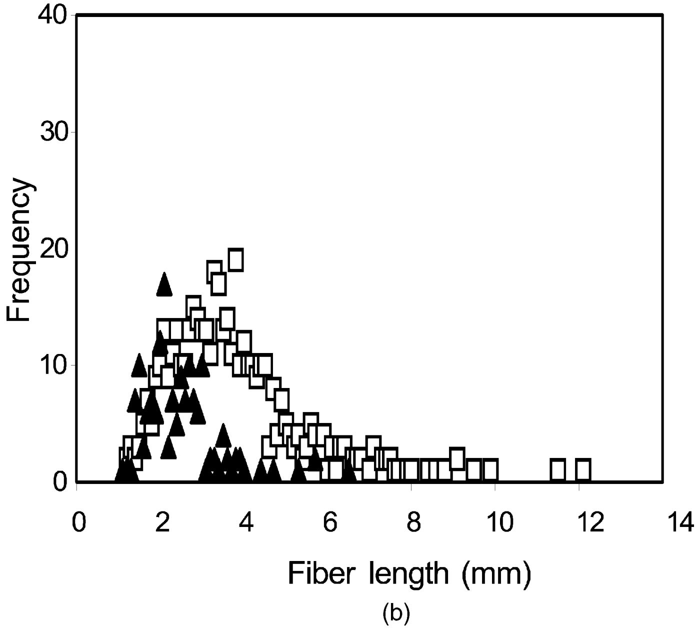


FIGURE 1 Fiber distribution curves for fique fibers chopped with several mesh sizes (□) and for the corresponding fibers extracted from composites (▲). Mesh sizes: (a) 4 mm, (b) 6 mm, and (c) 8 mm.

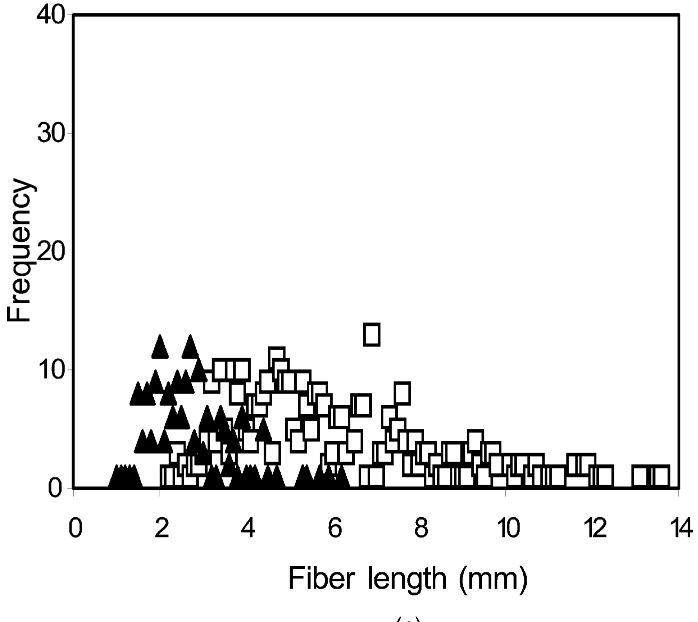


FIGURE 1 Continued.

mesh sizes used. The results show a clear length reduction for fibers extracted from composites, indicating that the processing conditions are the key factor for defining the final fiber size in the composites. This reduction can be related to friction between fibers and also between these and metallic parts of the twin-screw extruder during mixing process. Comparable results have been obtained by Gatenholm et al. [14] when studying the reduction of fiber length for samples of untreated cellulose fiber reinforced polystyrene composites with 40 wt% fiber, manufactured by injection molding. These authors

TABLE 1 Average Fiber Length for Chopped Fibers and for Fibers Extracted from Composites with a 20 wt% Fiber Content

	Length (mm)	
Mesh size (mm)	Chopped fibers (mm)	Fiber extracted from composites (mm)
4	2.9	1.9
6	3.7	2.5
8	6.5	2.8

suggested that another possible explanation for the reduction could be fiber degradation during molding.

Flexural properties of the 20 wt% untreated fique fibers composites as a function of fiber length are shown in Figure 2. The strength, σ_F, of the composites is lower than that of the PP matrix; these results being a consequence of the medium mechanical properties of fique fibers, and also of the poor fiber/matrix adhesion. The composite flexural strength does no show significant variations with the used mesh size, due to the large size reduction occuring during molding. The modulus, E_F, of composites is higher than that of neat PP. It reaches a maximum for 6 mm mesh size. This behavior could be related with dispersion problems generated during the mixing by using high initial fiber length. Similar difficulties for mixing fibers with high lengths have also been observed in polystyrene reinforced with short sisal fibers [15].

Fiber Content

Figure 3 shows the variation of flexural properties with fiber content for composites manufactured with chopped fibers of 4 mm mesh

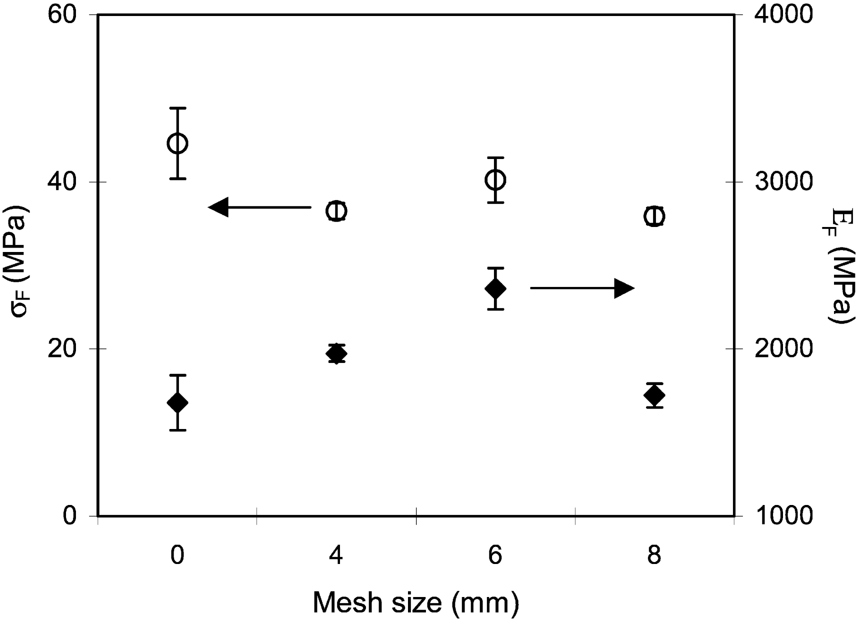


FIGURE 2 Variation of flexural properties with fiber length for composites with 20 wt% untreated fibers.

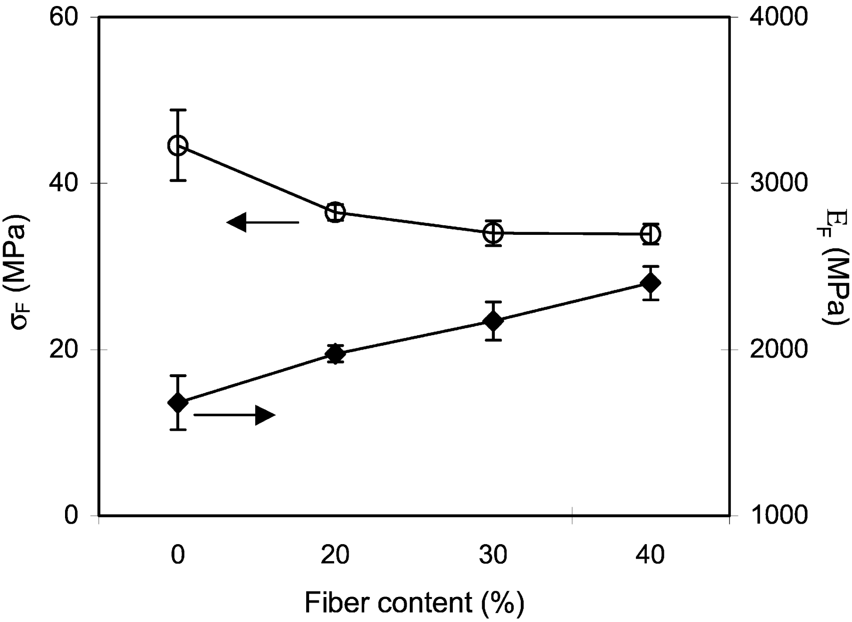


FIGURE 3 Variation of flexural properties of composites with fiber content for fibers chopped with 4 mm mesh size.

size. This mesh size was chosen as extensive mixing was easier to achieve. The composites had a lower flexural strength than that of the neat matrix, becoming lower with increased fiber loading. Contradictory results have been shown in the literature for polypropylene reinforced with other natural fibers such as sisal [10], jute [16], flax [17], and wood [18], whose tensile properties are higher than those for fique fibers. Besides the medium mechanical properties of fique fibers, the composite behavior can also be influenced by fiber-fiber interactions and their length reduction during processing, as mentioned earlier. However, as suggested by Bledzcki et al. [19], the low compatibility between fiber and matrix along the interface would be the main reason for the poor flexural strength of these composites.

Fiber/Matrix Modification

As Table 2 shows, fiber treatments do influence the mechanical properties of the fibers. Tensile modulus and strength increase for mercerized fibers with respect to untreated fibers. These results are associated with chemical and physical alterations on fique fibers [20]. As shown in a previous work [20], the MA treatment introduces an important reduction of tensile properties, possibly due to a process of

TABLE 2 Mechanical Behavior of Fique Fibers as a Function of Treatments Used

Fiber treatment	Average diameter (mm)	Tensile strength (MPa)	Modulus (GPa)	Elongation (%)
Untreated(*)	0.16 ± 0.01	237 ± 51	8.01 ± 1.47	6.02 ± 0.69
MA (*)(**)	0.16 ± 0.01	141 ± 51	8.88 ± 1.57	1.76 ± 0.50
M (*)	0.11 ± 0.01	373 ± 59	11.03 ± 1.41	7.80 ± 0.12
I	0.15 ± 0.02	239 ± 78	9.68 ± 2.43	4.67 ± 1.62

(*)Date extracted from Reference [20].

(**)The concentration employed corresponds to 10 wt% solution of maleic anhydride in acetone.

depolymerization or to changes in the crystalline structure of the fibers. With I treatment, the fiber showed slight changes of tensile properties, the Young's modulus being the main variation. During this treatment the reaction of isocyanate with –OH cellulosic groups of fique fibers occurs, Generating a chain of covalent bonds [21]. These bonds could affect the cellulose ordering inside the fibers, and the Young modulus of the fiber, respectively.

The free surface energy of fique fibers can be altered by surface treatments and compatibilizer addition. Some authors [11,20] have studied the relationships between these changes and the flexural behavior of different composites. Table 3 shows the polar components and total free surface energies for different fiber treatments and also for the neat PP matrix. According with these results, surface treatments reduce the hydrophilicity of fique fibers, allowing for better wettability by the PP matrix, that has a strong hydrophobic tendency. Authors such as Felix and Gathenholm [11] reported comparable results for PP matrix containing cellulose fibers.

TABLE 3 Effects of Treatments on Polar and Total Free Surface Energy for PP and Treated Fibers

Type of material	Polar component (mJ/m^2)	Total free surface energy(*) (mJ/m^2)
Matrix	1.1	26.0
Fiber treatment		
Untreated	22.6	44.4
MA	15.8	48.1
M	11.5	43.3
I	3.1	37.5

(*)Calculated by Owens-Wendt method.

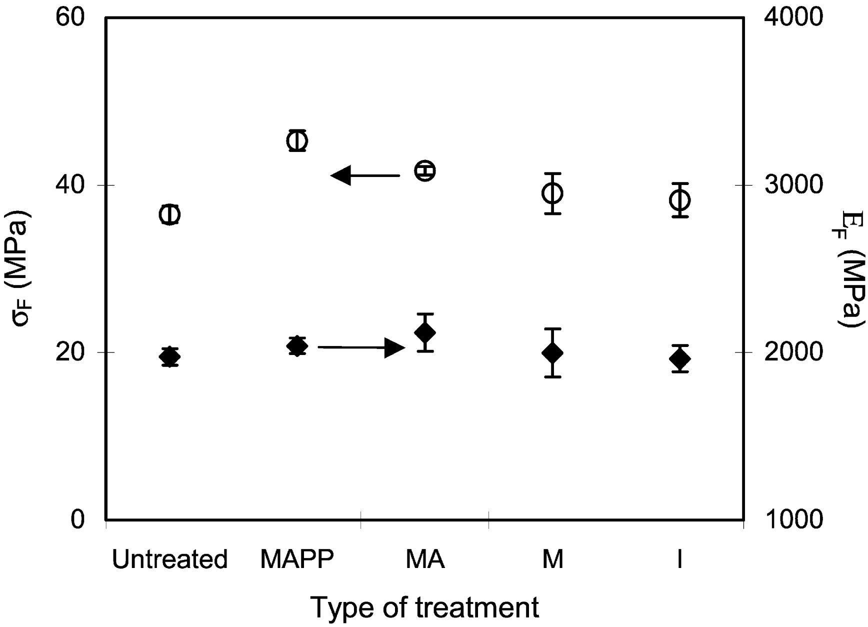


FIGURE 4 Flexural behavior of composites with 20 wt% treated fibers previously chopped at 4 mm mesh size.

The influence of different treatments on the mechanical behavior of composites with 20 wt% fiber is shown in Figure 4. The best flexural properties, that is the strength being even higher than for PP, are obtained for MAPP added to PP, surely as a consequence of the improved adhesion at the fiber-matrix interphase. With respect to surface treatments, the strength increased with respect to that for composites with untreated fibers. These results can be associated with the enhancement of fiber/matrix adhesion due to the shown increase on fiber wettability earlier. The MA fiber-treated composite registered an important increment of the flexural behavior, even with a higher modulus than that observed for mercerized composite. These results are contradictory, because mercerization treatment produces a significant improvement of the tensile properties of fique fibers, whereas for MA treatment, as shown in Table 2, a clear strength reduction and a slight modulus increase occur. The mercerization treatment increases the roughness of fiber surface by removal of some chemical structures [3,21], it is possible that at the treatment conditions employed in this work (20 wt% sodium hydroxide solution for 1 h), the surface alteration obtained could contribute to increase free space in the fiber/matrix interphase, so affecting the load transfer and consequently the mechanical behavior. With respect to MA treatment, it is important to consider that in this work the solution concentration is much lower than that employed in other studies, as for previous work [20] where it corresponded to 10 wt% solution of maleic anhydride in acetone or in the study of Nuñez et al. [22] of dynamic mechanical properties of treated woodflour composites, where the concentration employed was 0.6 M, and they reported an important reduction of storage modulus of the MA treated composites with respect to untreated ones. According to these results, it is possible to think that the solution concentration employed in this study allows to reduce the hydrophilic tendency of treated fibers (shown in Table 3), without noticeable modification of their mechanical properties. In short, the effectiveness of MA treatment could be affected by the solution concentration employed.

The I-treated fiber composite shows a slight increase of flexural strength with respect to the untreated fiber composite, yet lower than that obtained with MA treatment. A similar result has been observed by Joseph et al. [10] for sisal-reinforced composites. This increase can be associated with the enhancement of the fiber/matrix adhesion by reduction of hydrophilic behavior of fique fibers but also to the increase of fiber modulus by the effect of I treatment.

Another factor that can influence the mechanical behavior of composites is associated with alterations of the crystallization process of the matrix, including the formation of a transcrystalline layer generated from fiber surface into the rest of the melted matrix [23] or alterations of the nucleating process [24]. Several studies have demonstrated that changes occurring during the crystallization process, especially the transcrystallinity phenomena, can lead to higher mechanical properties of fiber-reinforced composites [25]. Similarly, Zafeiropoulos et al. [26], by using fragmentation test, reported that the presence of transcrystalline layers in flax/polypropylene composites enhanced the interface properties. The formation of a transcrystalline layer is associated with factors such as the variations of surface free energy [27], surface roughness [27], or surface treatment of reinforcement [28,29]. In previous work [30], the authors observed that the fique fibers can lead to formation of transcrystalline layer and the fiber treatments, such as MA, can enhance the crystallization process of PP matrix, especially nucleation, possibly due to changes in the free surface energy of the system. According to these observations, it is possible to suppose that the alteration of the PP matrix crystallization by the MA treated fiber can contribute to the changes of the mechanical behavior of the composites.

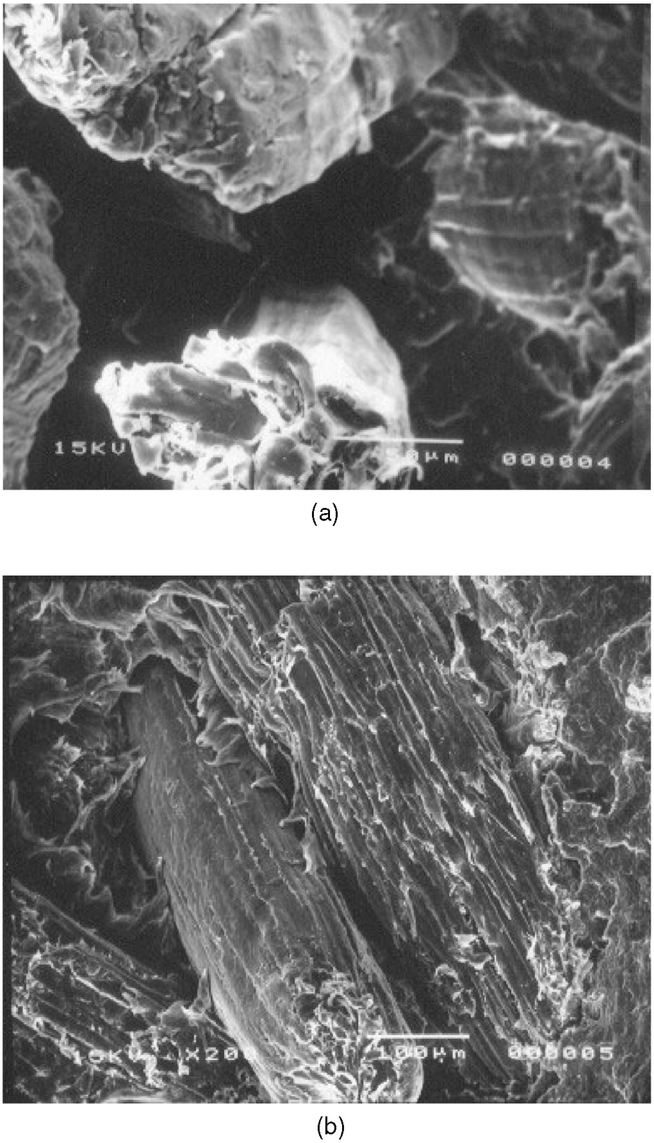


FIGURE 5 SEM micrographs of composites with 20 wt% fique fiber: (a) untreated fibers and (b) with compatibilizer agent MAPP.

Compatibilizer Agent

According to Figure 4, the composite with MAPP compatibilizer agent presents higher flexural strength than all the fiber-treated composites. Figure 5 presents the SEM micrographs of fracture surfaces for composites with untreated fibers and for those prepared with PP and MAPP as compatibilizer agent. For the untreated composite, a minimal presence of matrix on fiber surface exists and many empty spaces between fibers can be seen. On the contrary, the MAPP containing composite presents a reduction of these empty spaces and an important amount of matrix can be observed on the fiber surface, that indicates a strong interfacial adhesion between fiber and matrix caused by the interactions between anhydride groups of the matrix (neat PP mixed with MAPP) and –OH groups of fibers [31].

Physical Behavior

Table 4 shows the density of untreated and treated fibers and that of their composites. The changes introduced by fiber treatments are reflected on the values observed, especially for mercerized fibers, for which the reduction of fiber diameter and the variations on cellulose crystalline structure [32,33] clearly increase the fiber density. The density of the untreated fiber composite is intermediate to those of fiber and matrix. The values of fiber treated composites are slightly higher than that for untreated ones. These results indicate that these treatments can produce surface changes that may include the removal of some impurities as pectin or waxes.

According to previous work [20], mercerized fibers possess a higher density than the untreated fibers. However, the density of mercerized fiber composite is comparable to that obtained with other treatments, such as MA or I treatment. The increase of surface roughness of fiber by the effect of mercerization could lead to the presence of voids or cracks in composites, thus reducing their density. This fact could permit to explain the flexural properties discussed earlier.

Finally, the variations in the treated composite densities may relate to possible changes of the polymer morphology associated by size, type, and form of fibers employed [34].

Dynamic Mechanical Analysis

The variation of storage modulus, E', with temperature for neat PP matrix and untreated composites with different fiber contents is presented in Figure 6. For all samples, the storage modulus decreases

TABLE 4 Density of PP, Untreated Fique Fibers, and Composites with Fibers Chopped at 4 mm Mesh Size

	Density (g/cm^3)		
Type of material	PP	Fiber	Composite
Matrix	0.97 ± 0.01	—	—
Fiber treatment			
Untreated	—	0.87 ± 0.01	0.92 ± 0.01
MA	—	0.86 ± 0.01	0.95 ± 0.01
M	—	1.29 ± 0.01	0.96 ± 0.01
I	—	0.85 ± 0.01	0.95 ± 0.01

with increasing temperature. The addition of fique fibers shifts the storage modulus to higher values over the entire temperature range measured as a consequence of the higher rigidity of the fibers. Joseph et al. [35] have observed a similar behavior in a low-density polyethylene matrix reinforced with short sisal fibers. It is apparent that E′ values show significant drop at temperatures in the melting region of PP.

When comparing the viscoelastic behavior of neat matrix and composites (see square in Figure 6), it is worth noting the slight variation

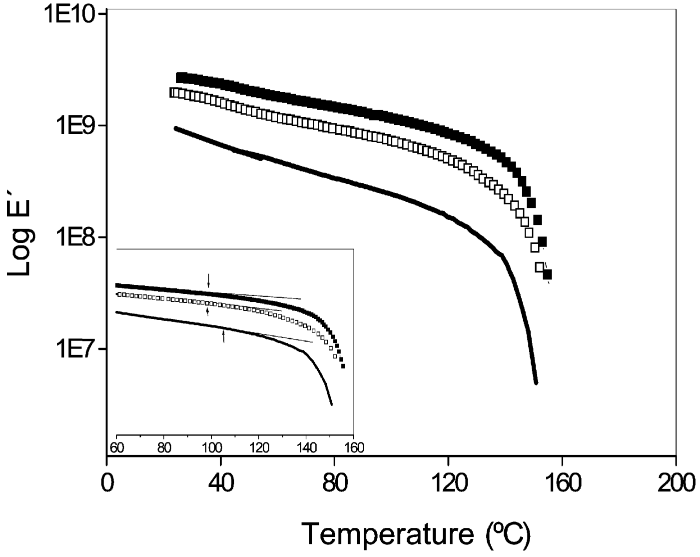


FIGURE 6 Dynamic mechanical behavior of neat PP (—) and composites with untreated fibers: (□) 20 wt% and (■) 40 wt%.

of E′ slope in the 90−110°C region. Indeed, whereas for PP matrix this variation occurs around 105°C, for fique fiber composites, the E′ slope change takes place at around 95°C. As shown in the literature [36−38], for crystalline polymers a relaxation corresponding to frictional viscosity between crystalline planes and/or movements inside crystals can occur between the glass transition and the melting temperature. Several authors [22,39−40] have observed a comparable relaxation for woodflour or natural fiber/polypropylene composites, attributing the changes to a lamellar slip mechanism and rotation in the crystalline phase. So that the authors are able to suggest that the displacement on the E′ slope variation on the 90−110°C region could be related to small variations in frictional mobility of PP crystals near the fibers.

CONCLUSIONS

In this study, the flexural behavior of untreated fique fiber reinforced polypropylene composites as a function of fiber size and content has been evaluated. Different fiber treatments such as mercerization, esterification, or isocyanate addition have been used. MAPP as a compatibilizer agent has also been employed.

The fiber length is strongly affected by the processing conditions, which lead to important reductions of fiber length and size distribution with respect to the original fiber dimensions, resulting in that the final fiber length in the composites is nearly independent of the initial size used.

Fique fibers increase the flexural modulus of composites relative to that for neat matrix. A clear increase of flexural strength was obtained by the addition of MAPP. This increase is associated with the enhancement of fiber/matrix adhesion, as shown by SEM analysis. Fiber treatments implemented on the fique fibers also lead to enhanced mechanical behavior. This is possibly related to an improved fiber/matrix interphase by reduction of the hydrophilic tendency of treated fique fibers relative to untreated ones. Additionally, the composite mechanical behavior as well as density are affected by changes of the fiber surface, fiber structure, and fiber properties. Indeed, in the case of mercerization, the tensile fiber properties can be enhanced but it could also produce the increased surface roughness, promoting the presence of voids in the composites.

The viscoelastic behavior of the composites has also been studied. The storage modulus of the composites shows slight variations with respect to that for PP matrix in the 90−110°C region. These variations could be associated with changes in the movements inside crystals in the fiber/matrix interphase.

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