

# Enhancement of Mechanical Properties and Interfacial Adhesion of PP/EPDM/Flax Fiber Composites Using Maleic Anhydride as a Compatibilizer

M. A. López Manchado,<sup>1</sup> M. Arroyo,<sup>1</sup> J. Biagiotti,<sup>2</sup> J. M. Kenny<sup>2</sup>

<sup>1</sup>*Institute of Polymer Science and Technology, C.S.I.C. C/Juan de la Cierva, 3 28006-Madrid (Spain)*

<sup>2</sup>*Materials Engineering Center, University of Perugia, Loc. Pentima Bassa, 21 05100 Terni (Italy)*

Received 13 August 2002; accepted 30 January 2003

**ABSTRACT:** In order to improve the compatibility between natural fibers and polypropylene (PP) and polypropylene-ethylene propylene diene terpolymer (PP-EPDM) blends, the functionalization of both matrices with maleic anhydride (MA) is investigated in this study. The morphological observations carried out by scanning electron microscopy show that the incorporation of small amounts of functionalized polymer considerably improves the adhesion at the fiber-matrix interface. In these cases, the fibers are perfectly embedded in the matrix in relation to the composites prepared with the pure homopolymers, and a significant increase in the composite strength is also observed, particularly, after the incorporation of both modified polymers (MAPP and MAEPDM). Thus, it is possible to correlate

better interfacial adhesion with the improvement of mechanical properties. It is assumed that the functionalization of the matrix reduces interfacial stress concentrations and may prevent fiber-fiber interactions, which are responsible for premature composite failure. The crystallization kinetics of PP were also analyzed by differential scanning calorimetry (DSC). It was observed that both flax fiber and rubber behave as effective nucleant agents, accelerating PP crystallization. Moreover, these results are particularly relevant when the grafted matrices are added to the composite. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2170–2178, 2003

**Key words:** Flax fibers; composites; functionalization of polymers

## INTRODUCTION

Fiber-reinforced thermoplastics are extensively used in many fields as a result of several convenient features, including their low cost, easy processing, environmental and working safety and recyclability. Natural fibers,<sup>1–6</sup> like jute, sisal, banana, flax, and others, have recently attracted the attention of scientists and technologists because of the advantages they offer in comparison to conventional fillers, and they are proof that it is possible to obtain materials that perform well using environmentally friendly reinforcements. In contrast with synthetic fibers, whose properties can be easily defined, the behavior of natural fibers depends on different factors, such as whether the fibers are taken from the plant stems or leaves,<sup>7</sup> the harvest period, weather variability, quality of soil, climate at the specific geographic location<sup>8</sup> and preconditioning.<sup>9,10</sup>

This growing interest in natural fibers is mainly due to their economical production, with few requirements for equipment, and it also due to the reduction of the total mass of the composite as a result of natural fibers' low density. Several studies reporting flax fiber

reinforced polypropylene composites<sup>11,12</sup> have shown that the incorporation of flax fibers improves the mechanical properties of the matrix and reduces the price of the material. Furthermore, they present safer handling and working conditions than other conventional fiber reinforcements. Another interesting characteristic of these fibers is their positive environmental impact; since they come from a natural resource, they are biodegradable and nonabrasive materials and can be easily eliminated after the life of the polymer. Due to their low density, the specific properties of these fibers are similar to those of synthetic fibers used as reinforcements in polymers, such as glass fibers.<sup>13,14</sup>

However, natural fibers present certain drawbacks, such as incompatibility with hydrophobic polymer matrices, a tendency to form aggregates during processing and poor resistance to moisture, which is reflected in a deterioration of the desirable properties, in particular toughness.<sup>15</sup> In order to improve the toughness of the composites, several elastomers can be used as impact modifiers for fiber reinforced PP composites.<sup>16–21</sup> It is well known that the presence of an elastomeric phase improves the impact strength of a composite but reduces its strength and elastic modulus. Stamhuis<sup>16,17</sup> demonstrated that the best results were obtained when the additives were partially encapsulated around the filler surfaces.

Another way to enhance the toughness of the composite is through the improvement of the interfacial

Correspondence to: J. M. Kenny (kenny@unlpg.it).

TABLE I  
Composition of Studied Composites

Sample Code	PP (wt. %)	MAPP (wt. %)	EPDM (wt. %)	MAEPDM (wt. %)	Flax Fiber (wt. %)	Glass Fiber (wt. %)
M1	80	0	0	0	20	0
M2	72	8	0	0	20	0
M3	56	0	24	0	20	0
M4	48	8	24	0	20	0
M5	56	0	16	8	20	0
M6	48	8	16	8	20	0
M7	80	0	0	0	0	20

adhesion at the fiber-matrix using coupling agents. Several authors have shown that the interaction at the fiber-matrix interface can be improved by adding small amounts of a grafted matrix. Among the different coupling agents, maleic anhydride is the most commonly used.<sup>22-28</sup> In general, the literature reports improvements in tensile strength, elongation at break and impact properties when maleic anhydride grafted matrices are used as compatibilizers. Moreover, excellent adhesion at the fiber-matrix interface has been observed. The studies of Long et al.<sup>18</sup> on filled PP systems showed that maleated styrene-ethylene/butylene-styrene triblock copolymer (SEBS-MA) and ethylene-propylene random copolymer (EPR-MA) act not only as toughening agents but also as compatibilizers between the filler particles and the PP matrix. The filler particles were encapsulated by the maleated elastomers, giving rise to improved impact properties.

For the reasons mentioned above, the aim of this work is to analyze the effect of chemical modification of both matrices, PP and EPDM, with maleic anhydride on the compatibility and properties of flax fiber-reinforced composites based on PP and PP-EPDM blend matrices.

## EXPERIMENTAL

### Materials

A commercially available grade of isotactic polypropylene (iPP) (MFI: 2.9 dg/min at 190°C and 5 kg and 0.90 g/cm<sup>3</sup> density), kindly supplied by Solvay (Brussels, Belgium), under the trade name of Eltex-P HV-200; a maleic anhydride grafted polypropylene (MAPP) with 5% maleic anhydride, supplied by Sigma-Aldrich (Milan, Italy); an ethylene-propylene diene terpolymer (EPDM) rubber with 5-ethylidene-2-norbornene (ENB) as a termonomer (68% ethylene content, Mooney viscosity, 55 ± 5 ML (1 + 8) at 125°C and 0.86 g/cm<sup>3</sup> density) supplied by Bayer (Leverkusen, Germany), under the trade name Buna EP T 6470 P and maleic anhydride grafted EPDM (MAEPDM) with 1% maleic anhydride content, supplied by Uniroyal Chemical (Amsterdam, The Netherlands), under the trade name of Royaltuf 498, were used in this work. Flax natural fibers, furnished by Finflax (Oulu, Fin-

land) (1.50 g/cm<sup>3</sup> density), and glass fiber (2.5 g/cm<sup>3</sup> density) were used as reinforcing agents.

### Composite preparation

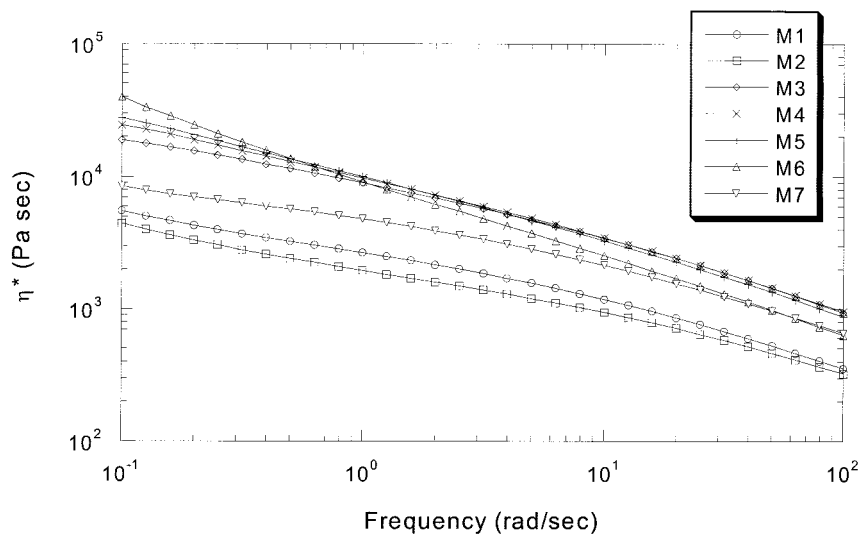
The compounds were prepared by means of hot-rolls, at a temperature of 180°C, for approximately 5 min from the incorporation of the fiber. Once the polymers were melted, the appropriate percentage of fiber, previously dried in an oven at 70°C, was added to the polymer blend. Immediately after mixing, the material was finely cut into pellets and injection molded in a Sandretto Micro 30 injection-molding machine to obtain standardized dog-bone specimens. In order to avoid thermal degradation of the fibers, the temperatures in the three zones of the equipment were 182, 184 and 186°C, respectively. A mold temperature of 25°C and a specific injection pressure of 1700 bar were used. The period of time for the packing and cooling stages were 30 and 25 s, respectively. The compositions of the composites used in this work are reported in Table I.

### Testing

The rheological characteristics of the composites were determined by using a Rheometric Scientific ARES N2 rheometer. Tests were conducted using parallel plate fixtures at 190°C in a range of angular frequency from 0.1 to 100 rad/s. The strain amplitude was maintained constant at 5%.

To analyze the interfacial adhesion between the fiber and the matrix, single fiber pull-out tests were conducted. The specimens were prepared by embedding a single flax fiber into melted thin discs of polymeric matrix (PP or PP-EPDM blend) by means of a Mettler FP-82 HT automatic hot-stage thermal control programmed at a temperature of 180°C. The fiber embedded lengths varied from 100 to 1000 μm. The pull-out tests were performed on a Lloyd LR30K dynamometer with a crosshead rate of 1 mm/min at room temperature.

The mechanical properties of the fiber-matrix composites were evaluated by tensile, flexural and impact experiments. Tensile and flexural tests were performed at room temperature on a Lloyd dynamometer



**Figure 1** Variation of complex viscosity with angular frequency at 190°C for flax fiber reinforced composites based on PP and PP-EPDM (70:30) blends.

model LR 30K, according to ASTM D 638M and ASTM D 790M, respectively. Tensile tests were carried out at a crosshead speed of 5 mm/min and the dimensions of the test specimens were 150 × 10 × 4 mm. Flexural tests were carried out at a crosshead speed of 1.92 mm/min with a span of 64 mm, and the nominal dimensions of the specimens were 80 × 10 × 4 mm. The support span to specimen depth ratio was 16:1. In both tests, all results were the average of at least five measurements.

Impact experiments were carried out according to ASTM D-256 (v-notched) in an Izod pendulum Ceast Resil 25 at room temperature with an impact speed of 3.48 m/s. Notches were prepared in a Ceast electrical notching apparatus, with a depth of 20% of the specimen thickness and “V” side grooves at 45° angles. The impact properties were taken as the average of at least seven measurements.

Thermal analysis experiments were performed using a DSC Perkin-Elmer Pyris 1 differential scanning calorimeter. Crystallization tests were carried out under isothermal conditions at 130°C. Samples of about 8 mg were melted at 200°C for 10 min in order to eliminate any previous thermal history in the material. Then they were rapidly cooled to the crystallization temperature,  $T_c$  (in our case, 130°C), and maintained at that temperature for the time necessary to complete crystallization of the matrix. The experiments were carried out in a nitrogen atmosphere, and after the isothermal crystallization tests, a dynamic scan at 10 °C/min was performed to check for the presence of a residual crystallization peak. By integrating the area under the isothermal exothermic peaks, plots of the degree of crystallization as a function of time were obtained. Subsequently, the melting temperature ( $T_m$ ), of the composites was considered to correspond to the maximum of the endothermic peak.

In order to analyze the formation and growth of polypropylene spherulites, the composites were observed by means of a Hund model Wetzlar H600 optical microscope, equipped with a Mettler FP-82HT automatic hot-stage thermal control and a video camera. The samples were melted and squeezed between two microscope cover glasses at 200°C for 10 min and then rapidly cooled to the crystallization temperature of 130°C.

The morphology of the samples was also analyzed by means of a Philips scanning electron microscope (SEM), model XL30 ESSEM, with an acceleration voltage of 15 KV. Fracture surfaces obtained from impact test were *sputtered* with gold prior to being observed by SEM.

## RESULTS AND DISCUSSION

The variation of complex viscosity ( $\eta^*$ ) as a function of angular frequency is presented in Figure 1. The change in shape of the flow curves shows a strong variation in the pseudoplastic behavior of the studied systems, ranging from the knee after the “Newtonian” region for the majority of the studied composites to a “power-law model” tendency in the case of the com-

**TABLE II**  
Rheological Parameters of Studied Composites

Sample Code	$\eta$ at 1 rad/sec (Pa sec)	Ellis Model		
		$\eta_0$ (Pa sec)	K (sec)	m
M1	2670	5382	0.9	0.57
M2	1965	4366	1.0	0.51
M3	8970	27941	3.6	0.56
M4	9770	50676	14.3	0.54
M5	9980	69666	25.0	0.55
M6	9130	$2.88 \times 10^7$	$1.49 \times 10^6$	0.56
M7	4810	9315	0.83	0.57

**TABLE III**  
Crystallization Parameters of Studied Composites

Sample	$n$	$K_n$ (min <sup>-n</sup> )	$\tau_{1/2}$ (min)
PP	2.54	$1.43 \times 10^{-3}$	11.3
M1	2.15	0.38	1.85
M2	2.33	0.37	1.32
M3	2.30	0.82	1.30
M4	2.30	0.82	0.94
M5	2.74	0.04	1.09
M6	2.31	0.34	1.37
M7	2.67	0.51	1.12

pound designated M6. Then, in order to model the flow behavior of the analyzed materials, rheological Ellis models,<sup>29,30</sup> which are expressed in the following equation, were proposed:

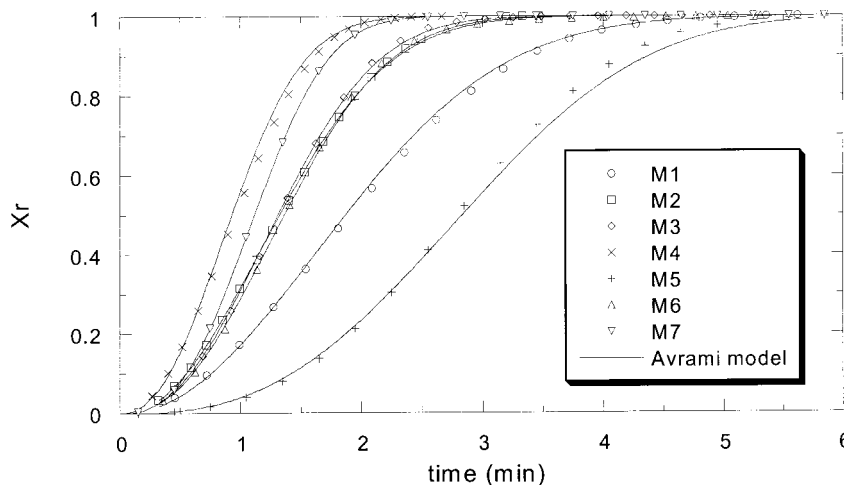
$$\eta = \frac{\eta_0}{[1 + (K\omega)^m]} \quad (1)$$

where  $\eta_0$  represents the zero-shear viscosity,  $\omega$  the angular frequency,  $K$  is a constant with the dimension of time and  $m$  is a dimensionless constant. The effects of the material composition are reported in Table II, where the fitted parameters of the proposed models are summarized. Taking into consideration the fact that the change of rheological behavior is not only a function of the modification effects but also of the nature of matrix *neat* components, a strong increase in viscosity values was observed when the elastomeric phase was added to the compounds. This effect was more evident in the case of the modified EPDM. Moreover, the change of flow behavior, which certainly leads to higher zero-shear viscosity values, occurs when both compatibilizers are present.

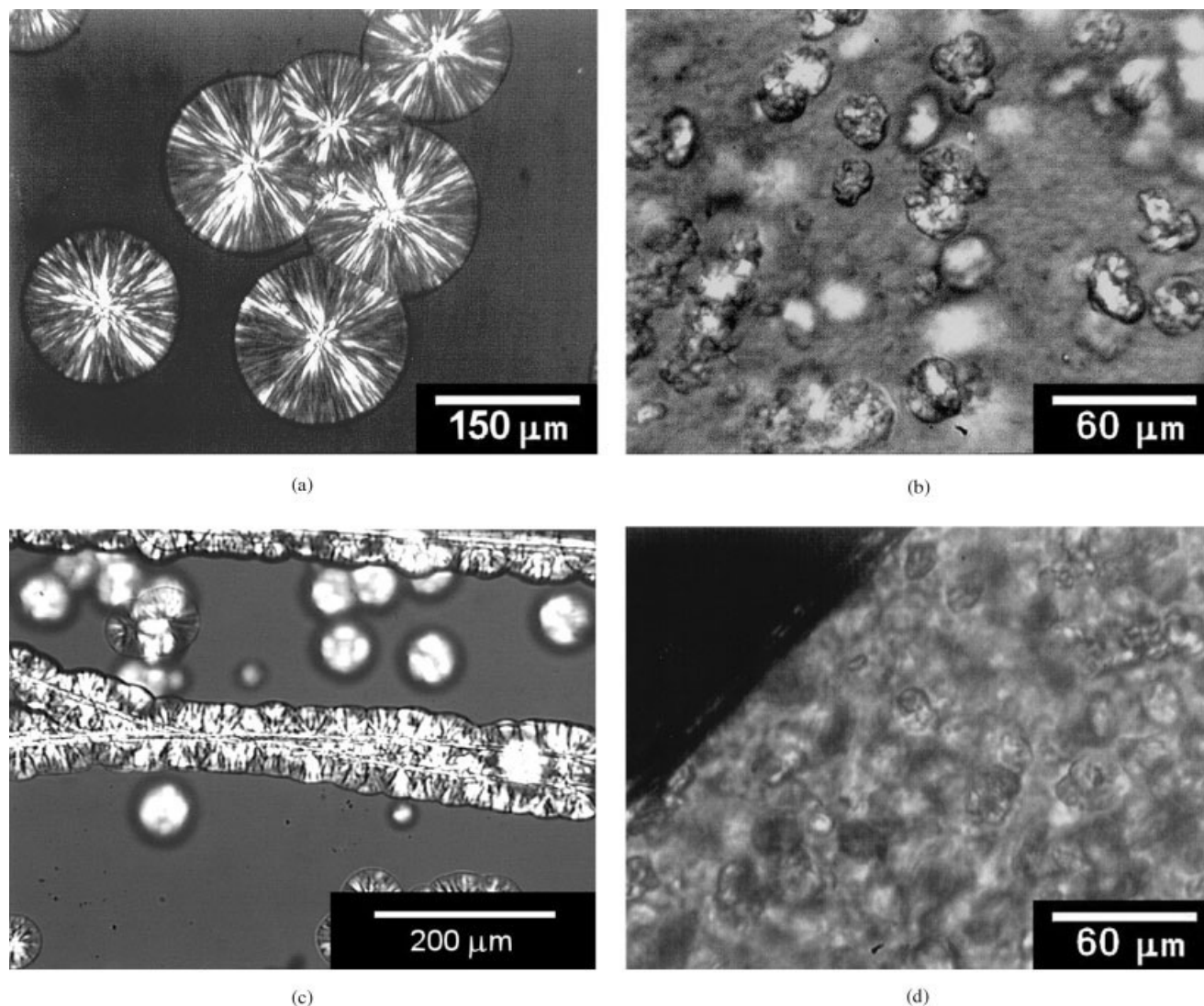
The crystallization kinetics of PP and its composites were analyzed by means of a differential scanning calorimeter (DSC) and the results obtained are summarized in Table III. Figure 2 shows the degree of

crystallization curves as a function of time of all studied samples obtained at 130°C. From these results, it can be deduced that EPDM acts as a nucleant agent, accelerating PP crystallization, which is clearly reflected in the marked decrease of the half time of crystallization. This nucleant effect of the elastomeric phase can be attributed to the modification of the PP matrix structure. Thus, a change in the average size and number of the spherulites is induced by the incorporation of the elastomeric particles, and this structural change is very important for interpreting the function of the elastomer as an impact modifier in the PP matrix. This was clearly observed during PP spherulitic growth in the presence of both fibers and elastomer by optical polarizing microscopy, taking microphotographs at different intervals of time [Fig. 3(a-d)]. It can be confirmed that the PP nucleation density increases in the presence of both fibers and elastomer, but the effect is more marked for the elastomer than for the flax fiber. Moreover, the phenomenon of transcrystallization on the flax surface can be easily observed. It is assumed that the highest level of transcrystallization was obtained at high degrees of undercooling and in the absence of the elastomer phase. In fact, when the matrix is a PP-EPDM blend, the transcrystallinity phenomenon seems to be hindered [Fig. 3(d)]. Similar results were reported in a previous study,<sup>31</sup> where the kinetic crystallization of polypropylene in ternary composites, based on fiber-reinforcing PP-EPDM blends, was analyzed.

It is interesting that the incorporation of low amounts of grafted matrix with the maleic groups accelerates the crystallization process even more, showing a considerable decrease of the half time of crystallization in all cases (see Table III). It can be assumed that the functional polar monomer used in this work behaves as an effective nucleant agent for the PP matrix, promoting the crystallization of the semicrystalline polymer. An explanation of these results can be found in the fact that a higher



**Figure 2** Degree of crystallization of flax fiber-reinforced composites based on PP and PP-EPDM (70:30) blends at 130°C.

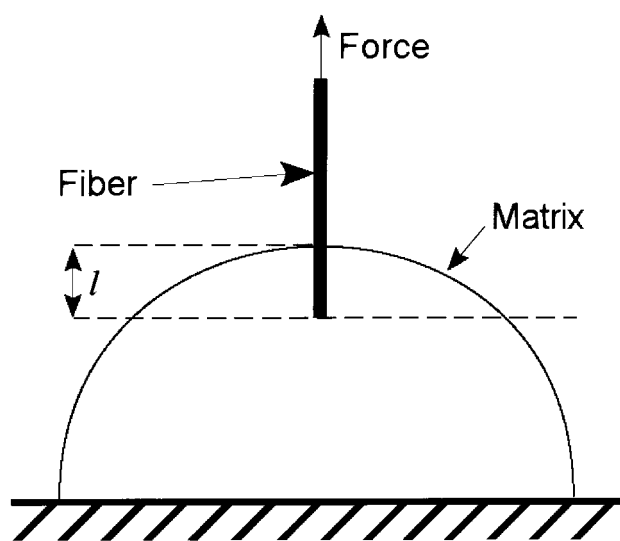


**Figure 3** Micrographs of crystalline growth at 130°C for: (a) neat PP after 2430 s, (b) PP-EPDM blend (70:30 wt %) after 360 s, (c) M1 after 180 s and (d) M3 after 95 s.

number of active nuclei are formed during the crystallization process. Moreover, an increase of PP crystallinity is observed when maleic groups are grafted into polymer chains.

In order to characterize the properties at the interface between the fiber and polymer matrix, single fiber pull-out tests were carried out. A schematization of the pull-out sample is shown in Figure 4. The diameter,  $d$ , and the fiber embedded length,  $l$ , were previously measured using the optical microscope previously described, as shown in Figure 5. The advantage of this assay is that the debonding force can be plotted as a function of the embedded length of the fiber. So, from each force-displacement curve, the force at the debonding,  $F$ , is determined and the interfacial shear strength (IFSS or  $\tau$ ) can be calculated according to the Kelly/Tyson equation:<sup>32</sup>

$$\tau = \frac{F}{\pi dl}$$



**Figure 4** Schematic diagram of the pull-out sample.

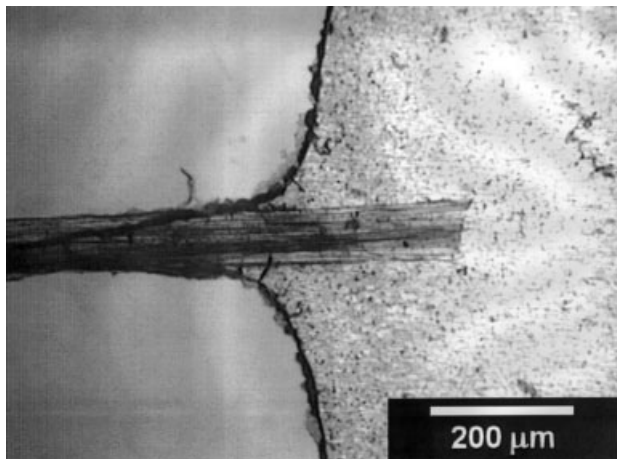


Figure 5 Optical polarizing microscopy of the flax fiber.

where  $F$  is the maximum debonding stress,  $d$  is the diameter of the fiber and  $l$  is the embedded length. A typical pull-out test is shown in Figure 6. The shape of the curve is typical of a mixed mode fracture process. The debonding starts at point A, and is extended along the fiber, while, at point B, debonding has been completed, but a part of the fiber may still be bonded, giving rise to a residual interfacial strength in the system. Similar results are reported in the literature.<sup>33</sup> About 20 to 30 single fiber tests were used to determine the statistical distribution parameters of IFSS. The data obtained from the tests were represented by a two-parameter Weibull equation (Fig. 7), which expresses the cumulative density function of the interfacial shear strength of the analyzed systems as

$$F(\tau) = 1 - \exp\left[-\left(\frac{\tau}{\tau_0}\right)^\alpha\right]$$

where  $\alpha$  is a dimensionless shape parameter related to the dispersion of data, and  $\tau_0$  is a location parameter representing an average value of the measured property. The results obtained for all materials studied are summarized in Table IV. It is worth mentioning that the addition of small proportions of maleic anhydride

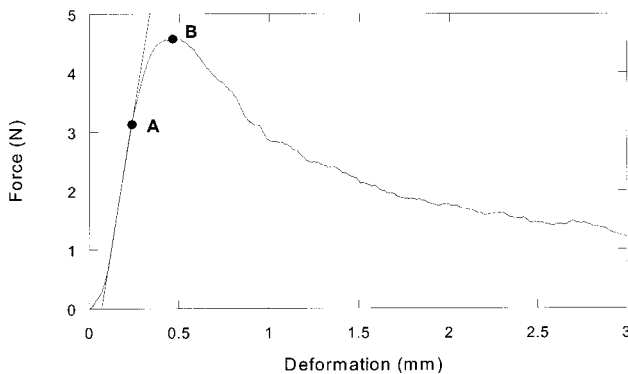


Figure 6 Typical pull-out test curve.

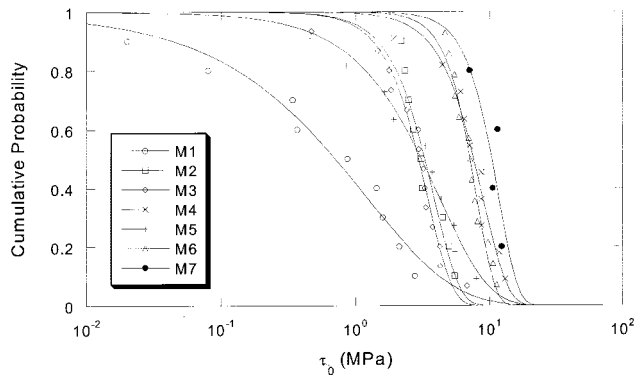
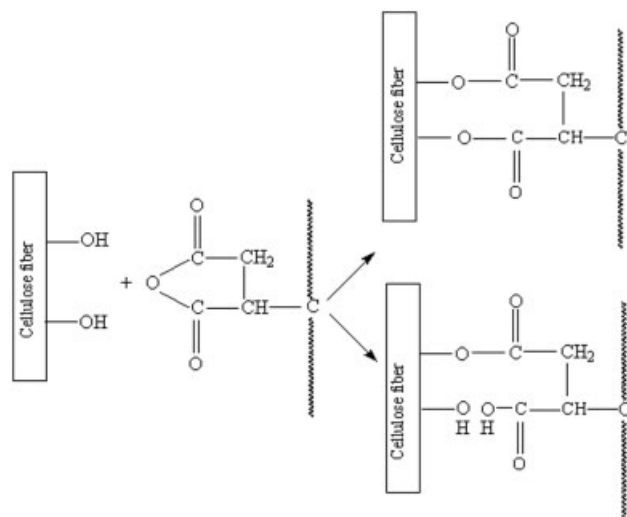


Figure 7 Interfacial shear strength distribution for the analyzed flax fibers.

modified matrices significantly increases the shear strength. This effect is more evident when the matrix is PP modified with MAPP addition (M2). These results can only be explained by the fact that the anhydride maleic groups behave as an effective compatibilizer, improving the adhesion at the fiber-matrix interface. That is, in the presence of maleic anhydride functional groups, the esterification of the flax fibers takes place, as can be observed in Figure 8. After this treatment, the surface energy of the fibers is increased to a level much closer to the surface energy of the matrix. Thus, a better wettability and a higher interfacial adhesion is obtained.<sup>34</sup> The mechanical properties of the flax fiber-reinforced PP and PP-EPDM composites with MAPP and MAEPDM compatibilizers are reported in Table V. As was expected, a clear diminution in both tensile and flexural PP composite strength is observed with the incorporation of the elastomer phase. On the other hand, the results show the positive effect of both compatibilizers, MAPP and MAEPDM, on the composite properties, MAPP being the most effective. The more evident effects were observed in the tensile and flexural strength. That is, the incorporation of small amounts of MAPP considerably increases the strength of the composites. However, it is interesting to point out that the composite with the highest strength is obtained when both compatibilizers are simultaneously added to the composite (increments above

TABLE IV  
Interfacial Shear Strength Properties of Flax Fibers

Sample	$\tau_0$ (MPa)	$\alpha$
M1	1.2	0.68
M2	3.8	2.31
M3	3.4	2.39
M4	8.9	2.36
M5	4.2	1.18
M6	8.0	3.26
M7	11.0	4.02



**Figure 8** Schematic representation of the chemical reaction between maleic anhydride functional group and hydroxyl group on the flax fiber.

70% are observed in the composite denominated as M6). These results can be explained by the formation of new interactions between the maleic anhydride groups inserted into both matrices, which gives rise to a more rigid material. It is assumed that an increase in the tensile strength means that the stress has been transferred from the matrix to the flax fibers. These results can be explained in terms of the better adhesion at the fiber-matrix interface due to the presence of compatibilizers. The interface so formed provides a deformation mechanism to reduce the interfacial stress concentration and may furthermore prevent fiber-fiber contacts, which are a source of high stress concentrations in the final composite. On the other hand, the stiffness of the composite measured in both tensile and flexural tests hardly varies with the incorporation of the compatibilizers, while an expected decrease was observed when the elastomer was added to the composite.

In addition, the elongation at break significantly increases in the presence of EPDM. This effect is attributed to the small elastomer particles dispersed in the PP ma-

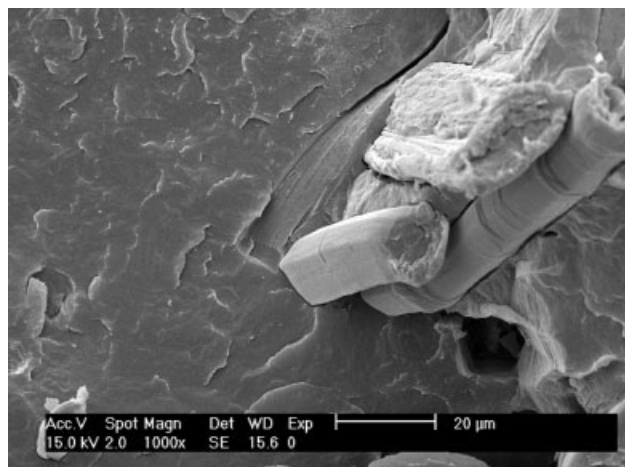
trix that act as stress concentrators, initiating the local yielding of the matrix and so avoiding the brittle catastrophic failure of the material.<sup>26</sup> However, a dramatic decrease on the elongation at break is observed when both grafted matrices are added to the composite. As can be expected, a strong adhesion at the fiber-matrix interface, even with small amounts of filler, would give rise to a decrease in elongation at break.

The mechanical characterization results are in accordance with those obtained by single pull-out tests and support a strong assumption that maleic anhydride groups grafted into the matrices behave as effective compatibilizer agents, improving the adhesion at the fiber-matrix interface. Therefore, a marked increase of the composite properties is obtained. This statement is particularly evident when the matrix is PP with MAPP (M2). The impact strength considerably increases in the presence of rubber. However, no changes are observed when compatibilizers are added.

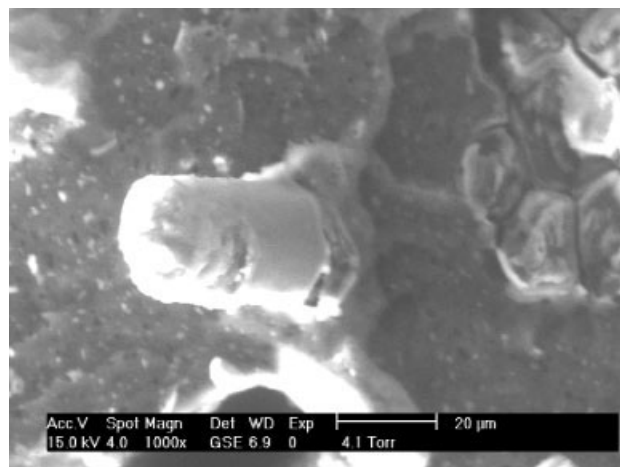
The analysis of the fracture surfaces of the composites by scanning electron microscopy (SEM) has allowed us to evaluate the effects of the incorporation of impact modifiers, EPDM and grafted matrices (MAPP and MAEPDM), on the morphology of the composite. The morphological observations are correlated to the mechanical measurements, showing an evident improvement of the interfacial adhesion in the composites with grafted matrices. As can be deduced from Figure 9, the flax fiber-reinforced PP composites without impact modifiers and compatibilizers show poor adhesion at the interface. These natural hydrophilic fibers do not show good chemical compatibility with the hydrophobic polymer matrices, as deduced from the clean surface of the fibers and their traces on the polymer matrix. This poor adhesion is deduced not only from the great length of the fibers which come out of the fracture surfaces of the samples but also from the high amount of empty hollows on the surfaces, due to the fibers that have been pulled out of the matrix. A slight improvement in terms of fiber/matrix adhesion was observed when the elastomeric phase was added to the blend by a general reduction of pulled-out fiber length, as shown in Figure 10. From

**TABLE V**  
Mechanical Properties of the Studied Composites

Sample	Tensile Properties			Flexural Properties		
	Young Modulus (MPa)	Tensile Strength (MPa)	Deformation at Break (%)	Bending Modulus (MPa)	Max. Strength (MPa)	Impact Strength (KJ/m <sup>2</sup> )
M1	2280 ± 100	33.9 ± 0.3	30.8 ± 0.7	2830 ± 45	43.3 ± 0.3	3.8 ± 0.1
M2	2435 ± 30	43.0 ± 0.5	42.5 ± 0.5	3400 ± 50	63.4 ± 0.5	4.3 ± 0.2
M3	1565 ± 85	17.5 ± 0.4	57.4 ± 0.5	2335 ± 25	30.7 ± 0.3	13.2 ± 1.1
M4	1755 ± 65	27.5 ± 0.1	25.7 ± 0.5	2500 ± 75	41.1 ± 0.4	13.6 ± 0.5
M5	1310 ± 60	19.5 ± 0.7	17.2 ± 5.2	1710 ± 35	29.5 ± 0.6	12.6 ± 0.7
M6	1595 ± 65	29.9 ± 1.3	20.6 ± 2.2	2380 ± 50	42.2 ± 0.2	12.4 ± 0.9
M7	2850 ± 75	52.4 ± 1.4	51.3 ± 16.2	3880 ± 90	69.1 ± 1.6	6.6 ± 4.1



**Figure 9** Fracture surface of flax fiber-reinforced PP composites.



**Figure 11** Fracture surface of flax fiber-reinforced PP-EPDM composites with MAPP.

the micrograph, it is also detectable that the fiber surface remains quite clean. Then, without the presence of chemical linkages, the better ability of the PP-EPDM matrix to transfer stresses to the fiber can be associated to a major physical hindrance effect due to the elastomer addition. This behavior was also underlined by the results of pull-out tests, shown in Table IV, where the composite M3 (PP-EPDM-flax) exhibited a great interfacial-shear-strength value with respect to composite M1 (PP-flax). However, the incorporation of compatibilizers significantly improves adhesion to the fibers. Figure 11 shows the microstructure of flax fiber-reinforced PP-EPDM composites with MAPP as a compatibilizer. The morphology is clearly different when compared to composites containing unmodified PP. The better fiber-matrix adhesion can be measured by the fact that the fibers are perfectly encapsulated in the matrix, making it more difficult to distinguish the fibers. The failure of these composites mainly occurs in the matrix and not at the filler surfaces, which would

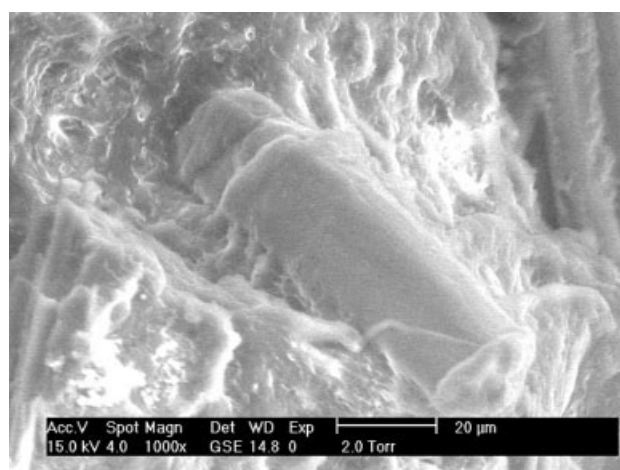
explain their higher mechanical strength. Figures 12 and 13 show the morphology of the flax fiber PP-EPDM composites with MAEPDM and with both MA-EPDM and MAPP, respectively. In both cases, a considerable improvement of the adhesion at the interface is observed, and there are hardly any voids in the fracture surface, which indicates that the fibers are so well trapped by the polymer matrix that fiber pull-out during impact tests considerably decreases. It can also be seen that there is good contact between the fibers and the polymer matrices, due to the better bonding promoted by the maleic groups and to the fibers protruding from the polymer matrix having been covered with a polymer layer.

### CONCLUSIONS

Functionalized PP and EPDM with maleic anhydride have been used in this study to improve the interfacial adhesion between hydrophilic flax fibers and these hy-

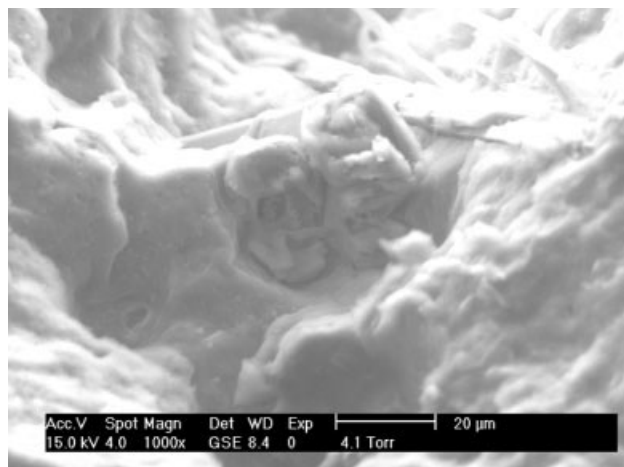


**Figure 10** Fracture surface of flax fiber-reinforced PP-EPDM composites.



**Figure 12** Fracture surface of flax fiber-reinforced PP-EPDM composites with MAEPDM.





**Figure 13** Fracture surface of flax fiber-reinforced PP-EPDM composites with MAPP and MAEPDM.

drophobic polymeric matrices. It has been proven that the addition of low proportions of maleic anhydride grafted PP and EPDM to their composites increases nucleation, favoring the PP crystallization process, which was reflected in a marked decrease in the half time of crystallization. The micrographs obtained by means of scanning electron microscopy (SEM) have shown that better adhesion at the fiber-matrix interface exists when grafted matrices are added to the composite. In fact, there were hardly any voids on the fracture surface, and the fibers were also perfectly encapsulated by the matrix, making it very difficult to distinguish them. In addition, mechanical measurements are in accordance with these observations, showing a considerable increase in the composite properties when the grafted matrices were added to the composite. These results were particularly evident for PP-MAPP matrix. According to these results, it is possible to establish a relationship between good interfacial adhesion and the improvement of mechanical properties of the composite. In a future study, the chemical treatment of flax fibers and its effect on the properties of the modified matrix composites will be analyzed.

Financial support from the Consejo Superior de Investigaciones Científicas (Spain) and the National Research Council of Italy (CNR) are gratefully acknowledged.

## References

- Hornsby, P. R.; Hinrichsen, E.; Taverdi, K. *J Mater Sci* 1997, 32, 1009.
- Roe, P. J.; Ansell, M. P. *J Mater Sci* 1985, 20, 4015.
- Mukherjee, R. N.; Pal, S. K.; Sanyal, S. K. *J Appl Polym Sci* 1983, 28, 3209.
- Gassan, J.; Bledzki, A. K. *Composites A* 1997, 28, 1001.
- Gassan, J.; Bledzki, A. K. *Comp Sci Tech* 1999, 59, 1303.
- Vázquez, A.; Dominguez, V.; Kenny, J. M. *J Therm Comp Mat* 1999, 12, 477.
- Bisanda, E. T. N.; Ansell, M. P. *J Mater Sci* 1992, 27, 1690.
- Barkakaty, B. C. *J Appl Polym Sci* 1976, 20, 2921.
- Chawla, K. K.; Bastos, A. C. *Int Conf Mech Beh Mat* 1979, 3, 191.
- Ray, P. K.; Chakravarty, A. C.; Bandyopadhyay, S. B. *J Appl Polym Sci* 1976, 20, 1765.
- Van den Oever, M. J.; Bos, H. L.; Van Kemenade, M. J. *Appl Compos Mater* 2000, 7, 387.
- Benevolenski, O. I.; Karger-Kocsis, J.; Mieck, K. P. *J Thermoplast Compos* 2000, 13, 481.
- Wells, H.; Bowen, D. H.; Macphail, I.; Pal, P. K. In *Proceedings of the 35<sup>th</sup> Annual Technology Conference, Reinforced Plastic/Composites Institute*; Univ. of Mississippi, 1980.
- Morton, W. E.; Hearle, J. W. In *Physical Properties of Textile Fibers*, 2<sup>nd</sup> ed.; John Wiley & Sons, Inc.: New York, 1975.
- Oskman, K.; Lindberg, H. *Holzforschung* 1995, 49, 249.
- Stamhuis, J. E. *Polym Compos* 1984, 5, 202.
- Stamhuis, J. E. *Polym Compos* 1988, 9, 72.
- Long, Y.; Shanks, R. A. *J Appl Polym Sci* 1996, 62, 639.
- Pukanszky, B.; Tudos, F.; Kolarik, J.; Lednický, F. *Compos Polym* 1989, 2, 491.
- Gupta, A. K.; Srinivasan, K. R.; Krishna Kumar, P. *J Appl Polym Sci* 1991, 43, 451.
- López-Manchado, M. A.; Biagiotti, J.; Kenny, J. M. *Polymer Composites* 2002, 23(5), 779–789.
- Dalvåg, H.; Klason, C.; Strömbal, H. E. *Inter J Polym Mater* 1985, 11, 9.
- Felix, J. H.; Gatenholm, P. *J Appl Polym Sci* 1991, 42, 609.
- Myers Chahyadi, G. E.; Coberly, C. A.; Ermer, D. S. *Int J Polym Mater* 1991, 15, 21.
- Myers Chahyadi, G. E.; González, C.; Coberly, C. A.; Ermer, D. S. *Int J Polym Mater* 1991, 15, 171.
- Han, G. S.; Ichinose, H.; Takase, S.; Shiraiishi, N. *Mokuzai Gakkaishi* 1989, 35, 1100.
- Oksman, K.; Clemons, C. *J Appl Polym Sci* 1988, 67, 1503.
- Bledzki, A. K.; Gassan, J. *Prog Polym Sci* 1999, 24, 221.
- Carriere, C. J.; Silvis, H. C. *J Appl Polym Sci* 1997, 66, 1175.
- Cox, W. P.; Merz, E. H. *J Polym Sci* 1958, 28, 619.
- López-Manchado, M. A.; Torre, L.; Kenny, J. M. *Appl Polym Sci* 2001, 81, 1.
- Kelly, A.; Tyson, W. R. *Mech Phys Solids* 1965, 12, 329.
- Stamboliuss, A.; Baillie, C.; Schulz, E. *Die Angew Makromol Chemie* 1999, 272, 117.
- Bledzki, A. K.; Reihmane, S.; Gassan, J. *J Appl Polym Sci* 1996, 59, 1329.