# Composite Materials Constituted by a Modified Polypropylene Fiber and Epoxy Resin

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ABSTRACT: A polyblend fiber constituted of polypropylene (PP) and an ethylene-vinyl acetate copolymer modified with mercapto groups was employed for the preparation of an epoxy resin-based composite. This composite presented outstanding impact properties as compared to one prepared with unmodified PP fibers. Scanning electron microscopy indicated the existence of matrix-modified PP fiber adhesion. The results obtained from dynamic mechanical analysis of these composites, such as damping values and the glass transition temperature, taken from the maximum damping temperature, confirm the existence of interfacial adhesion between the matrix and mercapto-modified PP fiber. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 69–73, 1999

**Key words:** composites; polypropylene fiber; polyblend fiber; dynamic mechanical properties; epoxy matrix

## INTRODUCTION

Polypropylene (PP) fibers are attractive candidates as reinforcing components for low-cost composite materials because of their low cost, relatively high fiber strength, and low density.<sup>1</sup> Unfortunately, these fibers exhibit poor adhesion to epoxy resin and other polar matrices because of the nonpolar nature of the fiber polymeric backbone. Many studies have been reported on fibersurface treatment to increase the polarity of PP or polyethylene (PE) fibers and impart better fiberepoxy matrix adhesion.<sup>2</sup> The chemical etching with strong oxidizing agents and plasma etching improve the pull-out adhesion of PE fibers to epoxy resin but lower the fiber strength.<sup>3,4</sup> Another interesting way to increase the polyolefin fiber polarity involves the preparation of a polyblend fiber by using a polar component in a minor proportion.<sup>5</sup>

In a previous report,<sup>6</sup> we developed a new polyblend fiber made from a mixture of PP and a mercapto-modified ethylene-vinyl acetate (EVA) copolymer. The surface of these modified PP fibers was analyzed by Fourier transform infrared spectroscopy using a diffuse reflectance technique, indicating the presence of a functionalized EVA copolymer component close to the fiber surface. Considering that mercapto groups easily react with epoxy groups,<sup>7</sup> the presence of these groups on the PP surface may improve the fiber-epoxy resin matrix adhesion, giving rise to composites with better mechanical performance.

This work concerns the efficiency of these mercapto-modified PP fibers as reinforcing agents for epoxy-based composites. For these studies, impact resistance and dynamic mechanical properties were evaluated.

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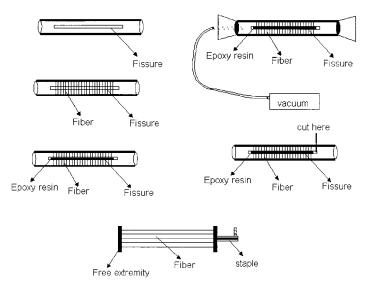


Figure 1 Schematic representation of the composite sample preparation.

## **EXPERIMENTAL**

## Materials

The epoxy resin (CY260) and curing agent (HY561), supplied by Ciba Geigy Química S/A (São Paulo, Brazil), were used as the matrix components in a proportion of 100 : 26 phr. PP (PPH206) was supplied by OPP Petroquímica S/A (Rio Grande do Sul, Brazil). A mercapto-modified ethylene-vinyl acetate copolymer (EVASH) was prepared in our laboratory by a transesterification reaction between mercaptoacetic acid and an EVA copolymer containing 18 wt % of vinyl acetate (Petroquímica Triunfo S/A, Rio Grande do Sul, Brazil). The reaction was performed in toluene solution and resulted in an EVASH copolymer having 24.9 mmol % of mercapto groups.<sup>8</sup> PP fiber and a PP-EVASH (95:5 wt%) blend fiber were prepared as previously described.<sup>6</sup>

#### **Fabrication of the Composites**

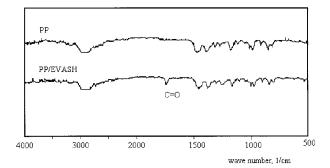
For the fabrication of unidirectionally reinforced composites with epoxy resin, the fiber was wrapped on a carton cylinder of 80-mm inner diameter and 200-mm length. The cylinder had a fissure of 5-mm width and 140-mm length, as illustrated in Figure 1. Each cylinder contained about 7 g of fiber. A mixture of the epoxy resin and curing agent was applied on the fiber portion located in the fissure region, in order to attach the fiber together. After applying a vacuum at the carton extremity to force the resin penetration

into the fissure, the fibers were cut in the fissure direction and the carton cylinder was removed. The set of fibers was secured with a staple at one extremity and impregnated with the mixture of the epoxy resin and curing agent. The excess of resin was removed with the help of an absorbing sheet. The fiber content in each cylinder corresponds to one layer of the composite specimen. To build the composite specimen, several layers of the preimpregnated set of fibers were arranged in one direction, one above the other as a "waffle," until the composite sheet reached a thickness of about 5.0 mm. The resulting preimpregnated composite specimens (prepregs) were submitted to a vacuum to eliminate absorbed gases and then cured at 120°C for 120 min at a pressure of 350 kPa. The fiber volume fractions in the composites varied between 40 and 45%, as indicated by the TGA measurements.

## Characterization

The impact resistance of the composites was determined on an EMIC A1C-1 impact tester at a speed of 3.45 m s<sup>-1</sup>, using a pendulum with nominal energies of 2.7 and 5.4 J. The measurements were made according to the ASTM D256 method, using rectangular unnotched specimens of 60  $\times$  10  $\times$  5 mm, with the fibers disposed in a transversal way.

Dynamic mechanical analysis (DMA) was performed on a DuPont TA 9900, in a flexural mode, at a heating rate of 5°C/min within the range of 25–200°C. Scanning electron microscopy (SEM) of



**Figure 2** DRIFTS of PP/EVASH polyblend fiber containing 5 wt % of EVASH (with a mercaptoacetate content of 24.9 mmol %).

the composite fracture was performed on a Zeiss-DSM 950. The surface was covered with a thin layer of gold.

## **RESULTS AND DISCUSSION**

In the previous work, we developed some PP/ EVASH blend fibers with different types and different amounts of EVASH.<sup>6</sup> The surface analysis by X-ray photoelectronic spectroscopy (XPS) of these blend fibers revealed that the main constituent of the fiber surface was pure PP. On the other hand, the surface analysis based on diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) indicated the presence of the absorption at 1740 cm<sup>-1</sup>, characteristic of the carbonyl groups of the EVASH component. The intensity of this absorption increased with the amount of EVASH in the blend fiber. Considering that the presence of the mercapto groups in the EVASH component near the fiber surface is important for a good interfacial adhesion between

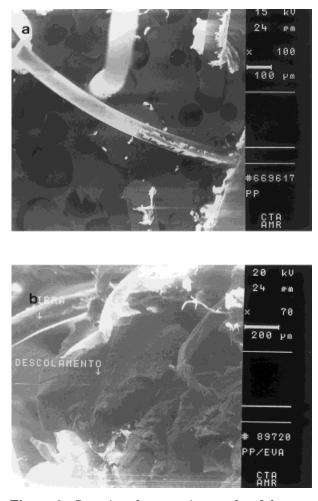
the epoxy matrix and the PP/EVASH blend fiber, we decided to employ a blend fiber sample which presented the highest intensity of the carbonyl absorption in the DRIFTS spectrum and the highest surface tension which is characteristic of polar groups at the surface. Therefore, we chose for our studies of the epoxy-based composites the fiber sample containing 5 wt % of EVASH whose DRIFTS spectrum is illustrated in Figure 2.

The basic properties of the PP fiber and the PP-EVASH blend fiber together with the impact strength values of the corresponding composites with the epoxy resin are summarized in Table I. As indicated in this table, the composite prepared with the PP-EVASH blend fiber presented a significantly higher impact resistance than that of the one containing PP fiber. The toughness of the composite depends largely on the partial properties of the matrix, fiber, and interface, as well as on the interfacial adhesion. EVA copolymers, for example, were reported to be good impact modifiers for PP, even at a low proportion (less than 5%).<sup>9</sup> The PS-EVASH fiber/epoxy resin composite developed in this work contains 40 vol % of the fiber. Considering that the modified fiber is composed of 5 wt % of EVASH, the total amount of the EVASH component in the composite corresponds to nearly 2.0 wt %. Therefore, the presence of this low amount of EVASH may be one of the factors which contribute to the toughness of the material.

Another characteristic that we must take into account is related to the interfacial adhesion. The presence of mercapto groups in the modified PP fiber increases the polarity of the fiber as indicated by the surface energy value and should promote a fiber-matrix adhesion. Such adhesion may be also related to the ability of these groups to react with the epoxy groups of the matrix.

 
 Table I
 Basic Properties of the Fibers Used in the Composite Preparation and Impact Resistance of the Corresponding Composites

Property	PP Fiber	PP-EVASH (95 : 5 wt %) Fiber
Ultimate tensile strength (MPa)	454	318
Young's modulus (GPa)	0.86	1.27
Elastic deformation (%)	26	14
Crystallinity degree (%)	54	50.0
Surface energy (dyne cm <sup>-1</sup> )	34	37
	PP/epoxy	PP-EVASH/epoxy
Impact strength (J/m)	259	951



**Figure 3** Scanning electron micrographs of the composite surface containing (A) PP fiber and (B) mercaptomodified PP fiber.

Figure 3 shows SEM photographs of the fractured surface in the impacted tested samples. The surface of the composite containing PP fibers presents many holes originated from the pull-out of the fibers, indicating poor interfacial adhesion. Such holes are not so evident in the PP–EVASH/ epoxy composite, indicating a better interfacial adhesion [(see Fig. 3(b)]. This adhesion ensures an effective stress transfer, increasing, of course, the impact strength of the material.

DMA constitutes a very attractive method for interface characterization. This technique gives two types of response to a low-strain periodic deformation: an elastic and a damping term. The latter is related to the energy dissipation and is very sensitive to all kinds of molecular motions that occur in a material. In the case of composites, when the fiber and matrix strongly interact at the

interface, the mobility of the macromolecular chains located in the fiber surface environment tends to decrease as compared to the mobility at other regions in the matrix. This phenomenon affects both damping and the glass transition temperature.<sup>10</sup> Figure 4 shows the loss tangent  $(\tan \delta)$  as a function of temperature for the epoxy resin matrix and the composites made with PP and PP-EVASH fibers. The magnitude of the main relaxation peak of the epoxy/PP fiber composite (peak B) decreases considerably when compared to the tan  $\delta_{\rm max}$  of the epoxy resin. The value of the damping peak temperature, corresponding to the glass transition of the material, presents also a substantial shift toward higher temperature. Since PP fibers are apolar, no specific interactions between the fiber and matrix could be expected. Therefore, the decrease of the tan  $\delta_{max}$ may be attributed to the restraint of the molecular motions of the matrix near the interface as a result of the differences between the thermal expansion coefficients of the components. This phenomenon causes also an increase of the glass transition temperature, as observed by Dong and Gauvin in DMA studies involving carbon fiber/ epoxy composites.<sup>10</sup>

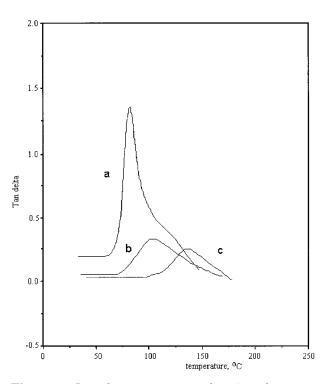


Figure 4 Loss factor,  $\tan \delta$ , as a function of temperature in (a) epoxy-cured resin, (b) PP fiber/epoxy resin composite, and (c) PP–EVASH fiber /epoxy resin composite.

Dynamic Properties	Epoxy Resin	PP/Epoxy Composite	PP-EVASH/Epoxy Composite
Storage modulus	$3.01\pm0.21$	$2.98\pm0.05$	$2.30\pm0.20$
$E'$ (GPa) tan $\delta$	$1.34\pm0.06$	$0.34\pm0.01$	$0.26\pm 0.02$
$T_g (^{\circ}C)^{a}$	$82.25\pm0.29$	$103.3 \pm 1.92$	$130.97 \pm 3.77$
B parameter <sup>b</sup>	—	1.21	2.01

 Table II
 Dynamic Properties and B Parameter of Epoxy Resin and Their Composites

 with PP and PP-EVASH Fibers

<sup>a</sup> Glass transition temperature determined from the maximum damping.

<sup>b</sup> B parameter calculated as follows: tan  $\delta_c = (1 - B\phi_f) \tan \delta_m$ .

The PP-EVASH fiber/epoxy composite presents a value of damping at a glass transition temperature lower than that of the PP fiber/epoxy composite. The glass transition point also shifts toward higher temperature. Since the volume fractions of the reinforcement components are comparable, the results observed with the composite prepared with the modified PP fiber may be explained by an improved interfacial adhesion. Table II lists the DMA data of these materials. Parameter B was reported by Ziegel and Romanov to estimate the contribution of the interfaces to the damping of the composites.<sup>11,12</sup> According to the theory, strong interactions at the interface result in the formation of a layer of the immobilized interphase. The relationship between parameter B and the damping properties is described by the following equation<sup>11,12</sup>:

$$\tan \delta_c = (1 - B\phi_f) \tan \delta_m$$

where  $\tan \delta_c$  and  $\tan \delta_m$  denote the damping of the composite and matrix, respectively, and  $\phi_f$  is the volume fraction of the reinforcement. Stronger interfacial interactions result in a thicker immobilized layer and higher values of parameter  $B.^{10}$  As presented in Table I, the parameter increases significantly in the composite prepared with the modified PP fiber, indicating better interface adhesion.

The initial modulus (E') value results from several factors, such as the matrix and fiber nature, fiber portion, stiffness of the components, and interfacial adhesion. Since the adhesion fibermatrix is more efficient in modified PP fiber-based composites, the lower value of E' may be attributed to the lower Young's modulus of the fiber component.

## **CONCLUSIONS**

The presence of EVASH in the PP-based blend fiber improves the interfacial adhesion of this component with the epoxy resin matrix. This adhesion was suggested by SEM and the dynamic properties and may explain the significantly higher impact resistance of this composite. In previous work, we demonstrated by XPS that the surface of the PP-EVASH blend fiber was essentially constituted by PP.6 However, by analyzing the same fiber surface by DRIFTS, we found the presence of the polar component (EVASH) at the surface. The last technique is able to detect components in a larger fiber thickness than can XPS. The proximity of the mercapto groups at the fiber surface may explain the improved interfacial adhesion of the epoxy resin/PP-EVASH fiber composite which is responsible for the outstanding impact performance.

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