# Physical Modification of Polypropylene. III. Novel Morphology of Polypropylene and Poly(ethylene-*co*-vinyl alcohol) with Epoxy Blend Fibers

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**ABSTRACT:** In this study, the novel morphology of polypropylene (PP) and poly(ethylene*co*-vinyl alcohol) (EVOH) blend fibers is described. More precisely, the blend fibers of PP–EVOH containing a small amount of EVOH (1, 3, 5, 7, and 9% by weight), with and without epoxy (1 wt %), have been melt-spun at a constant spinning velocity (500 m/min). For the as-spun fiber, both the initial modulus and the tenacity increased with the increase in the EVOH content. The blend fibers with three draw ratios (2, 3, and 4) drawn at room temperature. The scanning electron microscopic study showed that a draw ratio of 2 reveals little about the morphological changes, whereas a draw ratio of 4 showed a streak structure perpendicular to the fiber axis for PP–EVOH (91/9 wt %) blend fibers. In addition, epoxy (1 wt %) containing PP–EVOH (91/9 wt %) blend fiber showed latitudinal streaks. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1049–1057, 1999

Key words: polypropylene; blend fiber; poly(ethylene-co-vinyl alcohol); streak

## INTRODUCTION

A useful polypropylene (PP) results from the use of suitable additives, which constitute ways of modification for the types of the fibers obtained. The necessity of tailor-made additives for polypropylene fibers is related to fiber manufacturing process conditions and to application diversity. Major developments in this field have been recorded in the last 20 years.<sup>1</sup> The main restrictions on the use of polypropylene fiber are its lack of dye receptor sites, which makes it difficult to dye. In spite of the extensive research efforts of many researchers focused on developing dyeable polypropylene fibers, no truly commercial product is available on the market at the present.<sup>2–7</sup> Therefore, in recent years, the research of various polyblend fibers is being progressively developed. In order to obtain dyeable polypropylene fiber, we prepared polypropylene–poly(ethylene-co-vinyl alcohol) (PP–EVOH) blends and PP–EVOH blend fibers with and without the addition of epoxy as an additive. In the present article, we report on results of investigations regarding novel morphology of PP–EVOH blends and blend fibers with and without Epoxy. A detailed dyeability study is in progress to gain a more complete understanding of this subject, and results will be reported in a future article.

## EXPERIMENTAL

#### Materials

The isotactic polypropylene (PP), H880Z (MFI = 25), was supplied by SK Co., Ltd. (Korea). The

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**Figure 1** DSC thermograms of the PP–EVOH blends: (1) pure PP; (2) 99/1; (3) 97/3; (4) 95/5; (5) 93/7; (6) 91/9; (7) pure EVOH.

EVOH copolymer containing 38 mol % ethylene units was Soarnol K3825 (MFI = 25), a product of Japan Synthetic Chem. Ind. Co. The epoxy used was poly(bisphenol A-epichlorohydrin) ( $M_n$  = 6100;  $M_p$  = 130–140°C), a product of Aldrich Chemical Co., Inc.

## **Preparation of Blends**

The PP-EVOH blends of compositions 1, 3, 5, 7, and 9 wt % EVOH content were prepared by melt-mixing at a screw speed of 60 rpm and a

temperature range of 210-220°C in a singlescrew extruder (Brabender plasticoder; L/D= 30). The extrudate obtained from the extruder was cut into small granules in a granulator and used for spinning.

## **Preparation of Fibers**

Before melt-spinning, the pellets of blend were dried in a vacuum drier for 5 h at 80°C. The pellets were fed into a spinning machine (Fuji melt spinning tester MST-CII) with a spinning

Table I Thermal Properties of the PP-EVOH Blends

Composition (PP-EVOH)		P	Р		EVOH				
	$\frac{T_m}{(^\circ\mathrm{C})}$	$T_c$ (°C)	$\Delta H_f$ (J/g)	$\Delta H_c$ (J/g)	$\begin{array}{c} T_m \\ (^{\circ}\mathrm{C}) \end{array}$	$T_c$ (°C)	$\Delta H_f$ (J/g)	$\Delta H_c$ (J/g)	
100/0	170.4	108.5	70.0	82.4	_	_	_		
99/1	164.5	115.0	93.0	99.7				_	
97/3	165.3	115.7	85.3	93.0	174.3	153.6	0.87	1.32	
95/5	164.3	119.0	88.3	101.0	174.7	153.9	0.90	2.35	
93/7	164.2	123.5	81.0	95.6	175.3	154.2	0.92	3.08	
91/9	162.2	124.2	71.8	90.1	173.7	154.3	0.93	4.21	
0/100	—	—	_	_	174.8	154.8	65.7	60.2	

	PP				EVOH			
Composition (PP-EVOH-Epoxy)	$\frac{T_m}{(^\circ\mathrm{C})}$	$T_c$ (°C)	$\Delta H_f$ (J/g)	$\frac{\Delta H_c}{\rm (J/g)}$	$\begin{matrix} T_m \\ (^{\circ}\mathrm{C}) \end{matrix}$	$\begin{array}{c} T_c \\ (^{\circ}\mathrm{C}) \end{array}$	$\Delta H_f$ (J/g)	$\begin{array}{c} \Delta H_c \\ ({\rm J/g}) \end{array}$
100/0	170.4	108.5	70.0	82.4	_	_		_
(99/1)/1	165.8	114.2	78.1	85.8		_	_	_
(97/3)/1	165.2	118.5	86.1	93.5		153.1	_	1.25
(95/5)/1	165.0	120.0	81.7	97.0	174.8	153.7	0.65	2.38
(93/7)/1	164.1	122.7	71.9	86.1	173.6	153.9	0.72	3.17
(91/9)/1	164.5	123.4	61.2	94.9	173.1	154.0	0.74	4.41
0/100	—	—	—	—	174.8	154.8	65.7	60.2

Table II Thermal Properties of the PP-EVOH-Epoxy Blends

nozzle having 28 orifices each of 0.5 mm diameter; they were melt spun at an extrusion rate of 0.8 kg/h and a take-up rate of 500 m/min at a temperature of the spinning head of  $230^{\circ}$ C. At the room temperature (25°C), as-spun fibers were drawn at three different draw ratios (2, 3, and 4).

#### Measurements

The melting and crystallization behavior of the pure polymers and PP blends was analyzed on a differential scanning calorimetry (DSC) instrument at a heating rate of  $10^{\circ}$ C min<sup>-1</sup> and cooling rate of  $10^{\circ}$ C min<sup>-1</sup>. The dynamic mechanical

properties of the blends were measured using a Rheovibron DDV II at a frequency of 110 Hz. Compression-molded samples of dimensions  $3 \times 0.2 \times 0.03$  cm<sup>3</sup> were used for testing. The temperature range used was from -100 to +150°C. Mechanical testing of blend fibers were determined at room temperature using an Instron (4301) tensile tester, equipped with a 2 kgf load cell. The gauge length was 50 mm. All the tensile properties to be presented are the average of at least five tests. The photomicrographs of the starting blend and the fibers were taken by Hitachi SEM S-4200. Blend fibers were treated in



**Figure 2** Tan  $\delta$  curves at 110 Hz of the PP–EVOH blends: ( $\bullet$ ) pure PP; ( $\bigcirc$ ) 99/1; ( $\lor$ ) 97/3; ( $\bigtriangledown$ ) 95/5; ( $\blacksquare$ ) 93/7; ( $\Box$ ) 91/9; ( $\bullet$ ) pure EVOH.



**Figure 3** Tan  $\delta$  curves at 110 Hz of the PP–EVOH blends containing 1 wt % of epoxy: (**●**) pure PP; (**○**) 99/1; (**▼**) 97/3; (**▽**) 95/5; (**■**) 93/7; (**□**) 91/9; (**♦**) pure EVOH.





**Figure 4** Tensile strength (g/denier) versus the draw ratio for PP and PP–EVOH blend fibers at various composition (wt % EVOH): ( $\bullet$ ) PP; ( $\bigcirc$ ) 1; ( $\mathbf{V}$ ) 3; ( $\bigtriangledown$ ) 5; ( $\mathbf{I}$ ) 7; ( $\Box$ ) 9.

**Figure 6** Modulus (g/denier) versus draw ratio for PP and PP–EVOH blend fibers at various composition (wt % EVOH): ( $\bullet$ ) PP; ( $\bigcirc$ ) 1; ( $\blacktriangledown$ ) 3; ( $\bigtriangledown$ ) 5; ( $\blacksquare$ ) 7; ( $\square$ ) 9.



60 ₽ 50 T ₽ 0 Modulus (g/d) 40 0 Δ 30 0 ▽ 20 0 10 0 2 3 1 4 5 Draw Ratio

**Figure 5** Tensile strength (g/denier) versus the draw ratio for PP and PP–EVOH–epoxy (1 wt %) blend fibers at various composition (wt % EVOH): ( $\bullet$ ) PP; ( $\bigcirc$ ) 1; ( $\nabla$ ) 3; ( $\bigtriangledown$ ) 5; ( $\blacksquare$ ) 7; ( $\square$ ) 9.

**Figure 7** Modulus (g/denier) versus the draw ratio for PP and PP-EVOH-epoxy (1 wt %) blend fibers at various composition (wt % EVOH): ( $\bullet$ ) PP; ( $\bigcirc$ ) 1; ( $\nabla$ ) 3; ( $\bigtriangledown$ ) 5; ( $\blacksquare$ ) 7; ( $\Box$ ) 9.



(a) pure PP



(b) 99/1



(c) 97/3



(d) 95/5



Figure 8 SEM micrographs of fracture surface of PP–EVOH blends: (a) pure PP; (b) 99/1; (c) 97/3; (d) 95/5; (e) 93/7; (f) 91/9.

dimethyl sulfoxide (a selective solvent for EVOH) in an ultrasonic bath for 10 min and rinsed in distilled water for 2 min. All fibers were mounted on specimen holders (SEM mounts) using silver paint and coated with gold in a thermal evaporation units.

# **RESULT AND DISCUSSION**

# **Thermal Behavior**

Figure 1 shows the DSC thermograms of PP– EVOH blends. The melting temperatures for PP and EVOH appear separately, and the melting



(e) 91/9

**Figure 9** SEM micrographs of fracture surface of PP–EVOH blends containing 1 wt % of epoxy: (a) 99/1; (b) 97/3; (c) 95/5; (d) 93/7; (e) 91/9.

temperature of PP decreases as the content of EVOH is increased. According to Flory,<sup>8</sup> the decrease in the melting point is due to the decrease in the chemical potential of the crystalline phase for the two-phase system. The same tendency was also observed for PP–EVOH–epoxy (1 wt %) blends.

Analyzing the DSC results of PP-EVOH and PP-EVOH-epoxy blends listed in Tables I and II. From Figure the tables, it was found that PP and EVOH crystallize at 108 and 154°C, respectively. The crystallization temperature is slightly increased to high temperature as the content of EVOH is increased. The same tendency was also observed for PP–EVOH–epoxy (1 wt %) blends. In spite of the addition of a small amount of epoxy, it does not affect the thermal properties of the PP–EVOH–epoxy blend.

#### **Dynamic Mechanical Properties of Blends**

Figure 2 shows the variation of tan  $\delta$  versus temperature for the pure components and the blends. The tan  $\delta$  curve of poly(ethylene-*co*-vinyl alcohol) (EVOH) show a peak at 70°C due to the  $\alpha$ -transition arising from the segmental motion. This corresponds to the glass transion temperature  $(T_{q})$ of the EVOH. Polypropylene shows tan  $\delta$  peaks around 20°C, which correspond to the  $T_g$ . The blends shows single tan  $\delta$  peak around 10°C, which corresponds to the PP component. The  $T_g$ corresponding to the PP component is shifted to a lower temperature upon the addition of EVOH. The damping of the blends decreases with an increase in the content of EVOH. The decrease in the damping and tan  $\delta_{\max}$  with a decrease in the EVOH content is due to the increase in the crystalline volume of the system on increasing the content of EVOH, whose damping is always lower than PP. Figure 3 shows the variation of tan  $\delta$ versus temperature for the pure components and the blends containing 1 wt % epoxy. In Figure 3, there is difference among them in their  $\beta$  relaxation. The addition of epoxy to the blends cause them have a higher  $T_g$  than the blend without epoxy. In addition, the addition of epoxy to the blends increase more in the damping and  $\tan \delta_{\max}$ than without epoxy.

## **Mechanical Properties of Blend Fibers**

Figures 4 and 5 present the relationship of the tensile properties of the blend fibers as a function of the draw ratio for both those containing epoxy (1 wt %) and those without epoxy. They are a little different. These figures imply that the best conditions to give the highest tensile modulus and strength for each case are different. When carrying out these drawing experiments, it is worthwhile to point out that we set the drawing condition constant and then continuously increased the draw ratio until the fiber broke; this meant that fibers could not be drawn further.

Figures 6 and 7 exhibit that modulus of the PP-EVOH-epoxy blend fibers are higher than those of PP-EVOH blend fibers. It is attribut-

able to the reinforcement of epoxy in the PP– EVOH–epoxy blend fibers. These phenomena could be explained in the terms of the effect of streak structure in the blend fibers. The highest tensile modulus and strength obtained from the PP–EVOH (91/9) blend fiber with the addition of epoxy.

#### Morphology of the Blends

The morphology of the blends, as measured under a scanning electron microscopy, is shown in Figures 8 and 9. Figures 8 and 9 show the micrographs of PP-EVOH blends without and with 1 wt % of epoxy, respectively. These micrographs clearly show the two-phase morphology of the PP-EVOH blend, with EVOH forming the discrete phase. The size of dispersed-phase domains vary with blending ratio and the epoxy. At high EVOH contents, the EVOH droplets become large. By comparing the morphology of the PP-EVOH blends with the morphology of the blends containing 1 wt % epoxy by weight, it can be immediately seen that the presence of epoxy in these blends resulted in a increase in the diameters of the dispersed phase. This may be related to the high affinity, which the epoxy has for EVOH.

### Morphology of the Blend Fibers

The morphology of PP–EVOH (91/9 wt %) blend fibers was investigated using a scanning elec-



**Figure 10** SEM micrograph of the surface of as-spun PP–EVOH (91/9 wt %) blend fiber.



Figure 11 SEM micrograph of the dimethyl-sulfoxide-treated surface of as-spun PP-EVOH (91/9 wt %) blend fiber.



**Figure 13** SEM micrograph of the dimethyl-sulfoxide-treated surface of drawn PP-EVOH (91/9 wt %) blend fiber (draw ratio 4).

tron microscopy. Figures 10 and 11 show surfaces of the as-spun PP-EVOH (91/9 wt %) blend fibers. As-spun PP-EVOH blend fiber exhibited a smooth surface without any clear defect. The dimethyl-sulfoxide-treated as-spun PP-EVOH blend fibers does not alter the morphology of the fiber significantly (Fig. 11). Figures 12 and 13 show surfaces of the drawn (draw ratio of 4) PP-EVOH (91/9 wt %) blend fibers. When the blend fibers were highly drawn (draw ratio of 4), a streak structure was noticed, as shown in Figure 13. These streaks propagate perpendicular to the fiber axis and follow a helical path along the cylindrical fiber. We prepared 1 wt % of epoxy containing the PP–EVOH blend fiber to reduce the pitch distance (distance between consecutive streaks). Figure 14 shows surfaces of the drawn (draw ratioof 4) PP–EVOH (91/9 wt %)–epoxy (1 wt %) blend fibers. It can also be seen that streak structure appear for 1 wt % of epoxy containing PP– EVOH blend fibers having the same draw ratio. With the inclusion of additive amount of epoxy (1 wt %) in the PP–EVOH blend fiber, the separated phase between PP and EVOH were con-



**Figure 12** SEM micrograph of the surface of drawn PP–EVOH (91/9 wt %) blend fiber (draw ratio 4).



Figure 14 SEM micrograph of the dimethyl-sulfoxide-treated surface of drawn PP–EVOH (91/9 wt %)– epoxy (1 wt %) blend fiber (draw ratio 4).

siderably adhered, even though the streak structure was well defined.

## **CONCLUSIONS**

Among many attempts to obtain dyeable polypropylene fibers, the modification method of blend have been investigated. In one of attempts, we prepared PP-EVOH blends and PP-EVOH blend fibers with and without the addition of epoxy. Their mechanical properties and morphologies were strongly influenced by the presence of epoxy. The blend fiber's tensile modulus and strength are as good as, or better than, those of PP fibers. The morphological study shows a streak structure from the blend fibers.

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