Reactive Blending of Poly(ethylene terephthalate) with a Liquid Crystalline Copolyester and Polyhydroxyether

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ABSTRACT: Poly(ethylene terephthalate) modified with a dianhydride (PET-anhydride) was melt-blended with a liquid crystalline copolyester (Vectra A) in the presence of a small amount of a liquid crystalline polyhydroxyether. The mechanical properties of a blend consisting of PET-anhydride/Vectra A/polyhydroxyether were drastically improved compared to blends without polyhydroxyether or without anhydride. Meltspun fibers of PET-anhydride/Vectra A/polyhydroxyether in a 80/20/0.75 weight ratio displayed a much higher tensile modulus (17 GPa) and tensile strength (214 MPa) than did a 80/20 PET-anhydride/Vectra A blend (4 GPa and 60 MPa, respectively). A similar increase in modulus and strength was found for a 90/10/0.75 relative to a 90/10 blend. The tensile moduli of the blends can well be described by the Tsai-Halpin equation. A better fibril formation was observed, which was attributed to an improved viscosity ratio. Reactions between the various functional groups during melt processing were indicated by viscosity measurements. The polyhydroxyether may act as a reactive compatibilizer which improves the interfacial adhesion, chemically and/or physically. WAXD recordings of both blends showed a crystalline and highly oriented Vectra phase. The PET phase was unoriented and amorphous in a PET/Vectra blend and semicrystalline and weakly oriented in a PET/Vectra/polyhydroxyether blend. Postdrawing of the various blend fibers to $\lambda = 4$ increased the modulus by about 40% and the tensile strength by more than 100%, mainly through orientation of the PET phase. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1107-1123, 1999

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

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) have been studied extensively in blends with

thermoplastics.^{1,2} During processing, TLCPs can form oriented fibrils in the blend, which can act as a reinforcing component. Therefore, they are also called *in situ* composites. In addition to the *in situ* formation of reinforcing fibrils, the TLCP phase may lower the melt viscosity, which results in a lower energy consumption during processing and the possibility for thin-walled products. TLCPs and thermoplastics are in most cases incompatible and generally exhibit a poor interfacial adhe-

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sion.^{2,3} This is a limiting factor for the mechanical properties, especially the tensile strength. The adhesion can be improved by increasing the interactions between the phases, physically or chemically. Compatibilizers, for example, block copolymers, are used in blends to decrease the interfacial energy.^{4,5} This results in a finer dispersion of droplets in the matrix and can result in a better adhesion. However, it might be more difficult to deform these smaller droplets into fibrils.^{2,6,7} Compatibilization can also take place by specific interactions between the TLCP and the matrix polymer, like ion-dipole interactions,⁸ hydrogen bonding,⁹ chemical interactions,⁶ or a combination of these.^{7,10} A prerequisite for a compound to act as a reactive compatibilizer is incompatibility with both components, because the compound then tends to reside at the interface, where it should interact. Lee and DiBenedetto¹¹ proposed the idea of improving the interfacial adhesion, physically or chemically, by adding a second TLCP to a TLCP/thermoplastic blend. An interesting study concerning the compatibilizing of TLCP/thermoplastic blends, particularly TLCP/ PET blends, was conducted by Chin et al.^{6,12} They studied the effect of compatibilizers with epoxide functionalities. Addition of these compatibilizers resulted in higher stiffness, strength, and toughness. It was suggested that an epoxy-co-PET-co-LCP mixed copolymer was formed, which would reduce the interfacial tension between the phases and enhance the fibril formation. However, the formation of this copolymer, or particularly the reactions between epoxy and PET or epoxy and LCP, was not proven. Only the reduction of epoxide groups was proven by infrared spectroscopy, but as Chin et al. stated, these groups may undergo hydrolysis and other unknown reactions.

Our study was aimed at improving the properties of TLCP-thermoplastic blends through chemical interactions. In a previous article, we described the synthesis of a range of polyhydroxyethers which display liquid crystallinity.¹³ Besides for its reactive groups, the polyhydroxyether was chosen because of the relatively easy synthesis and easy adjustment of the structure. However, attempts to use these functionalized TLCPs as a reinforcing phase, able to react with a thermoplastic polyester as a matrix, did not give the desired results. Nevertheless, the functionalized TLCP appeared very useful as a reactive third component in a blend of poly(ethylene terephthalate) (PET) and a liquid crystalline copolyester. The polyhydroxyether contains pendent hydroxy groups that are able to react with functional groups in both PET and the liquid crystalline copolyester, according to the literature. Reactions in the melt have been reported for the polyhydroxyether based on bisphenol A (known as phenoxy) with PBT^{14-16} as well as with liquid crystalline polyesters.^{17,18} In this study, the thermal behavior and compatibility of the blends was investigated using modulated DSC, reactions that could take place during processing were monitored by viscosity changes, and the blends were investigated with respect to morphology and mechanical properties of extruded fibers.

EXPERIMENTAL

Materials

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 TLCP with functional groups, referred to as polyhydroxyether, was prepared¹³ from 4,4'-biphenol and the diglycidylethers of 4,4'-biphenol and 1,4-dihydroxybenzene (50/50 mol/mol). It has a liquid crystalline melt in the range of 270-290°C and an inherent viscosity (IV) of 0.4 dL/g (C = 0.2 g/dL, in dimethylacetamide at 25°C). The matrix polymer was PET, kindly supplied by M&G Richerche S.p.A. (Pozzilli, Italy). Two types of PET were used, both with an IV of 0.6 dL/g (C = 0.25 g/dL, in 60/40 w/w phenol/1,1',2,2'-tetrachloroethane at 25°C). One type has no additives and will be referred to as PET; the other 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.¹⁹ The anhydride groups can react with hydroxy end groups or ester groups in the PET. A third type of PET, Arnite D04 300, referred to as Arnite, was obtained from DSM (IV = 1.0 dL/g). The chemical structures of the polymers are shown in Scheme 1.



Scheme 1

Processing

The blend components were tumble-mixed and dried for at least 16 h in a vacuum at 120°C. Two methods were used to produce blend fibers:

Method A: The different blend compositions were fed to a Collin single-screw 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 were drawn to different draw ratios.

Method B: The different blend compositions were fed into a Leistritz LM 30.34 corotating twin-screw extruder, with a kneading section. Zone temperatures were 215, 240, and 290°C; the die exit temperature was 270°C. The extruded strands were quenched in a water bath, chopped, and dried. The dried blend was fed into a capillary viscometer and melted at 310°C for 5 min, after which the temperature was lowered to 270°C and fibers were spun through a capillary with diameter d = 1.04 mm and length L = 45 mm and drawn to different draw ratios. The fairly high temperature of 310°C appeared to be necessary to melt all the 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 drawn fiber: $DR = d_{die}^2/d_{fiber}^2$.

Thermal Properties

Thermal properties were studied using modulated differential scanning calorimetry (MDSC).²⁰ A DuPont 2200 DSC was used. With MDSC, the heat capacity (C_p) jump and the enthalpic effects can be separated, which may make the determination of the glass transition temperature (T_g) more accurate.²¹ After the first heating run, from 0 to 300°C, the sample was quenched and a second heating run was performed, all under a dry nitrogen flow. A modulation with an amplitude of 1.5°C and an oscillation period of 60 s was used, with an average heating rate of 3°C/min. The peak in the derivative of the heating signal (dC_p/dT) was taken as the glass transition temperature.

Rheology

Viscosity measurements as a function of temperature, shear rate, and time were performed on the same capillary viscometer as used in processing method B. A capillary of 1.04 mm diameter and a length of 45 mm was used.

Mechanical Properties

The produced fibers were mechanically tested on a Zwick tensile tester. A strain rate of 10%/min was applied. Clamps with a special clothing, designed for yarns, were used, to prevent breakage at the clamps. The samples were conditioned at 23°C and 50% RH before measuring. The tensile modulus was determined from the best linear fit through the initial region of the stress–strain curve. The reported tensile strength is an average of at least six measurements. The dynamic tensile modulus was determined on an apparatus designed at TNO.²² Measurements were taken at 10 Hz and 25°C. A static strain of 0.25% and a dynamic strain amplitude of 0.03% were applied.

Wide-angle X-ray Diffraction (WAXD)

Flat-film diffractograms were recorded in a transmission mode using Ni-filtered CuK α radiation (wavelength 1.54 Å). The recording was taken at



Figure 1 Modulated DSC thermograms (reversible heat flow) of PET/polyhydroxyether blends; (a) first heating run; (b) second heating run. The corresponding blend composition of PET/polyhydroxyether is given at each curve. The T_g 's are indicated by the vertical dashes.

40 kV and 32 mA; exposure times of 7–15 h were used, depending on the thickness of the fibers.

Morphology

Fibers were cryogenically fractured in liquid nitrogen, and the samples were coated with a gold layer. The fiber cross sections were examined using a Philips XL20 scanning electron microscope. An acceleration voltage of 15 kV was applied.

RESULTS AND DISCUSSION

Compatibility

A DSC study was performed to establish the compatibility between the polyhydroxyether and PET. Since the polyhydroxyether was available only in lab-scale quantities, the polymers were blended in solution, instead of melt mixing. Various ratios of polyhydroxyether and PET were dissolved as a 10 wt % solution in a mixture of 60/40 w/w phenol/1,1',2,2'-tetrachloroethane at 100°C. The polymer solution was precipitated in methanol using an ultra-turrax, dried in a vacuum oven, and characterized by modulated DSC. The fast precipitation method is likely to force the components to be mixed on a molecular scale. However, if the components are incompatible, after the first heating run, such a blend will phase separate and two glass transitions (T_g 's) should appear in the second heating run.^{23,24}



Figure 2 Glass transition temperatures of PET/polyhydroxyether blends, as determined by MDSC: (\bullet) first heating run; (\blacksquare) second heating run. The dashed line represents the T_{σ} according to the rule of additivity.

The first and second heating runs of PET/polyhydroxyether blends are displayed in Figure 1. The first runs of almost all compositions show a smooth single glass transition at a temperature in between those of the pure components [Fig. 1(a)], which points to a single phase. Only in the first run of the 90/10 blend is the transition irregular, which can be interpreted as two overlapping glass transitions, caused by an inhomogeneous blend. In the first run of the compositions 90/10, 80/20, and 65/35, a small exothermic jump around 115°C was observed, which could not be identified. In the second heating run, all compositions show a smooth single glass transition [Fig. 1(b)]. This suggests that PET and the polyhydroxyether are compatible, at least when the blend has been melted once. The T_g 's are plotted against the composition in Figure 2. The T_g showed a positive deviation from the rule of additivity (dashed line in Fig. 2) at polyhydroxyether contents up to 20 wt %, and a negative deviation from additivity at higher contents. Duplicate experiments of the 90/10 and 80/20 compositions showed that there is some spreading in the results, probably due to small differences during the precipitation from solution. A clear trend in the development of T_g with composition could therefore not be identified.

Blends of PET-anhydride with polyhydroxyether also displayed a single T_g in the second heating run, similar to PET/polyhydroxyether blends. The presence of anhydride did not lead to systematic differences in the glass transition temperatures compared to blends without anhydride. The phenomenon of both positive and negative deviations from additivity has been observed before in blends,²⁵ where it was explained by the occurrence of reactions between the components. Here, it may be explained by transesterification reactions and/or by hydrogen bonding between the hydroxy of the polyhydroxyether and the ester group in PET (and the dianhydride, in the case of PET-anhydride). This changes the chemical structure of the components, which changes the T_{g} , dependent on the extent of the reactions that



Figure 3 Relation between shear viscosities η and shear rate γ of (closed symbols) PET–anhydride and (open symbols) Vectra at (\bigcirc) 270°C, (\triangle) 280°C, and (\square) 290°C.



Figure 4 Relation between shear viscosities η and shear rate γ of (\blacktriangle) Arnite, (\blacksquare) PET–anhydride, (\bigcirc) PET, and (\Box) Vectra at 290°C.

can take place at the different compositions. In the subsection Rheology, the occurrence of reactions is discussed further. At first, it is quite unexpected that the liquid crystalline polyhydroxyether seems compatible with PET. It can be explained by reactions occur-



Figure 5 Shear viscosity at 82 s⁻¹ and 290°C, as a function of time, of (---) PET–anhydride, (---) PET–anhydride/polyhydroxyether 80/1, (—) Vectra, and (—) Vectra/ polyhydroxyether 20/1.

	PET–Anhydride/Vectra/ Polyhydroxyether		PET/Vectra/ Polyhydroxyether	Arnite/Vectra/ Polyhydroxyether
Processing				
method A	90/10/0	80/20/0	80/20/0	80/20/0
	90/10/0.5	80/20/0.5	80/20/0.75	80/20/0.75
	90/10/0.75	80/20/0.75		
	90/10/1	80/20/1		
	90/10/1.5	80/20/2		
Processing				
method B	90/10/0	80/20/0	_	
	90/10/0.25	80/20/0.25		
	90/10/0.75	80/20/0.75		

Table I Compositions of the Produced Blend Fibers

ring between the components, through which they are chemically changed; this may result in a better compatibility. In the literature, there are a few reports on the compatibility of the polyhydroxyether based on bisphenol A ("phenoxy") with PET. Based on DSC and DMTA results, Seymour and Zehner¹⁶ and Harris et al.²⁶ found that PET and phenoxy were incompatible, even when the blend had been in the melt state, while Robeson and Furtek¹⁵ found an indication for compatibility in melt-extruded PET/phenoxy blends.

Equations that describe the T_g as a function of the composition of compatible blends, such as the Gordon–Taylor equation²⁷ or the Fox equation,²⁸ are not very useful to apply to the present system because of the changes in chemical structure. For Vectra/phenoxy blends, Choi et al.¹⁷ found incompatibility over the complete composition range. Whether Vectra is also incompatible with liquid crystalline polyhydroxyethers is not clear. Solution blending of Vectra with polyhydroxyether was not performed, since Vectra is only soluble in very aggressive and toxic solvents. Because of the small amounts of polyhydroxyether available, extrusion melt blending could not be performed with suitable compositions. One Vectra/polyhydroxyether blend was prepared by extrusion, with a 20/1 w/w ratio (see Rheology). A T_g could not be detected by DSC; DMTA analysis showed a glass transition at 105°C, both for pure Vectra and the Vectra/polyhydroxyether blend. Since the glass transitions of both components are very near each other, it is not possible to give an indication of their compatibility from these experiments.

Rheology

The viscosities of the blend phases are an important factor for the LCP fibril formation.² Viscosity measurements were performed as a function of temperature and shear rate and also as a function of time, to indicate reactions that are taking place during processing. Figure 3 shows the shear viscosities against shear rate of the pure components, PET-anhydride and Vectra, at three temperatures. The viscosity of Vectra decreases with increasing temperature and shear rate, which is a usual behavior. The shear-thinning effect is in agreement with region III of the so-called threeregion flow curve²⁹ for LCPs. The viscosity of PET-anhydride shows a less pronounced shearthinning effect, but more striking is the effect of temperature: The viscosity is higher at higher temperature. This unusual behavior may be explained by chain-extension reactions of the anhydride compound in PET, taking place during premelting, before the actual measurement. The reaction rate increases with temperature, which accounts for a higher molecular weight and viscosity at higher temperatures. Figure 4 shows the shear viscosity at 290°C of the different types of PET and Vectra. The shear viscosity of PETanhydride and Arnite are higher than the shear viscosity of Vectra; PET (without anhydride) has the lowest viscosity. Only at shear rates higher than about 10^3 s^{-1} , the Vectra viscosity is lower than the PET viscosity, due to a larger shear thinning effect of Vectra. Comparable viscosities of the blend components is most favorable for fibril formation of a dispersed phase in a matrix.

To monitor possible reactions that are taking place, viscosity measurements were performed as a function of time. Figure 5 shows the shear viscosity at 290°C and a shear rate of 82 s⁻¹ as a function of time of Vectra and PET–anhydride, as well as of their blends with a small amount of polyhydroxyether. The ratio of components in

these binary blends was taken to be roughly the same as their ratio in the mechanically tested ternary blends, that is, 20/1 for Vectra/polyhydroxyether and 80/1 for PET-anhydride/polyhydroxyether. The viscosity of Vectra is constant; those of a blend of Vectra/polyhydroxyether 20/1 and PET-anhydride are almost constant; the small decrease with time can be attributed to degradation reactions. The results indicate that no reaction has taken place between Vectra and polyhydroxyether. On the other hand, the viscosity of a PET-anhydride/polyhydroxyether 80/1 blend increased substantially, suggesting that reactions with hydroxy groups of the polyhydroxyether have occurred, which led to a chain extension. It was attempted to prove this reaction directly by infrared spectroscopy on extracted fractions, but it is not certain that PET and polyhydroxyether can be separated perfectly by extraction. Therefore, no conclusions could be drawn from these experiments.

A PET/polyhydroxyether 80/1 blend, without anhydride, was also measured. The viscosity of this blend also increased with time, which suggests that not exclusively anhydride groups but also the ester and/or the carboxylic acid end groups in PET can react with the hydroxy groups in the polyhydroxyether.

In Figure 5, it can be observed that the viscosities of the blends start at lower levels than do the pure components. This is explained by the fact that before the viscosity measurements the blends have been prepared by melt extrusion, which may have caused some degradation.

Mechanical Properties

The compositions of the produced blend fibers and the production method are summarized in Table I. To determine the effect of the processing conditions, two different processing methods were used. The tensile modulus, strength, and elongation at break were determined from the stressstrain curves. The dynamic tensile modulus was also determined, because the accuracy of the DMTA measurement enables a good comparison of the various values.

Fibers Prepared by Processing Method A

Figure 6(a) shows the dynamic tensile modulus (10 Hz, 25°C) as a function of the draw ratio of blends of PET–anhydride/Vectra 90/10 prepared



Figure 6 (a) Dynamic tensile modulus (*E*) as a function of draw ratio of blends of PET-anhydride/Vectra 90/10 with different amounts of polyhydroxyether, prepared by method *A*: (\bullet) 90/10; (\blacktriangle) 90/10/0.5; (\blacksquare) 90/10/1; (\checkmark) 90/10/1.5. (b) Dynamic tensile modulus (*E*) as a function of draw ratio of blends of PET-anhydride/Vectra 80/20 with different amounts of polyhydroxyether, prepared by method *A*: (\bullet) 80/20; (\bigstar) 80/20/0.5; (\blacksquare) 80/20/0.75; (\bigstar) 80/20/1; (\checkmark) 80/20/2. Lines are drawn to guide the eye.

by method A, with different amounts of polyhydroxyether. The moduli are not dependent on the draw ratio and are higher when polyhydroxyether is included, except for the 90/10/1.5 blend. A highest value of 6.3 GPa was obtained in the 90/10/ 0.75 blend. At higher polyhydroxyether contents, the modulus decreased. For the 80/20 blend series [Fig. 6(b)], the dynamic tensile modulus increased with increasing draw ratio when polyhydroxyether was included. This effect was most pronounced in the 80/20/0.75 blend. A maximum dynamic tensile modulus of 11.1 GPa was obtained. The results of the static stress-strain



Figure 7 (**A**) Static tensile modulus *E* and (**II**) tensile strength σ of (a) 90/10 PET– anhydride/Vectra fibers and (b) 80/20 PET–anhydride/Vectra fibers as a function of the amount of polyhydroxyether. The draw ratio is around 20. Closed symbols: before postdrawing; open symbols: after postdrawing at 150°C ($\lambda = 4$).

measurements, displayed in Figure 7(a,b), show the effect of polyhydroxyether on the properties of 90/10 and 80/20 blend fibers, respectively, with an extrusion draw ratio of about 20. The maximum tensile strength was 87 MPa for a 90/10 blend, observed at 0.75 to 1 wt % polyhydroxyether. The static tensile modulus shows a maximum of 4.9 GPa at 0.75 wt % polyhydroxyether. For the 80/20 blend, a maximum tensile strength of 131 MPa and a tensile modulus of 10.3 GPa were observed at 0.5 wt % polyhydroxyether. The elongation at break was about 1.5-2% for both the 90/10 and 80/20 blends and did not show a specific dependence on the added amount of polyhydroxyether.

Fibers Prepared by Processing Method B

Figure 8 shows the dynamic tensile moduli of PET-anhydride/Vectra/polyhydroxyether blends

obtained by processing method B. In the 90/10 series [Fig. 8(a)], the dynamic tensile modulus of the 90/10/0.25 blend was increased slightly compared to the 90/10 blend, while there was a large increase in modulus up to 9.8 GPa for the 90/10/ 0.75 blend. The 80/20 series [Fig. 8(b)] showed a similar trend. In the 80/20/0.25 blend, the dynamic tensile moduli were considerably increased compared to the 80/20 blend, while in the 80/20/0.75 blend, the highest moduli were reached, with a maximum of 16.7 GPa. From the stress-strain measurements, the maximum tensile strength was 144 MPa for the 90/10/0.75 blend and 214 MPa for the 80/20/0.75 blend, while the static modulus values were 12.3 and 18.1 GPa, respectively. The elongation at break was about 1-1.5% for both the 80/20and 90/10 blend series, slightly lower than the elongation at break of fibers from method A.



Figure 8 (a) Dynamic tensile modulus (E) as a function of draw ratio of blends of PET-anhydride/Vectra 90/10 with different amounts of polyhydroxyether, prepared by method $B: (\bigcirc) 90/10; (\triangle) 90/10/0.25; (\Box) 90/10/0.75$. (b) Dynamic tensile modulus (E) as a function of draw ratio of blends of PET-anhydride/Vectra 80/20 with different amounts of polyhydroxyether, prepared by method $B: (\bigcirc) 80/20; (\triangle) 80/20/0.25; (\Box) 80/20/0.75$. Lines are drawn to guide the eye.

Comparing the processing methods, the highest properties were obtained with method B. This may be caused by several factors, like different mixing methods, different shear rates, and elongational rates applied. The drawing efficiency (which is determined among others by the distance between the die exit and the take-up unit and the die dimensions) was much higher in method B. In addition to these factors, the time available for reactions, that is, the residence time in the melt, might also play a role in improving the properties. This point will be addressed in the subsection Reactions.

Postdrawing

Postdrawing of fibers at temperatures above the T_{σ} is a suitable method to increase the modulus and strength of fibers and well known for PET fibers.^{30,31} PET-anhydride/Vectra 80/20 blend fibers with various amounts of polyhydroxyether were postdrawn to determine if any improvement in the properties could be obtained. The drawing temperature was 150°C; a lower drawing temperature (closer to the T_g of PET) was not possible because in that case the fibers broke at very low draw ratios. Figure 7(b) shows the static tensile modulus and the tensile strength before and after postdrawing of fibers from method A, postdrawn to about $\lambda = 4$ (the fibers had an extrusion draw ratio of about 20). The static tensile modulus was increased by about 40% to 14 GPa, while the strength was increased by more than 100% to 308 MPa. The dynamic tensile modulus could be increased from 11.1 to 15.6 GPa. Postdrawing of fibers from method B resulted in a smaller increase in properties. The dynamic tensile modulus increased from 16.7 to 18.6 GPa, while the tensile strength did not increase significantly.

Morphology

To observe the orientation of the different components, WAXD patterns were recorded of blend fibers (prepared by method A) and fibers of the pure components, with a draw ratio of about 10. A PET-anhydride fiber showed no crystalline reflections, only a broad halo, indicating that the fiber is amorphous and unoriented. A Vectra fiber displayed sharp equatorial reflections at 15.1, 4.47, and 3.55 Å and a meridional reflection at 6.73 Å; this fiber is crystalline and highly oriented. In an 80/20 PET-anhydride/Vectra blend, only the Vectra reflections were visible [see Fig. 9(a)], which indicates that the PET phase in this blend is amorphous and unoriented. On the other hand, in the 80/20/0.75 blend, the WAXD pattern shows reflections of both PET and Vectra, indicating that the PET phase is (partly) crystalline in this blend [see Fig. 9(b)]. Apparently, the polyhydroxyether induces crystallization of the PET phase. Furthermore, the PET reflections show a weak orientation of the crystalline PET phase, while the Vectra phase is highly oriented in the same way as in the pure Vectra fiber. The results imply that in the 80/20/0.75 PET-anhydride/Vectra/polyhydroxyether blend PET will contribute more to the modulus than in the 80/20 PET-

(b)



(c)



Figure 9 Flat-film wide-angle X-ray diffractograms of blend fibers (DR = 10): (a) PET-anhydride/ Vectra 80/20; (b) PET-anhydride/Vectra/polyhydroxyether 80/20/0.75; (c) as (b), but postdrawn at 150°C to $\lambda = 4$. The orientation direction of the fibers is vertical.

anhydride/Vectra blend, although Vectra still accounts for the major part of the modulus. During postdrawing, the PET phase is oriented, while the orientation of the Vectra phase is not changed, as was observed from a WAXD recording of a postdrawn fiber [see Fig. 9(c)], which shows a high orientation of both the PET and the Vectra phases.

The addition of a small amount of polyhydroxyether to the blend has a marked effect on the morphology. Fiber cross sections were examined by SEM. Figure 10 shows SEM micrographs of 80/20 PET-anhydride/Vectra blends with 0, 0.75, and 2 wt % of polyhydroxyether, respectively, at a draw ratio of about 10. Without polyhydroxyether, the Vectra phase is present as spherical or ellipsoidal particles, with a diameter of 3–15 μ m. With 0.75 wt % polyhydroxyether, long, thin Vectra fibrils are present in the matrix, with a diameter of 0.5–2 μ m. With 2 wt % of polyhydroxyether, the fibrils are thicker, $2-5-\mu m$ diameter. The aspect ratio (length/diameter) of the fibrils is the highest in the blend with 0.75 wt % polyhydroxyether, estimated to be about 20. The 90/10 PET-anhydride/Vectra blends, shown in Figure 11, follow the same trend: With 0.75 wt % polyhydroxyether, the LCP fibrils have the highest aspect ratio and the smallest fibril diameter, comparable to the 80/20 blends. All the blends show a small extent of skin-core morphology: Near the skin of the extruded strand the fibrils are thinner than in the core.

The *in situ* fibril formation is influenced by various material and processing conditions. The process of deformation and breakup of LCP droplets in a thermoplastic matrix is determined by counteracting forces: the deforming shear stress τ and the interfacial tension σ/R , where σ is the interfacial energy and R is the droplet radius. The ratio of these two forces is the dimensionless capillary number³²:

$$Ca = \tau R/\sigma$$

Only when the capillary number exceeds a critical value are LCP fibrils formed. The critical capillary number, $Ca_{\rm crit}$, is influenced by the viscosity ratio and the flow type (shear or elongational). Grace³³ determined a window where fibril formation occurs. He found an optimum viscosity ratio around 1, although fibril formation even appeared to be possible when the viscosity of the matrix is





a)





Acc V. Spot Magn 15 0 KV 4 8 4000x 9 7 PE L/Vectra/phe 80/20/2 DIR-20

c)

Figure 10 SEM micrographs of fracture surfaces of cryogenically broken 80/20 PET– anhydride/Vectra blend fibers (DR about 10) with (a) 0 wt %, (b) 0.75 wt %, and (c) 2 wt % polyhydroxyether. Magnification of left micrographs: $1000\times$; Magnification of right micrographs: $4000\times$.



Figure 11 SEM micrographs of fracture surfaces of cryogenically broken 90/10 PET-anhydride/Vectra blend fibers (DR about 10) with (a) 0 wt %, (b) 0.75 wt %, and (c) 1.5 wt % polyhydroxyether. Magnification $1000 \times$.

lower than the viscosity of the LCP. Furthermore, elongational flow is more favorable for fibril formation than is shear flow. Another important factor is that fibril formation is easier when the dispersed-phase fraction is larger. A larger dispersed fraction causes coalescence of droplets into droplets with a larger radius, which are more easily deformed.

The fibril formation in PET/Vectra blends is clearly enhanced through addition of polyhydroxy-

ether. Apparently, the capillary number has been changed by the addition of polyhydroxyether. A very plausible explanation for the results and the role of the polyhydroxyether and the anhydride compound therein is the following: During extrusion, the anhydride groups of PET-anhydride will react with the hydroxy groups in the polyhydroxyether, which results in longer chains and branched chains and, thus, in a higher viscosity of the matrix. This higher viscosity is favorable for fibril formation: The shear stresses that the matrix applies to the Vectra droplets are higher; this will give easier fibril formation and, consequently, higher mechanical properties. If this explanation is true, a PET with a higher molecular weight, and thus a higher viscosity, will give PET/LCP blends with higher mechanical properties.

Therefore, an 80/20 PET/Vectra blend was prepared with a high molecular weight PET (Arnite) to see whether this results in high mechanical properties. Furthermore, a PET/Vectra/polyhydroxyether blend was prepared using PET without the anhydride compound. The bar diagram in Figure 12 shows the tensile modulus of 80/20 PET/Vectra blends with PET, PET-anhydride, and Arnite, respectively, prepared according to method A. The Arnite/Vectra blend reached a dynamic tensile modulus of 11 GPa (at 25°C and 10 Hz), which is about as high as the modulus of the PET-anhydride/Vectra/polyhydroxyether 80/20/ 0.75 blend. This shows that a high matrix viscosity is favorable for fibril formation. Adding polyhydroxyether to the Arnite/Vectra blend did not increase the modulus further; it even decreased the modulus. During extrusion of this Arnite/Vectra/polyhydroxyether blend, the pressure fluctuated and fibers of irregular thickness were obtained. The polyhydroxyether apparently works better with the lower molecular weight ("fiber grade") PET. The addition of polyhydroxyether increases both the modulus of PET/Vectra and PET-anhydride/Vectra blends, but the modulus of the latter was increased more, which shows the extra effect of the anhydride.

It can be concluded that the polyhydroxyether improves the properties of a PET/TLCP blend when a fiber-grade molecular weight PET is used, by increasing the viscosity of the matrix and thereby improving the conditions for TLCP fibril formation. This effect is even larger when the anhydride compound is present.



Figure 12 Maximum dynamic tensile moduli (10 Hz, 25°C) of blend fibers of Vectra with PET, PET–anhydride, and Arnite, respectively, in a 20/80 weight ratio, (left) with and (right) without 0.75 wt % of polyhydroxyether.

Mechanical Modeling: The Tsai-Halpin Equation

The tensile moduli of the blends can be modeled with the Tsai-Halpin equation.³⁴ This equation describes the tensile moduli of unidirectional composites (with discontinuous fibers and a perfect adhesion) as a function of the fibril fraction and of the aspect ratio of the fibrils:

$$rac{E}{Em} = rac{1+AB arphi_f}{1-B arphi_f}$$

in which

$$A = \frac{2L}{D} \qquad B = \frac{Ef/Em - 1}{Ef/Em + A}$$

E is the tensile modulus of the composite; E_m and E_f , the moduli of the matrix and the reinforcing phase, respectively; φ_f , the volume fraction; and L/D, the aspect ratio of the fibrils. When the aspect ratio goes to infinity (when the fibers become continuous), the rule of mixture is approximated:

$$E = (1 - \varphi_f) E_m + \varphi_f E_f$$

The aspect ratio of the fibrils in the 90/10/0.75and 80/20/0.75 blend fibers spun in the capillary viscometer (method *B*) was estimated from the SEM micrographs to be about 20. Figure 13 shows the rule of mixture and the Tsai–Halpin curve, using an aspect ratio of 20, a matrix modulus of 4.8 GPa, and a fiber modulus of 80 Gpa, which are actually measured values for PET–anhydride and Vectra fibers, respectively. The weight fractions were converted to volume fractions using densities of 1.33 g/cm³ for PET–anhydride and 1.40 g/cm³ for Vectra. From the figure, it is observed that the experimental moduli agree well with the Tsai–Halpin curve.

Lin and Yee³⁵ developed a modification of the Tsai–Halpin model, in which the draw ratio was taken as a parameter, since the aspect ratio is a function of the draw ratio (λ). The parameter A was given by $2\lambda^{3/2}$, which means that the TLCP phase deforms affinely with the matrix, without shear. Figure 14 shows that the experimental moduli of 90/10 and 80/20 PET/Vectra blends with 0.75 wt % polyhydroxyether show a remarkably good fit using a fiber modulus of 80 Gpa and a matrix modulus of 4.8 GPa. The drawing of these fibers apparently caused a very efficient deformation of the Vectra particles.



Figure 13 Tensile moduli according to (drawn line) the rule of mixture, (dashed line) the Tsai–Halpin equation, and (symbols) experimental data, of PET–anhydride/Vectra blend fibers with 0.75 wt % of polyhydroxyether.

Reactions

The differences between the fibers from methods A and B may arise, apart from the different conditions already mentioned, from the different residence times in the melt. The average residence time in the extruder in method A is calculated to be 40 s, while in method B, the material is melted for 5 min at 310°C. This gives the blend more time



Figure 14 Tensile modulus as a function of draw ratio according to the modified Tsai-Halpin equation³⁵ (drawn lines) and experimental data for (\blacktriangle) 80/20 and (\blacksquare) 90/10 PET-anhydride/Vectra blends with 0.75 wt % of polyhydroxyether.

to react, which can lead to a higher modulus and strength and a lower elongation at break in the case of method B. Figure 15 shows the various reactions that can take place between the functional groups that are present in the blend. Due to the complexity, it is practically impossible to determine the extent of each reaction. Furthermore, there might be some hydrogen bonding between the hydroxyl and carbonyl groups, which are quite strong interactions as well. The anhydride and carboxylic acid groups are the most reactive functionalities, while the secondary hydroxy groups in the polyhydroxyether have locally the highest concentrations. The reactions between these groups are assumed to be the most prominent, an assumption which is supported by the viscosity measurements. When more polyhydroxyether is added, more reactions will take place. The maximum mechanical properties are obtained at 0.75 wt % polyhydroxyether. Apparently, at this composition, the optimum amount of reaction takes place, to account for a high matrix viscosity but still a deformable matrix. At a polyhydroxyether content of 2 wt % and higher, undrawable and insoluble fibers are obtained, which indicates that crosslinking takes place. If it is assumed that, in a 80/20/2 PET-anhydride/Vectra/polyhydroxyether blend, all secondary hydroxy groups react with all the anhydride func-



Figure 15 Possible reactions of functional groups in a PET–anhydride/Vectra/polyhydroxyether blend.

tionalities, it can be calculated that PET–anhydride contains 0.7 wt % of PMDA, which is in the range of the value given by the supplier. In this case, the polyhydroxyether chain becomes grafted with either PET or other polyhydroxyether chains, which, in turn, contain reactive anhydride or hydroxy groups. This can lead to crosslinking rather quickly, which means that the PET phase cannot be sheared or elongated anymore and good fibers cannot be obtained. The occurrence of reactions seems the most important factor for the improvement of properties. The use of a liquid crystalline polyhydroxyether may not be necessary. The liquid crystalline character does not seem to have a very important effect in this blend system. The use of other types of polyhydroxyether, and the question whether the interfacial adhesion has been improved, will be discussed in a following article.³⁶

CONCLUSIONS

It was shown that the tensile modulus and tensile strength of blends of PET/TLCP blends could be drastically improved by adding a small fraction of a liquid crystalline polyhydroxyether. The dianhydride, ester, and the end groups of the modified PET are able to react with the pendent hydroxy groups in the polyhydroxyether. Reactions with the TLCP could not be proven. The method works well with a relatively low molecular weight PET (IV = 0.6 dL/g). Through reactions with polyhydroxyether, the viscosity of the matrix is increased and fibril formation of the TLCP is enhanced. Fibers with a tensile modulus of 16.7 GPa and a tensile strength of 214 MPa could be obtained. The tensile moduli can well be described by the Tsai-Halpin equation. It might also work with a polyhydroxyether which is not liquid crystalline. The liquid crystalline character does not seem to have a very important effect in this blend system. The occurrence of reactions seems the most important factor for the improvement of properties. The polyhydroxyether might account for an improved adhesion between the PET and TLCP phase, although this could not be demonstrated.

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