

# Polyblend Fibers from Polypropylene and Mercapto-Modified EVA

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**ABSTRACT:** Polyblend fibers were made from mixtures of polypropylene (PP) and ethylene–vinyl acetate copolymers (EVA) or their mercapto-modified products [poly(ethylene-co-vinyl acetate-co-vinyl mercaptoacetate)] (EVASH). The presence of few EVA or EVASH in the PP fibers results in an increasing of the elastic modulus, indicating a reinforcing action of these functional polymers. The composition surface of the modified PP fibers was analyzed by X-ray photoelectron spectroscopy and diffuse reflectance infrared Fourier transform spectroscopy. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2243–2249, 1997

**Key words:** polyblend fiber; polypropylene; EVA copolymers; surface analysis

## INTRODUCTION

Fiber-reinforced materials constitute an important class of engineering composites with high mechanical performance. Improvement on their properties is governed to a large extent by several factors including the degree of interfacial bonding between fiber and matrix resin.<sup>1</sup> Among the fibers with potential application in composite developments, polypropylene (PP) fibers offer interesting properties such as abrasion and chemical resistance, low density, and low moisture absorption.<sup>2</sup> Unfortunately, this material does not present good adhesion and dyeing properties because of the absence of active sites along the backbone. Several studies concerning surface treatment have been reported in order to improve wettability and adhesion to the matrix of other polymers.<sup>3–5</sup>

These surface modifications include chemical oxidation and plasma treatment. For example, plasma treatment of polyethylene fibers has been reported to improve the adhesion ability to epoxy resins.<sup>6,7</sup>

Another versatile way to improve mechanical, dyeing, thermal, and surface properties involves the manufacture of polymer blend fibers.<sup>8</sup> By blending PP with a polymer containing appropriate functional sites, it is possible to develop fibers with good adhesion and mechanical and dyeing properties. In this respect, poly(ethylene-co-vinyl acetate) (EVA) should be a good candidate for improving adhesive properties to PP fibers because of the presence of the acetate groups as active sites. In addition, as recently reported, this copolymer acts as an impact modifier for isotactic PP<sup>9</sup> and may also be used as a compatibilizing agent in PP/polyethylene blends.<sup>10</sup>

The purpose of this article is to study the mechanical, morphological, and surface properties of fibers prepared from blends of PP with a small

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**Table I** Molecular Characteristics of EVASH

Sample Code	Starting EVA	Mercaptoacetate Group Content (mmol/100 g)
A1	EVA18	20.0
A3	EVA18	19.0
A4	EVA28	18.0

amount of EVA or their mercapto-modified products [poly(ethylene-*co*-vinyl acetate-*co*-vinyl mercaptoacetate; EVASH)]. The introduction of SH groups along the EVA chain has been performed in our laboratories by direct reaction of mercaptoacetic acid with hydrolyzed EVA<sup>11,12</sup> or EVA copolymers.<sup>13</sup> The presence of SH groups along the EVA backbone may enhance the adhesive properties of this compound. Indeed, the interfacial activity of EVASH has been observed in several blend compatibilization studies.<sup>14–16</sup>

## EXPERIMENTAL

### Materials

Isotactic PP (PPH 206) (melt flow index [MFI] = 22 g/10 min at 230°C, weight-average molecular weight = 240,000) was supplied by OPP, Brazil. EVA copolymers EVA18 (VA content = 18 wt %; MFI = 0.7 g/10 min at 150°C) and EVA28 (VA content = 28 wt %; MFI = 6.4 g/10 min at 80°C) were supplied by Petroquímica Triunfo S. A. and Politeño S. A., respectively. EVASH samples used in polyblend fibers were prepared by the transesterification reaction of EVA18 or EVA28 with

mercaptoacetic acid in toluene, according to the procedure previously described.<sup>13</sup> The molecular characteristics of the EVASH copolymers are listed in Table I.

### Preparation of Fibers

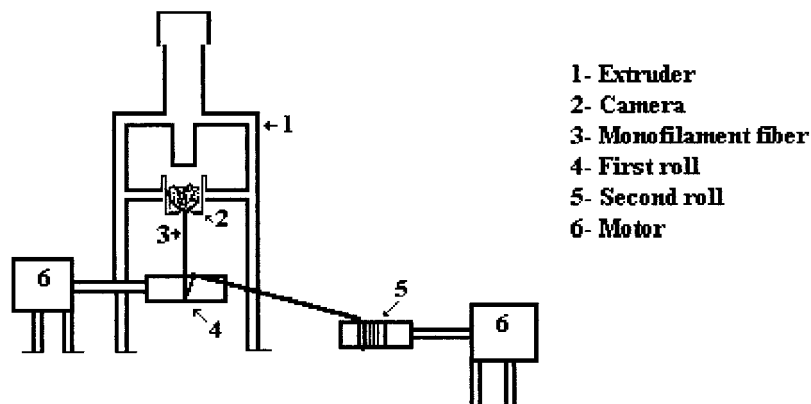
Extrusion and melt spinning assembly are illustrated in Figure 1. The polymeric materials (PP, PP/EVA, or PP/EVASH) were vessel blended before melt blending with a piston-type extruder at 190°C ( $D = 32.5$  mm;  $L = 200$  mm;  $L/D = 6.15$ ). The extruded monofilament was then drawn by two rolls. The first roll, working at 60 rpm, was 3.2 m away from the die of the spinning capillary. The second roll was located at 1 m from the first roll. The velocity of this second roll was varied in order to obtain different draw ratios (DR). The spinning DR was determined by measuring the decrease in diameter of the fibers. Before measurements, the fibers were conditioned at 25°C and RH  $\approx$  50%.

### Mechanical Testing of the Fibers

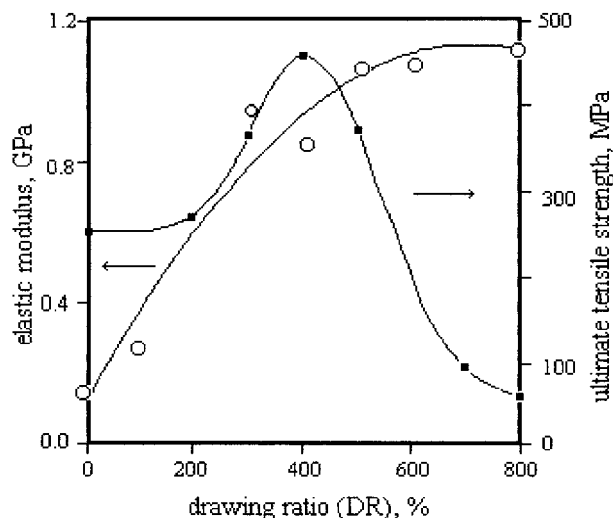
Tensile properties of the monofilament fibers were obtained with an Instron mod. 1130 with a gauge length of 10 mm and at a crosshead speed of 25 mm/min. The specimens for testing were prepared according to ASTM D-3379/75. All of the results are averages of at least 10 measurements.

### Characterization

Differential scanning calorimetry (DSC) measurements were conducted with a Du Pont TA 9900 apparatus. The analyses were performed un-



**Figure 1** Extrusion and melt spinning assembly used in the fiber preparation.



**Figure 2** Tensile properties of PP fiber as a function of DR.

der a nitrogen flow of 100 mL/minute. A first scan was made at a heating rate of 10°C/minute from room temperature up to 200°C, where it was kept for 10 min. Then, it was cooled to -70°C at a cooling rate of 10°C/minutes and heated again at the same rate up to 200°C.

The fiber surface was analyzed by Fourier transform infrared (FTIR) spectroscopy, with a 1750 FTIR Perkin-Elmer spectrometer equipped with a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) accessory. Samples were placed in the focus point of the diffuse reflectance cell for maximum reflection. The reflection spectra were recorded between 4000 and 500  $\text{cm}^{-1}$ , at a resolution of 4  $\text{cm}^{-1}$ . A scan number of 200 was used in all experiments.

X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos XSAM-800 dual-chamber

spectrometer with a Mg anode at a vacuum of  $10^{-9}$ – $10^{-10}$  Torr. The surface composition was calculated from the integral intensities of the XPS lines, as described elsewhere.<sup>17</sup> Surface tension was determined with the help of a Krüss Tensiometer, using a water/ethanol solution, according to ASTM D2578-67.

## RESULTS AND DISCUSSION

### Mechanical Properties

The tensile properties of PP fibers as a function of DR are illustrated in Figure 2. The elastic modulus increases with the DR, indicating an increase of stiffness. The ultimate tensile strength ( $\sigma_B$ ) displays a maximum at around 400% DR with a value of about 450 MPa. Similar values (390–460 MPa) have been reported in the literature for PP monofilament fibers.<sup>18</sup> On the basis of these results, we decided to use a 400% DR on the studies of mechanical properties of the PP/EVA or PP/EVASH polyblend fibers.

PP/EVA blend fibers were prepared with different amounts of EVA18 and EVA28 copolymers. The results concerning tensile properties are compared in Table II. The addition of EVA18 or EVA28 increases the elastic modulus of the material and decreases the elastic deformation, indicating a reinforcing action of these copolymers. The best values were achieved with the EVA18 sample. Similar reinforcing behavior was found in PP/liquid crystal polyblend fibers, which was attributed to the fibrillar morphology of the liquid crystal polymer (LCP) formed during the drawing process.<sup>19–21</sup>

The  $\sigma_B$  values of the PP/EVA fibers are lower

**Table II** Mechanical Properties of PP/EVA Polyblend Fibers

Fiber	EVA Content (phr)	Ultimate Tensile Strength (MPa)	Elastic Modulus (GPa)	Elastic Deformation (%)
PP		454	0.86	26
PP/EVA18	1	375	1.14	21
PP/EVA18	2	431	2.17	11
PP/EVA18	5	210	1.31	16
PP/EVA28	1	247	0.95	12
PP/EVA28	2	283	1.01	13
PP/EVA28	5	138	0.76	18

**Table III Mechanical Properties of PP/EVASH Polyblend Fibers**

Fiber	EVASH Content (phr)	Ultimate Tensile Strength (MPa)	Elastic Modulus (GPa)	Elastic Deformation (%)
PP		454	0.86	26
PP/A1 <sup>a</sup>	1	447	2.06	18
	2	235	0.88	18
	5	318	1.27	14
PP/A3 <sup>b</sup>	1	231	0.82	18
	2	444	1.33	21
	5	69	0.35	17
PP/A4 <sup>c</sup>	1	436	1.51	28
	2	392	1.63	20
	5	371	1.91	22

<sup>a</sup> A1, EVASH prepared from EVA18; mercaptoacetate content, 20.0 mmol/100 g.

<sup>b</sup> A3, EVASH prepared from EVA18; mercaptoacetate content, 19.0 mmol/100 g.

<sup>c</sup> A4, EVASH prepared from EVA28; mercaptoacetate content, 18.0 mmol/100 g.

than that found for pure PP fiber. This behavior is more pronounced when EVA28 is used and may be attributed to a poor interfacial adhesion between both components. Higher tensile properties were observed with PP fiber containing 2 phr of the EVA copolymer.

EVA18 and EVA28 copolymers were submitted to reaction with mercaptoacetic acid in order to produce mercapto-modified derivatives, such as EVASH. These functionalized copolymers were also blended with PP to obtain fibers with functional sites, which should be useful in the development of PP fibers-based composites. The mechanical properties of these PP/EVASH blend fibers are presented in Table III. In general, an increase on the elastic modulus was observed for all modified fibers, which also suggests a reinforcing action of the EVASH samples.

PP/EVASH fibers, the functional polymer of which was prepared from EVA28 copolymer (PP/A4 fibers), display higher elastic modulus and ultimate tensile strength than those obtained

from PP/EVA28 blend or pure PP. The best value of modulus was achieved with 5 phr of EVASH, whereas the higher value of  $\sigma_B$  was observed with the addition of 1 phr of the functional copolymer. The presence of SH polar groups along the EVASH backbone may increase the entanglements of the EVASH chains promoted by the interactions between the polar groups. This effect should also contribute to the increase of the ultimate tensile strength. The  $\sigma_B$  decreases with the increase of the EVASH content, probably because of the incompatibility of this material with the PP matrix.

EVASH prepared from EVA18 copolymer results in PP/EVASH fibers with higher elastic modulus than that of pure PP, but lower than that observed for PP/EVA18 blend fiber (see PP/A1 and PP/A3 fibers in Table III). In this case the best values of  $\sigma_B$  and elastic modulus were achieved when 1–2 phr of EVASH was used.

Because the mechanical properties of the fibers are largely influenced by the DR, we decided to

**Table IV Mechanical Properties of PP and PP/EVASH Fibers Obtained at Different DR**

Property	DR of PP Fiber (%)			DR of PP/EVASH Fiber (%)		
	300	400	500	300	400	500
Ultimate tensile strength (MPa)	367	454	360	423	318	381
Elastic modulus (GPa)	0.95	0.86	1.07	2.32	1.27	1.10
Elastic deformation (%)	26	26	15	12	14	23

**Table V DSC Melting Behavior of PP Fibers and Their Polyblend Fibers with EVA or EVASH**

Melting Properties	PP Fiber	PP/EVA18 100 : 5 phr	PP/EVA28 100 : 5 phr	PP/A3 100 : 5 phr	PP/A4 100 : 5 phr
Melting temperature (°C)	177	174	174	170	170
Crystallinity degree (%)	54	49	51	50	51

investigate the effect of different DR on the performance of PP/EVASH fibers. For this study, the PP/A1 polyblend fiber with 5 phr of EVASH was used. The results, summarized in Table IV, revealed that the PP/EVASH fiber requires lower DR to achieve better mechanical properties. Indeed, higher elastic modulus and  $\sigma_B$  were observed when the modified fiber was drawn at a 300% DR. Increasing the DR, the EVASH domains seem to lose their morphological characteristic for a good reinforcement.

### Melting Behavior

The DSC endothermic peaks for PP, PP/EVA, and PP/EVASH fibers were studied, and the results are summarized in Table V. The peak melting temperature decreased from 177°C for PP fiber to 174°C when 5 phr of EVA18 or EVA28 was present in the fiber. The crystallinity degree of the blends was determined by relating the heat of fusion of the fibers with that of individual PP pellets, which was taken as 51.6%. The crystallinity degree also decreases for the EVA-modified fibers. PP/EVASH fibers also display a decrease in melting temperature. The influence of EVA or EVASH on the melting temperature of the PP component may be attributed to a partial miscibility of blend components in the melt state.

### Surface Analysis

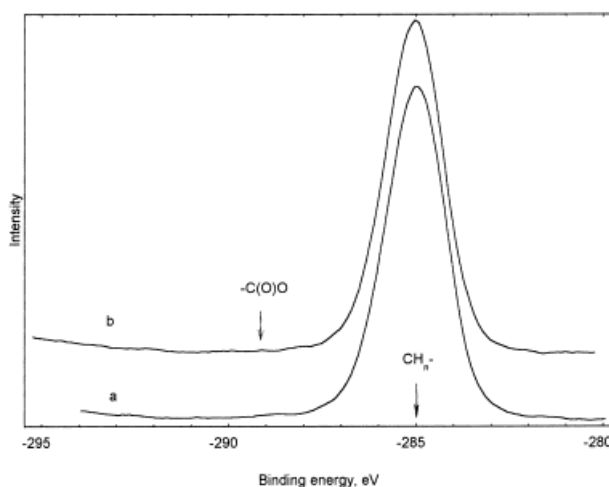
The surface chemistry of a modified fiber plays a decisive role in determining the adhesion properties and performance of the material. In this work, the surface of a PP/EVASH fiber sample was analyzed by FTIR and XPS.

The XPS spectra of neat PP and PP/EVA or PP/EVASH fibers are basically identical. As observed in Figure 3(a), the spectrum of PP contain only single  $C_{1s}$  line at 285.0 eV. The appearance of a weak signal of oxygen in the survey spectrum may be caused by the presence of some contamination at the PP surface. The  $C_{1s}$  core line of the

PP/EVA28 blend also shows a single line of carbon [Fig. 3(b)]. The absence of the carboxyl component at 289.2 eV suggests the complete attenuation of the signal from EVA or EVASH. The results of the quantitative analysis of some samples are summarized in Table VI. The similar surface composition of PP and their blends indicates that the surface overlayer of the blend fibers is composed mainly of PP.

The surface segregation of a component in a multicomponent polymer systems depends on the surface energy<sup>22</sup> and the viscosity of the components.<sup>8</sup> Normally, the near-surface region is enriched with the lower surface energy component. On the other hand, when incompatible polymers with different viscosities flow through a tube, the lower-viscosity component will tend to shift toward the wall and the higher-viscosity component will shift toward the center of the tube. Considering the MFI data of the PP and EVA samples presented in the experimental part, it is understandable that the PP component (higher MFI value) should preferentially shift to the wall.

The surface energy of the polyblend compo-



**Figure 3**  $C_{1s}$  core level spectra for (a) neat PP fiber and (b) PP/EVA28 polyblend fiber containing 5 wt % of EVA28.

**Table VI Surface XPS Results of PP, PP/EVA, and PP/EVASH Blend Fibers**

Sample	PP		PP/EVA28 (100 : 5)		PP/EVASH(A4) (100 : 5)	
	Peak Position (eV)	Atom (%)	Peak Position (eV)	Atom (%)	Peak Position (eV)	Atom (%)
C <sub>1s</sub>	285.0	98.4	285.0	97.8	285.0	98.9
O <sub>1s</sub>	532.3	1.6	532.3	2.1	532.3	1.0

nents is summarized in Table VII. Both EVA18 and its mercapto-modified product (A3) display surface energy equal or superior to the PP component, which agrees with the XPS results. In the case of EVA28 and the corresponding EVASH (A4), the values of surface energy are lower than that of the PP fiber, but the differences may be not enough to promote a surface segregation of these copolymers during the drawing process.

In addition to XPS analysis, several different sampling techniques of FTIR spectrometry are also useful in the surface analytical studies of fibers, such as Fourier transform infrared photoacoustic spectroscopy (FTIR/PAS)<sup>23–25</sup> and DRIFTS.<sup>25–27</sup> DRIFTS was chosen to analyze the PP/EVASH fiber surface, the spectra of which are demonstrated in Figure 4. The band of the carbonyl ester group at 1740 cm<sup>-1</sup> may be observed in all spectra of the PP/EVASH fibers. Its intensity increases as the EVASH concentration in the fiber increases. It is important to emphasize that DRIFTS provides an overlayer composition analysis of a surface as deep as a few microns,<sup>25</sup> whereas the XPS technique is able to analyze the overlayer composition of thickness about 50 Å. Therefore, the presence of the carbonyl absorption in the DRIFT spectra is explained by the ability of this technique to detect components at the near-surface depth.

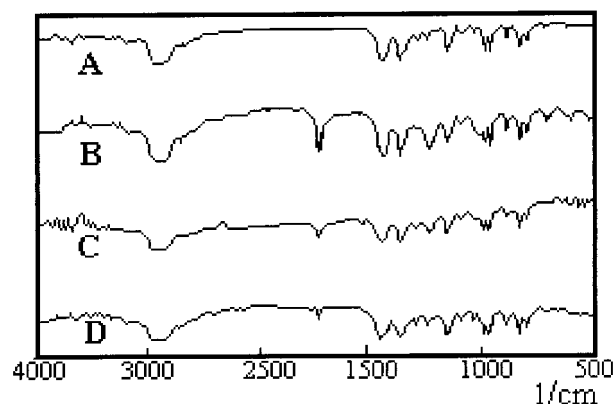
**Table VII Surface Tension of the Polyblend Components**

Polymer	Surface Tension (dyn/cm)
PP fiber	34
EVA18	34
EVASH (A3)	39
EVA28	31
EVASH (A4)	30

## CONCLUSION

Polyblend fibers constituted by the PP matrix and a small amount of EVA or their mercapto-modified products (EVASH) display higher elastic modulus than the PP pure fiber, suggesting a reinforcing action of these polar copolymers. The addition of only 2 phr of EVA18 (with 18 wt % VA) resulted in a substantial improvement on the elastic modulus without affecting the ultimate tensile strength. EVA28 (with 28 wt % VA) did not exert the same influence. In this case, the elastic modulus presented a small increase with the addition of 1–2 phr of EVA28, but the ultimate tensile strength barely decreased. The presence of the mercapto groups along the EVA18 or EVA28 backbone resulted in a superior reinforcement of the PP polyblend fibers. A better combination of ultimate tensile strength and elastic modulus was achieved with the addition of as low as 1–2 phr of the mercapto-functionalized EVA samples.

The overlayer composition of PP/EVASH fiber determined by XPS analysis is mainly constituted



**Figure 4** DRIFTS of (A) neat PP fiber, and PP/EVASH polyblend fibers (PP/A4) with (B) 5 wt %, (C) 2 wt % and (D) 1 wt % of EVASH.

by PP. The analysis of the same fiber surface by the DRIFTS technique revealed the presence of the polar component close to the surface. These discrepant results were attributed to the larger fiber thickness that DRIFTS is able to analyze. From both techniques, we can conclude that EVA or EVASH components in the polyblend fiber are located close to the surface with a very thin layer of PP wrapping the fiber. The proximity of the polar groups (related to the minor component in the blend) at the fiber surface may provide some adhesion properties to these materials. In this sense, some research concerning the application of these modified PP fibers in epoxy-based composites is in progress. The results of these studies are forthcoming.

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