# Influence of the Type of Polyhydroxyether on Mechanical Properties of PET/TLCP/Polyhydroxyether Blends

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ABSTRACT: In a more elaborate article, it was described that blends of poly(ethylene terephthalate) (PET), a liquid crystalline copolyester, and small amounts of a liquid crystalline polyhydroxyether showed an increase in tensile modulus and strength compared to the blends without polyhydroxyether. The results were obtained using a polyhydroxyether composed of 75 mol % biphenyl and 25 mol % phenyl units. In this article, the use of two other types of polyhydroxyether is described, one based on the  $\alpha$ -methylstilbene unit and the other based on bisphenol A. Addition of either of these polyhydroxyethers to the PET/thermotropic liquid crystalline polymer (TLCP) blends increased the tensile modulus and strength of extruded fibers in a similar way as upon addition of the liquid crystalline polyhydroxyether. Improvement of the viscosity ratio and thereby improvement of the fibril formation, by reactions of the functional hydroxyl side groups in the polyhydroxyethers, appears to be the most important factor for the improvement of the mechanical properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1125–1131, 1999

**Key Words:** reactive blending; poly(ethylene terephthalate); PET; LCP; polyhydroxyether

## **INTRODUCTION**

Previously, it was shown that the mechanical properties of blends of poly(ethylene terephthalate) (PET), modified with a dianhydride, and a thermotropic liquid crystalline polymer (TLCP) could be improved by a factor 4 –5 by adding a small amount of a polyhydroxyether.<sup>1</sup> The improvement was achieved due to reactions taking place between the anhydride and secondary hydroxyl groups, which changes the rheological conditions (and possibly improves the adhesion between the phases). The results were obtained with a liquid crystalline polyhydroxyether based on 75 mol % biphenyl and 25 mol % phenyl units.<sup>2</sup> In this article, two other types of polyhydroxyether were used in the PET/TLCP blend to establish

1. Whether another mesogenic group in the polyhydroxyether has any effect on the improvement of the properties of the blend; for this purpose, a polyhydroxyether based on the  $\alpha$ -methylstilbene unit was used, and

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2. Whether the liquid crystallinity of the polyhydroxyether is important in improving the blend properties. For this purpose, the polyhydroxyether based on bisphenol A, known as Phenoxy, was used.

## **EXPERIMENTAL**

#### Materials

One of the polyhydroxyethers was prepared<sup>2</sup> from 4,4'-dihydroxy- $\alpha$ -methylstilbene and its diglycidyl ether. It will be referred to as  $\alpha$ MS-polyhydroxyether. It has an inherent viscosity of 0.6 dL/g (C = 0.2 g/dL, in dimethylacetamide at 25°C). The other polyhydroxyether, trade name Paphen, type PKHJ, was purchased from Phenoxy Specialties (Rockhill, SC). It is referred to as Phenoxy. The chemical structures of the polyhydroxyethers are shown in Scheme 1.

The TLCP used was Vectra A900, here referred to as Vectra, an aromatic copolyester prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6naphthoic acid (HNA), with a melting temperature of 280°C, produced by Hoechst Celanese (Frankfurt, Germany). The matrix polymer, PET, was kindly supplied by M&G Richerche S.p.A. (Pozzilli, Italy). This PET has an intrinsic viscosity of 0.6 dL/g and was modified with 0.4 wt % of pyromellitic dianhydride (PMDA) and will be referred to as PET–anhydride. PMDA is an additive used for the upgrading of the molecular weight of PET.<sup>3</sup> The compatibility experiments were performed using PET of the same intrinsic viscosity, from the same producer, but without PMDA.

#### Processing

The blend components were tumble-mixed and dried for at least 16 h in a vacuum at 120°C. In the previous article, two methods were used to produce blend fibers<sup>1</sup>; in this article, the first of these methods (method A) was used: The different blend compositions were fed into a Collin singlescrew extruder, equipped with a four-way Ross static mixer, containing a sequence of 10 mixing elements. The subsequent extruder zones were set at 160, 290, and 310°C. The temperature of the mixing section was 300°C, and the die exit temperature, 270°C. The screw speed was 20 rpm. The strands coming out of the extruder (die diameter 2.5 mm) were drawn to different draw ratios. Sheets of the blends were extruded through a flat die (thickness 1 mm, width 10 cm), using the same temperature zones as when extruding the fibers. The fairly high temperature of 310°C appeared to be necessary to melt all crystallites in the Vectra, while the quite low die exit temperature of 270°C was needed to obtain a sufficient melt strength; at higher exit temperatures, the strands could not be drawn. The draw ratio was determined by the ratio of square diameters of the die and the drawn fiber:  $DR = d_{die}^2/d_{fiber}^2$ . The compatibility, morphology, tensile moduli, and tensile strengths were determined using the procedures and methods as described previously.<sup>1</sup>

### **RESULTS AND DISCUSSION**

#### Compatibility

The compatibility of PET with Phenoxy and with the  $\alpha$ MS-polyhydroxyether was studied in 50/50 compositions with DSC. PET without anhydride was used. The blend was prepared from solution.<sup>1</sup> The DSC thermograms of the first and second heating runs are shown in Figure 1. The PET/  $\alpha$ MS-polyhydroxyether blend has a single  $T_g$  in both heating runs, in between the  $T_g$ 's of the pure components, which indicates a single phase and, thus, compatibility. The PET/Phenoxy blend shows two glass transitions in the first run, at



**Figure 1** DSC thermograms of 50/50 w/w blends of (a) PET/ $\alpha$ MS-polyhydroxyether and (b) PET/Phenoxy; first and second heating runs are shown.

about the  $T_g$ 's of the pure components, which indicates two phases and incompatibility. However, in the second run, only one glass transition was found, which points to a single phase. Apparently, the blend becomes compatible in the melt, possibly through transesterification reactions between the two components. Seymour and Zehner<sup>4</sup> and Harris et al.<sup>5</sup> found that PET and Phenoxy were incompatible, even when the blend had been in the melt state, while Robeson and Furtek<sup>6</sup> found indications for the compatibility of PET and Phenoxy for extruded blends. Concerning the compatibility of Vectra and Phenoxy, Choi et al.<sup>7</sup> found that they were immiscible in the whole composition range.

#### **Mechanical Properties**

One blend composition was prepared with  $\alpha$ MSpolyhydroxyether. A larger number of blend compositions were prepared with Phenoxy. Figure 2 shows the tensile strength and modulus for a 80/20 PET-anhydride/Vectra blend with 0.75 wt % of either of the polyhydroxyethers. The strength and modulus increase in the same way as with the polyhydroxyether previously studied<sup>1</sup> (based on



**Figure 2** ( $\blacksquare$ ) Tensile strength and (▲) modulus for PET–anhydride/Vectra 80/20 fibers with (a) 0.75 wt %  $\alpha$ MS-polyhydroxyether and (b) 0.75 wt % Phenoxy, as a function of the draw ratio.

75/25 biphenyl/phenyl); the elongation at break was similar as well: about 2%.

Figure 3 displays the maximum-achieved stiffness and strength as a function of Phenoxy content for 80/20 PET-anhydride/Vectra blends. All the blends with Phenoxy showed a higher tensile modulus and strength than did the blends without Phenoxy, with a clear optimum at 0.75 wt %: 8.3 GPa and 159 MPa, respectively. Comparing this Phenoxy to the previously studied polyhydroxyether,<sup>1</sup> the maximum-achieved modulus is somewhat lower while the maximum-obtained strength is somewhat higher, but the trend is similar.

PET-anhydride/Vectra 90/10 blends with Phenoxy showed a similar increase in modulus

and strength, with a (less pronounced) optimum at 0.75 wt % Phenoxy. A tensile modulus of 3.1 GPa and tensile strength of 61 MPa was reached for a 90/10/0.75 blend. In the 95/5 composition, there is almost no increasing effect of the Phenoxy. The 95/5/0.75 blend displayed a modulus of 2.54 GPa and strength of 40 MPa, compared to 2.25 GPa and 33 MPa for the 95/5/0 blend, respectively.

## Morphology

The morphology of cryogenically fractured fiber cross sections was examined by scanning electron microscopy. In PET–anhydride/Vectra blends without Phenoxy, the Vectra phase was present



**Figure 3** (■) Maximum tensile strength and (▲) modulus of 80/20 PET–anhydride/ Vectra blends as a function of Phenoxy content.

as spherical particles in the PET matrix. Addition of a small amount of Phenoxy enhanced the fibril formation of the Vectra. Figure 4 shows highly drawn fibers of 80/20 blends with 0.5, 0.75, and 1.5 wt % Phenoxy. In the 80/20/0.5 blend, there are still some ellipsoidal Vectra particles present. In the 80/20/0.75 blend, the Vectra fibrils have the largest aspect ratio (length/diameter). Another notable feature is that no fiber pull-out was observed at the fracture surface. In blends with the liquid crystalline polyhydroxyether, this was not observed.<sup>1</sup> This might point to an improved adhesion between the fibril and matrix. However, the absence of fiber pull-out is not reflected in a substantially higher tensile strength for the 80/20/ 0.75 blend. The effect of the draw ratio on an 80/20/0.75 blend is shown in Figure 5. At low draw ratios, the Vectra phase is present as spheres or ellipsoids. It shows that together with the presence of Phenoxy an elongational flow (applied through drawing) is necessary for good fibril formation.

#### Adhesion

The reactive blend system could possibly lead to an improvement of the interfacial adhesion between PET-anhydride and Vectra. The polyhydroxyether and the anhydride are quite reactive and may even react with the stable ester bonds in Vectra. Interchange reactions in Vectra/Phenoxy mixtures were reported by Choi et al.<sup>7</sup> These reactions were indicated by viscosity measurements and infrared spectroscopy. Nevertheless, in our study, viscosity measurements as well as infrared spectroscopy did not indicate any reactions between the Phenoxy and Vectra. These different results might be caused by the fact that Choi et al. used a 50/50 blend ratio and longer mixing times.

A direct measurement of the interface adhesion is very difficult and has not been successful yet for TLCP/thermoplastic blends. Mostly, it was attempted to examine the fracture surface of the tensile test pieces using SEM. This was briefly mentioned above. Other methods to obtain an indication of the adhesion include contact angle measurements, peel testing, and transverse tensile testing of sheets. The last two methods were attempted in this study. Unfortunately, both methods did not lead to a successful determination of the interface adhesion.

## CONCLUSIONS

Two types of polyhydroxyether, one based on the  $\alpha$ -methylstilbene group and one based on bisphenol A (Phenoxy), were examined with respect to their effect on the mechanical properties of PET–anhydride/Vectra blends. Both polyhydroxyethers showed compatibility with PET, although for Phenoxy, only after melting of the blend, which indicates that reactions take place between Phenoxy and PET in the melt. Adding a small amount of



(c)

Figure 4 SEM micrographs of fracture surfaces of cryogenically broken PET-anhydride/Vectra 80/20 blend fibers, containing (a) 0.5 wt %, (b) 0.75 wt %, and ( c) 1.5 wt % Phenoxy. The fibers are maximally drawn (DR = 50-70). Magnifications: left figures 1000×; right figures 8000×.

either type of polyhydroxyether increased the tensile strength and tensile modulus of extruded fibers of the PET-anhydride/Vectra blends. The optimum added amount was 0.75 wt %. Studies of the fiber cross sections by SEM show an enhanced fibril formation. The trend as well as the achieved values are well comparable with the results obtained with the liquid crystalline polyhydroxyether (based on 75



Figure 5 SEM micrographs of fracture surfaces of cryogenically broken PET–anhydride/Vectra/Phenoxy 80/20/0.75 fibers at several draw ratios.

mol % biphenyl and 25 mol % phenyl) previously studied.<sup>1</sup> It can be concluded that the reactions between the polyhydroxyether and PET–anhydride and possibly between the polyhydroxyether and Vectra are of decisive importance for the improvement of the mechanical properties, by optimizing the viscosity ratio and thereby improving the fibril formation. The type of polyhydroxyether that is being used is of minor importance.

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