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Studies on blends of a thermotropic liquid crystalline polymer and polybutylene terephthalate

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Summary

Structure-property relationships of blends of a thermotropic polyester-type main-chain LCP and polybutylene terephthalate (PBT) were investigated. LCP was melt blended with three different PBTs and the blends were processed by injection moulding or extrusion. Mechanical and thermal properties of the blends were determined and the blend structure was characterized by scanning electron microscopy (SEM). LCP acted as mechanical reinforcement for PBT and improved also its dimensional and thermal stability. The stiffness of PBT increased with increasing LCP content, but at the same time the blends became more brittle. In extrusion the orientation of LCP phases could be further enhanced by additional drawing, which led to significant improvements in strength and stiffness at LCP contents of 20-30 wt.-%.

Introduction

Thermotropic main-chain liquid crystalline polymers (LCPs) consist of linear rigid rod-like molecules that are capable of aligning to a very high degree during melt flow, and thus form a highly ordered melt phase. The orientation is retained when the polymer melt is cooled, resulting in a highly ordered fibrous structure and anisotropic properties. The good mechanical strength and dimensional and thermal stability of thermotropic LCPs are based on this fibrous structure (1,2). The degree of orientation of the LCP fibres can be modified through choice of processing conditions, especially by mould design or by applying shear or elongational forces to the molten polymer. This makes the processing of LCPs important (3,4). LCP mouldings exhibit a layered structure and a skin/core morphology, which vary with the processing conditions. Near the surface there is a skin layer with abundant highly ordered fibres, while in the core there is less orientation and fibre formation. Because of the fibrous morphology LCPs are often called self-reinforcing polymers, SRPs (3-6).

Through blending of thermotropic main-chain LCPs with engineering thermoplastics, the highly ordered fibrous structure and good properties of LCPs can be transferred into the more flexible matrix polymer. LCPs are blended with thermoplastics mainly in order to reinforce the matrix polymer or to improve its dimensional stability. A small amount of a thermotropic LCP also renders some thermoplastics

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easier to process due to the relatively low melt viscosity. LCPs may modify several other properties of thermoplastics as well.

Blends of thermotropic LCPs and thermoplastics consist of two separate phases, which in most cases are immiscible. If the polymers are fairly similar e.g. a polyester-type LCP and a polyester, they may be at least partly miscible (7,8).

Similar skin/core structures to those of pure LCPs are found in the blends. In the skin layer there are more oriented fibre-like LCP domains, while in the core the LCP domains are less oriented or in spherical form (9-11). The formation of fibrillar LCP domains in the matrix depends on the ability of the rigid rod-like LCP molecules to orient in the direction of the melt flow. This orientation is then retained when the material is solidified, and a highly ordered fibre structure is obtained. The size, shape and distribution of the LCP domains in the matrix depend on the LCP content, processing conditions, viscosity ratio of the blend components and the rheological characteristics of the matrix. In addition, the mutual compatibility of the polymers and the interfacial adhesion between them play important roles (12-16).

In particular, sufficient shear forces are needed to obtain good mixing and sufficient extensional flow to deform the dispersed LCP domains into fibrillar shape. Increased orientation of the LCP microfibrils by additional drawing will usually greatly improve the mechanical properties of the blend (17-21).

In the solid state the blends of LCPs and thermoplastics will exhibit a composite-like fibre structure if sufficient orientation of the molten LCP phases is achieved during processing (22,23).

Many researchers have studied blends of thermotropic LCPs and various thermoplastics during recent years. Studies on blends of LCP and PBT have been reported e.g. by Kimura and Porter (8) and Kiss (22).

In this paper, the possibility to modify the properties of polybutylene terephthalate by melt blending with a thermotropic polyester-type main-chain LCP is studied. In particular, the structure-property relationships of both extruded and injection moulded PBT/LCP blends are discussed.

Experimental

Materials

The liquid crystalline polymer used in the experiments of this work was Vectra A 950 produced by Hoechst Celanese. This is a totally aromatic polyester-type thermotropic main-chain LCP consisting of p-hydroxybenzoic acid (HBA) and 2,6-hydroxynaphthoic acid (HNA). The following specifications are given by the manufacturer: density 1.40 g/cm^3, melting point 280 °C, tensile strength 165 MPa, elastic modulus 9700 MPa and elongation at break 3.0% (24). In this paper, the amount of LCP blended with the thermoplastic is sometimes indicated merely by number; thus PBT/30 indicates 30 wt.-% of LCP in PBT.

Three different grades of polybutylene terephthalate were used as matrix polymers. For injection moulding purposes 0, 10 and 30 wt.-% of the above mentioned LCP was blended with Vestodur 3000 from Hüls (PBT 1) and Rynite RE 6400 from Du Pont (PBT 2). PBT 2 is a toughened grade with higher impact strength but lower stiffness than the other two grades. For extrusion experiments 0, 5, 10, 20 and 30 wt.-% of the same LCP was blended with an extrusion grade PBT, Grilpet XE 3060 from EMS (PBT 3).

Blending

LCP was mixed with PBT manually in a barrel, with both polymers in pelletized form. Before the melt blending stage the mixed pellets were carefully dried in a Conair Micro-D dehumidifying dryer (5 hours at 120 °C).

The melt blending of the materials was usually performed by a Berstorff ZE 25x33D corotating twin screw extruder at temperatures ranging from 285 to 290 °C, and with a screw speed of 150 rpm. The hot extrudate was immediately quenched in a water bath and pelletized again. Exceptionally, LCP and PBT 1 were melt blended in a Buss MDK/E 46 Co-kneader instead of a twin screw extruder. The temperature profile was again from 285 to 290 °C, and the screw speed 110 rpm.

Injection Moulding

The blends and the pure polymers were injection moulded into the form of test specimens after thorough drying in a dehumidifying dryer. Injection moulding was carried out with an Engel ES 200/40 injection moulding machine. Pure polymers were processed at conditions recommended by the manufacturers and the blends at 280 - 290 °C.

Extrusion

The blends were extruded to strands of different diameter with a Brabender Plasti-Corder PLE 651 laboratory single screw extruder connected to a belt capstan. The hot extrudate was immediately quenched in a water bath, and drawn at different speeds of the take-up machine to form strands of different diameter. The speed of the belt capstan ranged from 10 to 40 m/min. The draw ratio for each strand was determined as the ratio between the die and strand cross-sections (S_O/S_S). The dimensions of the round hole capillary die were length (L) 30 mm, diameter (D) 5 mm. The cylinder temperatures ranged from 280 to 285 °C.

Testing and Analysis

Standard test bars of the injection moulded specimens were used for tensile, bending and impact tests. Before testing, all samples were conditioned by applying ISO 291 at test-room conditions (about 23 °C and 50% relative humidity) for at least 88 hours.

Tensile properties were measured according to ISO 527 with an Instron 4204 testing machine equipped with a computer. For the injection moulded samples a strain rate of 5 mm/min was used for the determination of both tensile strength and elastic modulus. The tests were performed without an extensometer with a gauge length of 115 mm. The dimensions of the test bars were length 154 mm, width of narrow part 10 mm and thickness 4 mm. For the extruded strands a test speed of 3 mm/min and a gauge length of 100 mm were used.

Flexural properties were studied with the same equipment according to ISO 178 by the three-point-bending test. The dimensions of the test bars were length 112 mm, width 10 mm and thickness 4 mm. The test speed was 5 mm/min.

Charpy impact strength was determined for unnotched test specimens at room temperature according to ISO 179 by using a Zwick 5102 pendulum-type testing machine. The dimensions of the specimens were 50x6x4 mm, and a pendulum of 40 kpcm was used.

Heat deflection temperature (HDT) was determined for selected samples according to ISO 75 by using a Zwick 4204 testing machine. The measurements were performed by method A using a load of 1.82 N/mm^2 and raising the temperature by 2 °C/min. The dimensions of the test bars were 112x10x4 mm.

Morphology of the fractured surfaces of the blend samples was investigated with a JEOL JXA-840A scanning electron microscope (SEM). The samples were fractured after dipping in liquid nitrogen, and the fractured surfaces were coated with a layer of gold about 15 nm thick.

Results and Discussion

Injection Moulded Blends

Mechanical properties and heat deflection temperatures (HDT) of the injection moulded blends of LCP with PBT 1 and PBT 2 are presented in Tables 1 and 2.

The addition of LCP increased the strength and stiffness of the PBT matrix significantly. Tensile strength of PBT 1 increased 50 % and elastic modulus about 80 % after an addition of 30 wt.-% of LCP. For PBT 2 the relative improvements were even higher (60 % and 130 % respectively). The addition of LCP, however, made the material more brittle, which can be seen from the dramatic decreases in Charpy impact strength and elongation at break. The impact strength was relatively poor even in the blends of the tougher PBT, which is probably due to the lack of interfacial adhesion between the blend components. LCP thus made the blends stiff but brittle.

Table 1. Tensile and impact properties and HDT values of the injection moulded blends of PBT 1 and LCP.

Material	Tensile Strength (MPa)	Elastic Modulus (MPa)	Strain at break (%)	Charpy Impact Str. (kJ/m^2)	HDT (A) (°C)
PBT	54	2629	275	not broken	49
PBT/10	68	3041	4.6	32	53
PBT/30	79	4943	2.4	14	85

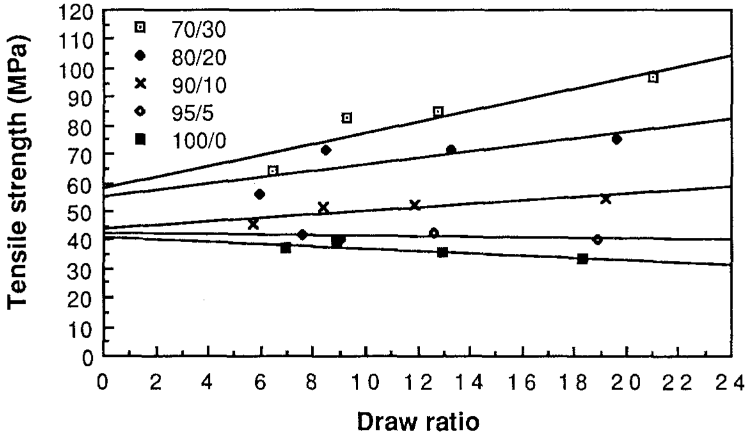
Table 2. Flexural and impact properties and HDT values of the injection moulded blends of PBT 2 and LCP.

Material	Maximal Strength (MPa)	Flexural Modulus (MPa)	Charpy Impact Strength (kJ/m^2)	HDT (A) (°C)
PBT	50	1468	not broken	46
PBT/10	62	1890	18	48
PBT/30	79	3338	11	87

LCP improved also the thermal properties of PBT, which can be seen as an increased heat deflection temperature. The HDT value of PBT 2 increased from 46 to 87 °C with 30 wt.-% of LCP (Table 2). In addition, the dimensional stability of PBT was improved, which appeared as a smaller mould shrinkage.

Extruded Blends

Similar blends of Vectra A 950 and PBT 3 manufactured in a twin screw extruder were extruded to strands of different diameter with a single screw extruder. This was done to study whether the orientation of the LCP phases and the fibre formation in the blends could be improved by applying axial elongation to the extrudate by additional drawing. Tensile properties of the extruded blends of PBT 3 and LCP at different blend compositions are presented vs. draw ratio in Figure 1.



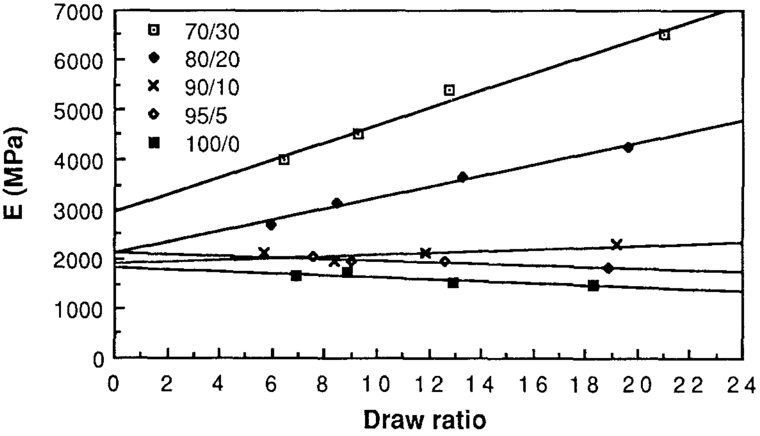


Figure 1. Tensile strength and elastic modulus of the extruded blends of PBT 3 and LCP vs. draw ratio at different blend compositions.

The tensile strength and elastic modulus for pure PBT were about 40 MPa and 1700 MPa. After an addition of 30 wt.-% of LCP the tensile strength increased to a value almost 2.5-fold and the elastic modulus nearly four-fold. These improvements were achieved with a draw ratio of 21.

LCP provided mechanical reinforcement in all blends studied. LCP addition increased both the strength and stiffness of the thermoplastic matrix polymers, while strain at break was generally decreased. The magnitude of the reinforcing effect depended significantly on LCP content, but also on draw ratio. The effect of draw ratio on strength and stiffness became more important at higher LCP contents as can be seen in Figure 1. This effect was not found in the case of pure PBT, whose tensile properties remained constant at these draw ratios. Higher draw ratios than used in this study could be expected to lead to higher stiffnesses even at relatively low LCP contents. Qualitatively similar results were obtained in our earlier studies for the blends of the same LCP with PET, PP and PPS (15, 21).

Morphology

The mechanical properties achieved were closely related to the blend morphology. The reinforcing effect of LCP on the thermoplastic matrix polymers was achieved through a in-situ formed composite-like fibre structure, as seen from the SEM micrographs. Good reinforcement is achieved when LCP phases are deformed into fibres oriented in the flow direction. The resultant blend morphology, i.e. the size, shape and especially the degree of orientation of the LCP domains, is finally determined by the last processing step.

The blends consisted of two discrete phases and exhibited a clear skin/core structure (Figure 2) that was more evident in injection moulded than in extruded blends. In the skin region LCP formed thin oriented fibres, while in the core the LCP domains were less oriented or in spherical form. The thickness of the LCP fibres and spheres was mostly 1-3 μm in PBT/LCP blends. Although the lengths of the LCP fibrils could not be measured accurately, they ranged from about 5-10 μm at lower LCP contents (5 and 10 wt.-%) to at least tens or hundreds of μm's at higher LCP contents and draw ratios. The orientation and length of the LCP fibres in the skin region can be seen more clearly in Figure 3, which is a SEM micrograph of the longitudinally fractured surface of an extruded PBT/30 wt.-% LCP blend.

Figure 2. SEM micrograph of the fractured surface of extruded blend of PBT 3 with 30 wt.-% of LCP: skin (left) and core (right) (x2000).

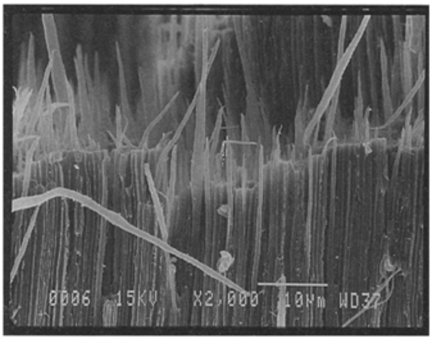


Figure 3. SEM micrograph of the longitudinally fractured surface of extruded PBT 3 / 30 wt.-% LCP blend (x2000).

At small LCP contents the LCP phases are able to form only a few thin fibres and no significant reinforcement is achieved; however, at larger LCP contents there are enough oriented LCP fibres in the matrix to carry a significant amount of the load and reinforce the matrix. In addition, the compatibility and interfacial adhesion between the two polymers are of great importance in the reinforcing effect. In particular, the ratio of the melt viscosities is important for good dispersion and fibre formation.

Generally, the size of the LCP domains increased with increasing LCP content. The formation of LCP fibrils was enhanced with increasing LCP content and in extrusion also with the draw ratio. Most of the LCP domains existed as fibres near or in the skin layer. At 20-30 wt.-% of LCP, fibril-like LCP domains also existed in the core of the extruded strand.

The improvements in mechanical properties were greater for the extruded than for the injection moulded blends. LCP domains are more easily oriented in extrusion, where more effective elongational forces exist to deform them in the longitudinal direction. Thus in extrusion even small LCP particles were fibrillated. The injection moulded bars were also much thicker than the extruded strands, and it is well known that, in moulded LCP specimens, the proportion of the unoriented core relative to the oriented skin increases with the thickness of the specimen.

SEM studies did not reveal any significant miscibility between LCP and the matrix polymers.

Conclusions

A thermotropic polyester-type main-chain LCP was melt blended with polybutylene terephthalate, and the blends were processed by injection moulding or extrusion. In general, LCP acted as a mechanical reinforcement for the matrix polymers and improved their dimensional and thermal stability. The stiffness of the thermoplastics increased with increasing LCP content, but at the same time the blends became more brittle. In extrusion the orientation of LCP molecules could be further enhanced by additional drawing. Significant improvements in strength and stiffness were found at LCP contents of 20-30 wt.-% even with rather small draw ratios. Strain at break and impact strength were, however, strongly reduced after LCP addition. The blends were thus stiff in the fibre direction but brittle in the transversal direction. This is partly due to the anisotropic blend structure, but probably the main reason is the poor interfacial adhesion between the blend components. The latter could be increased by proper compatibilization. In this work no compatibilizers were used, but the subject will be studied.

The mechanical properties achieved were closely related to the blend morphology. Under certain conditions LCP formed a composite-like fibre structure in the thermoplastic matrix, with thin oriented LCP fibres in the skin region and spherical or ellipsoidal LCP domains in the core (skin/core morphology). The morphology created depends on characteristics of the blend components such as viscosity ratio, but also on the conditions selected for blending and processing. The size of the LCP domains increased with increasing LCP content and the formation of LCP fibrils was enhanced with higher LCP content and draw ratio. At 20-30 wt.-% of LCP, fibril-like LCP domains existed even in the core of the extruded strand. SEM studies did not reveal any significant miscibility between LCP and the PBT matrix.

LCP/PBT blends showed rather similar properties to those of LCP/PET blends reported earlier (15,16,21). However, the HDT values were higher for LCP/PBT blends, although the value of pure PBT was lower than that of PET.

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