Morphological and Mechanical Properties of PET–LCP Blend Fibers

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SYNOPSIS

Blends of poly(ethylene terephthalate-co-p-oxybenzoate) (PET–PHB) with poly(ethylene terephthalate) (PET) have been studied in the form of as-spun and drawn fibers. Mechanical properties of drawn blend fibers (DR-6.0) up to 10 wt % liquid crystalline polymer (LCP) component exhibit significant improvement in modulus and strength. With the addition of 10 wt % LCP content in PET matrix, the modulus increases from 11.78 to 17.72 GPa, and the strength increases from 0.76 to 1.0 GPa in comparison to the PET homopolymer. With further addition of LCP content, the properties drop down. Scanning electron microscopy studies of drawn blend fibers show that up to 10 wt % LCP content the blends contain the LCP domains in the size range of 0.07–0.2 μm and are well distributed in the PET matrix. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCP) are well known for their unique mechanical and rheological properties.[1] Due to their rigid molecular structure, they can easily be oriented in the melt by an external field to form a liquid crystalline phase. When processed in the liquid crystalline state, these materials generally possess excellent mechanical properties in the direction of orientation. Furthermore, their melt viscosities under processing conditions (i.e., high deformation and deformation rates) are often one or two decades lower than that of comparable flexible polymers.[2,3] Blending of TLCPs with isotropic polymers might result in materials which can be used as an alternative for short fiber reinforced thermoplastic composites[1,4] or can serve as a matrix material for composites.[5] The potential advantages of *in situ* composites[4] are that problems occurring during the melt processing of conventional short fiber reinforced composites, such as fiber breakage, wear of the equipment, and rise of viscosity, can be avoided. On the contrary, the melt viscosity of the blend would be lowered significantly upon addition of a TLCP. The TLCP, which is initially dispersed as spheres or droplets, can be elongated in adequate flow fields to give *in situ* reinforcement. Fine fibrils can be formed, with larger length and smaller diameter than, for instance, glass fibers, and they can effectively reinforce the matrix, as has been demonstrated by a number of authors.[6-12]

Recent studies concerning blends of a TLCP with flexible polymers include polycarbonate,[13-15] polyamide,[3,8,10] poly(ethylene terephthalate) (PET),[6,7,9,12] 1polystyrene,[1,11] and some engineering plastics, such as poly(etherimide), poly(ethersulfone), and poly(ether–ether–ketone) as matrix materials.[2,3,11] In many of these studies, the authors report the above-mentioned features of fibril-like structures, mechanical reinforcement (at least in the processing direction), and a drop in melt viscosity by one or two orders of magnitude.

This study investigates the influence of the processing and the LCP contents on the morphology and mechanical properties of PET–LCP drawn blend fibers. An attempt has been made to give a plausible justification to the mechanical properties of the drawn blend fibres obtained in different sets of conditions in two-stage drawing.

Table I   Characteristics of LC Copolyester Chips

Sample	$[\eta]^{a}$ (dl/g)	T_g^{b} (°C)	$T_{(k-M)}^{c}$ (°C)	$T_{(N-I)}^{d}$ (°C)
PET/60 PHB	0.67	(i) 70–80 (ii) 190–210	210–250	> 320

^{a} Intrinsic viscosity was found out in a phenol–tetrachloro-ethane (60 : 40; w/w) mixture at 25°C.
^{b} Glass transition temperatures (T_{g1} and T_{g2}).
^{c} Crystalline–mesophase transition range.
^{d} Nematic–isotropic transition.

EXPERIMENTAL

Materials

Intrinsic viscosity of poly(ethylene terephthalate) (PET) in phenol-tetrachloroethane (60 : 40 weight fraction solution) at 25°C is 0.67 dL/g. Liquid crystalline copolyester (LCP) used was PET/60 PHB, and its characteristics are given in Table I.

Melt Spinning

A laboratory model, melt spinning unit was used for producing as-spun monofilaments. The melt spinning conditions are given below:

Spinneret temperature = 285°C for all the blends

Initial velocity = 1.2 m/min

Take-up speed = 200 m/min

Quench air temperature = ambient air temperature

The composition of the blend samples prepared is given in Table II.

Table III   Sets of Drawing Conditions

SET	First Zone Temperature (°C)	DR	Second Zone Temperature (°C)	DR
1	95	1.4	130	3.8
2	95	1.4	130	4.0
3	120	3.0	220	2.0
4^{a}	95	1.4	130	4.0
5^{a}	120	3.0	220	2.0

^{a} Feed speed was 10 m/min, whereas in sets 1–3 feed speed was 50 m/min.

Drawing

Drawing was carried out in a two-zone drawing machine under the following conditions (Table III).

The major reason for selecting the particular drawing temperatures for as-spun PET–LCP blend fibers is that the major component in blend fibers is PET. Therefore, PET drawing conditions were used for blend fibers. In sets 1 and 2 in Table III, the first zone temperature is above the T_g, and the second zone temperature is kept above the first zone temperature. In set 3, the first zone temperature is above the T_g, the second zone temperature is significantly above the first zone temperature, and the temperature is kept above the second T_g of PET/60 PHB and also near its crystalline-nematic transition.

Characterization Methods

Tensile tests were performed on an Instron machine model 4112. All tests were carried out on single filaments using a gauge length of 50 mm and crosshead

Table II   Composition of Blend Samples

Sample PET/LCP	Weight of PET (%)	Weight of LCP PET/ (60PHB) (%)
100/0	100	0
97.5/2.5	97.5	2.5
95/5	95	5
90/10	90	10
85/15	85	15
80/20	80	20
50/50	50	50

Table IV   Mechanical Properties of As-spun PET–LCP Blend Fibers

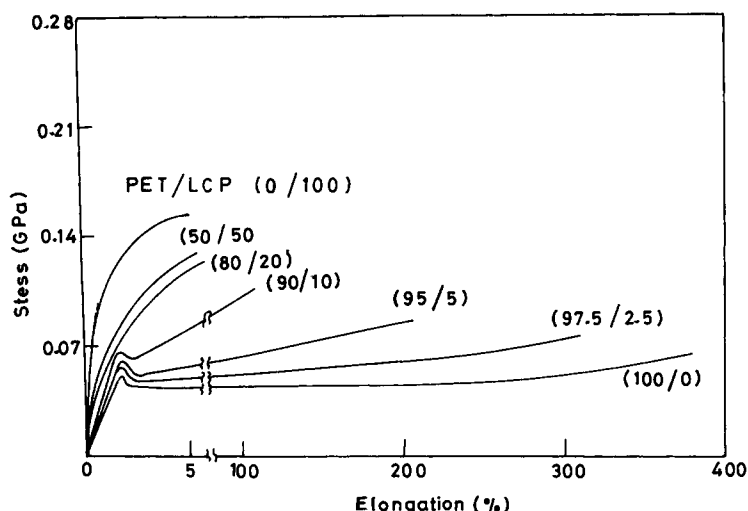| Sample PET/LCP	Strength (GPa)	Modulus (GPa)	Ext. (%)
100/0	0.052	2.12	383
97.5/2.5	0.057	2.26	313
95/5	0.064	2.57	207
90/10	0.069	3.26	110
80/20	0.12	3.46	55
50/50	0.13	4.54	5.5
0/100	0.15	8.5	5.5

Figure 1   Stress–strain curves of as-spun PET–LCP blend fibers.

speed of 50 mm/min. The average of 50 readings were reported for each sample.

A stereoscan 360, Cambridge instruments system was used to study the fracture surface of drawn blend fibers. For these studies filaments were fractured in liquid nitrogen and coated with gold under vacuum.

Table V   Effect of Draw Ratio[a] and Temperatures for Various Blend Fibers

Set[b]	Total (DR)	Sample PET–LCP	Strength[c] (GPa)	Modulus[d] (GPa)	Ext.[e] (%)
1	5.32	100/0	0.58	9.76	35.39
		97.5/2.5	0.60	10.68	32.66
		95/5	0.62	11.16	30.98
		90/10	0.65	11.69	30.63
		85/15	0.59	11.54	27.34
		80/20	0.35	11.46	21.14
		50/50	0.28	11.38	5.20
2	5.6	100/0	0.63	10.67	25.76
		97.5/2.5	0.65	11.37	21.46
		95/5	0.66	12.24	21.88
		90/10	0.69	12.57	19.56
		85/15	0.60	12.50	18.85
3	6.0	100/0	0.76	11.78	16.27
		97.5/2.5	0.80	12.18	14.41
		95/5	0.87	13.34	13.36
		90/10	0.94	14.95	12.96
		85/15	0.77	14.29	10.05

[a] For drawing conditions, refer to Table III.
[b] Feed speed, 50 m/min.
[c] Standard deviation $(\sigma_v) \times 10^{+2}$ in the range of 1.7–4.6.
[d] σ_v in the range of 0.29–0.61.
[e] σ_v in the range of 0.32–0.60.

RESULTS AND DISCUSSION

Mechanical Properties

Stress–strain curves for the as-spun blend fibers are shown in Figure 1, and data is given in Table IV. The as-spun blend fibers with over 20 wt % LCP exhibit no yield point but show highly improved values of strength and modulus. The blend fibers with 50 wt % LCP have a strength of about 0.14 GPa as compared to 0.05 GPa for as-spun PET fibers. The improvement in tensile properties may be related to good dispersion and strong interfacial adhesion[16] between PET and LCP. The 50% as-spun blend fibers show a significant drop in the extension at break from 380% (as-spun PET fiber) to 5%, indicating dominant behavior of LCP component in the blend. At lower weight percent of LCP content, the deformation is dominated by PET, and there is a flow between PET and LCP components, whereas at

Table VI   Birefringence Values for Drawn Blend Fibers

| Sample PET–LCP	Birefringence DR (5.6)	DR (6.0)
100/0	0.187	0.212
97.5/2.5	0.206	0.226
95/5	0.214	0.232
90/10	0.225	0.237
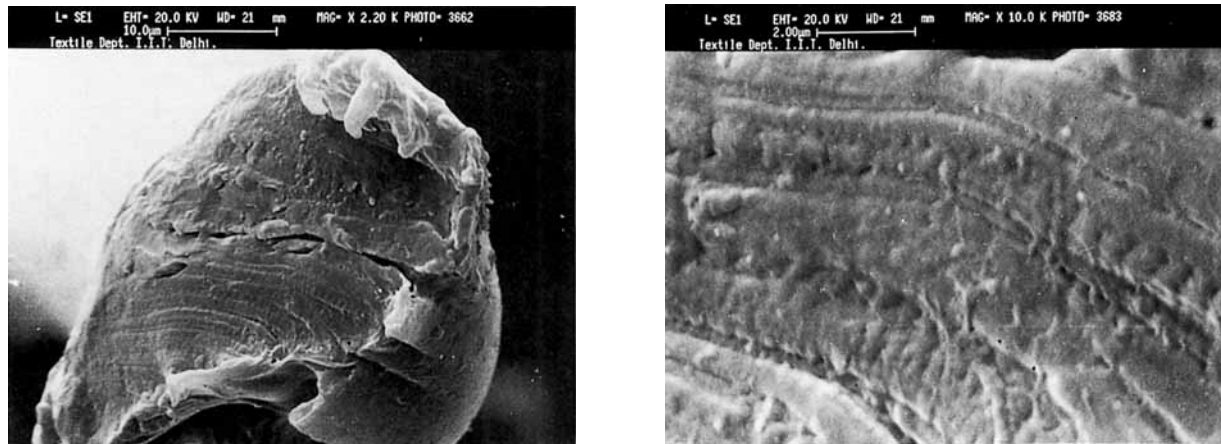
(a)
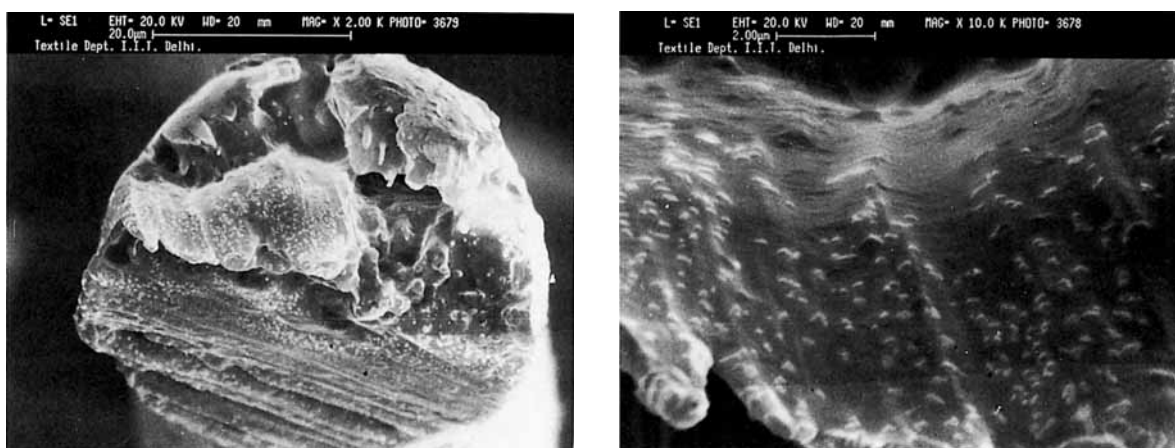
(b)

Figure 2   SEM photomicrographs of drawn PET–LCP blend fibers: (a) PET–LCP (100/
0), (b) 90/10, (c) 80/20, (d) 50/50.

higher weight percent of LCP content, the LCP particles are less deformed, due to the discrete phase in a matrix of blend fibers. This is exactly reflected in scanning electron microscopy (SEM) photomicrographs (Fig. 2).

The effect of draw ratio (DR) and LCP content on the strength, initial modulus, and ultimate elongation are shown in Table V. It can be seen that the modulus and strength of blend fibers produced at total draw ratio of 5.32, 5.6, and 6.0 increase linearly up to the addition of 10 wt % LCP content, possibly due to an increase in LCP orientation. This is supported by birefringence studies. As shown in Table VI, there is a significant increase in birefringence
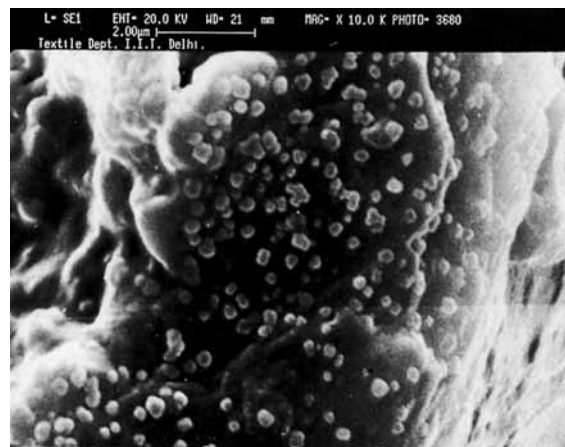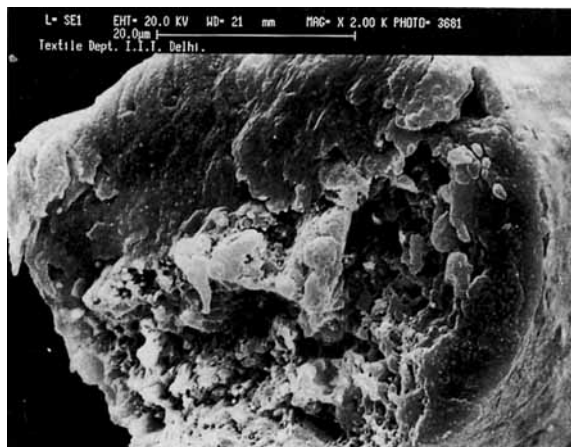
(c)
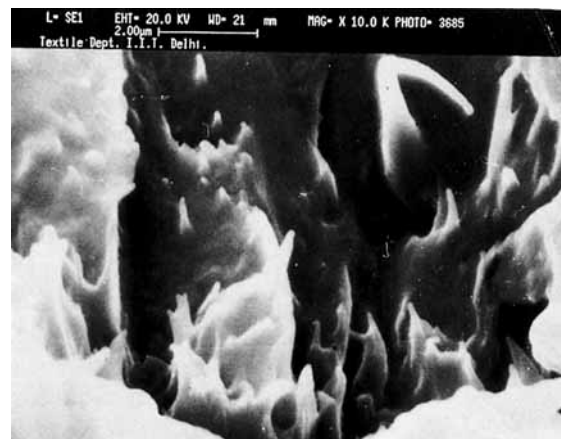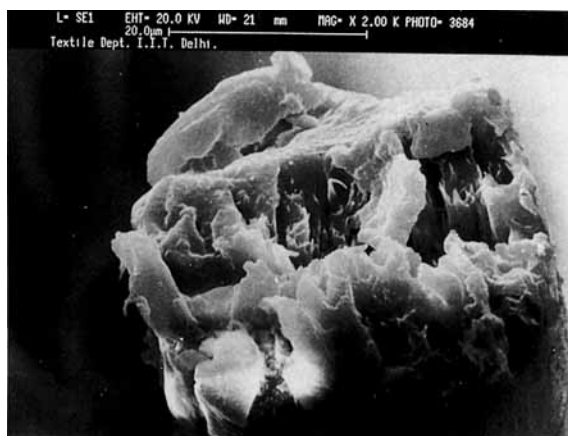
(d)

Figure 2   (*Continued from the previous page*)

values (Δn) for the drawn blend fibers with 10% blend having Δn of 0.237. Being a minor component, LCP can form highly elongated domains parallel to the flow direction, improving the overall orientation and thus giving rise to higher Δn values in the drawn blend fibers. The effect of draw ratio and first and second zone temperatures on the mechanical properties of blend fibers is shown in Table V. Sets 1 and 2 show that with the increase in LCP content up to 10 wt % there is a moderate increase in me-

chanical properties, and with further increase in LCP content, the properties deteriorate. The possible justification can be as follows: When as-spun blend fibers are drawn up to draw ratio of 1.4 in the first zone, around its T_g, and then subjected to a maximum draw ratio in the second zone, when second zone temperature is just above the first zone temperature, the maximum draw ratio attainable is reduced in the second zone. As the second zone temperature is just above the first zone temperature,

the stabilization of the structure would not take place in the second zone. Hence an oriented molecule, yet not incorporated into a crystal lattice, would be thermodynamically unstable at the elevated temperature of the second zone drawing stage and would tend to revert to either an unordered form or a folded chain crystalline form. Due to a relatively unrestrained relaxation, the resulting structure will have a low extent of tautness in the tie molecular chains, which will also be smaller in number. Therefore, modulus and strength will both be lowered.

With the increase in LCP content, the induced orientation increases, whereas the crystallinity of PET component in blend fibers, calculated from differential scanning calorimetry (DSC) studies,[17] increases slightly from 41% (PET–LCP : 100/0) to 43% (90/10), but further addition of LCP decreases the crystallinity to 37% (50/50). It is presumed that at a low degree of crystallinity, the steric hindrance offered by the LCP domains would give rise to a greater degree of orientation retention following stretching, which will lead to an improvement in the mechanical properties till phase separation or poor interfacial adhesion between the two polymers occurs at a higher weight percent of LCP.

Set 3 shows the same trend as depicted in sets 1 and 2, but the increase in the properties is quite steep up to 10 wt % of LCP content, and in 15% blend the properties drop down. When as-spun blend fibers are drawn up to the draw ratio of 3 in the first zone, above its T_g, the mobility of the macromolecules is high and the relaxation of orientation of fiber will be retarded due to higher draw ratio and because of rigid-rod LCP molecules. The structure developed in this region will be thermodynamically stable. The LCP molecules are probably embedded in the interfibrillar region, and when this material is fed to the second zone, at higher temperature, the LCP domains will induce orientation, and overall orientation will increase. The proportions of folded macromolecular sections may decrease and the proportions of straightened sections and crystallinity may increase.

In higher weight percent of LCP drawn blend fibers, the load propagation may depend on the aggregate of LCP molecules and the length distribution of tie chain molecules. Because of phase segregation, the fiber is drawn mainly due to polyester chains, and this may lead to broad distribution of tie chain molecules, and they will not cooperate in bearing a load exerted on the fiber. Consequently, breakage or slippage will take place, resulting in lower strength. The lowering of strength may also be related to the presence of microvoids at the interface. It is evident from the above results that the maximum improvement in the properties occurs in the PET–LCP (90/10) blend fiber. In order to achieve the maximum improvement in mechanical properties, the 10% blend fibers were drawn at lower drawing speeds. The effect of draw ratio on the strength, modulus, and elongation at break is given in Table VII.

The strength of the 10 wt % LCP fiber increases linearly, when the draw ratio is increased from 1.4 to 6. The modulus also increases in the same manner as the strength. The elongation at break decreases as the draw ratio increases.

Scanning Electron Microscopy

Scanning electron micrographs of the fracture surface of drawn blend fibers are presented in Figure 2 [(a)–(d)]. Fracture surface of drawn PET fiber [Fig. 2(a)] shows a homogeneous surface. The fracture surface of drawn PET–LCP 90/10 blend fiber [Fig. 2(b)] at lower magnification (2000) shows evidence

Table VII   Effect of Draw Ratio (DR)[a] in Second Zone for PET–LCP (90/10) Blend

First Zone		Second Zone			End Properties		
Temp. (°C)	DR	Temp. (°C)	DR	Total DR	Strength (GPa)	Modulus (GPa)	Ext. (%)
95	1.4	130	1	1.4	0.09	3.39	114.3
95	1.4	130	2	2.8	0.27	5.79	75.8
95	1.4	130	3	4.2	0.39	10.87	56.2
95	1.4	130	4	5.6	0.68	12.49	15.5
120	3.0	220	1.8	5.4	0.85	14.29	15.6
120	3.0	220	1.9	5.7	0.96	15.37	12.8
120	3.0	220	2.0	6.0	1.03	17.72	10.8

[a] Feed speed, 10 m/min.

of LCP particles dispersed in the PET matrix. At higher magnification (10,000), the LCP with a diameter of 0.07–0.2 μm particles are seen in the PET matrix. The fracture surface of drawn blend fibers [Fig. 2(b)] shows that the LCP particles have some matrix polymer spread over their surfaces, there are no open rings around the particles of LCP, and neat holes are not generated by the withdrawn LCP particles. This kind of morphology is rarely shown for the LCP-reinforced ductile polymers except for the case of chopped-fiber reinforced composites treated with a coupling agent or heat. It is indicative of the improvement in interfacial adhesion between the two polymers, and it could be due to the partial miscibility of the two polymers. As the LCP content increases to 20 wt % [Fig. 2(c)], the size of inclusion increases to 0.2–0.5 μm owing to the agglomeration of the droplet in the molten state. Figure 2(c) shows that there appears to be a tendency to form LCP fibrils in the PET matrix, whereas 50/50 blend [Fig. 2(d)] shows a clear phase separation and a bundle of fibrils with dimensions of 0.5–2 μm are distinctly shown in the fracture surface. Most of the reported literature[15,18–20] on LCP–thermoplastic blend system indicate much larger sizes (0.5–5 μm) of LCP domains.

It is clear from the above observation that in the blends up to 10 wt % LCP content, the LCP domains are well distributed in the PET matrix, indicating good mixing of the two components. We believe it could be due to the partial miscibility of the PET-rich phase of the LCP with PET homopolymer.

CONCLUSIONS

Mechanical properties of drawn blend fibers (DR-6.0) up to 10 wt % LCP composition exhibit significant improvement in tensile modulus (17.7 GPa) and strength (1 GPa) as compared to that of drawn PET fiber at 11.7 and 0.78 GPa, respectively. Above 10% LCP composition the strength and modulus decreases. Improvement in mechanical properties, when the LCP is a minor component, occurs for two reasons: (a) formation of highly elongated domains parallel to the flow direction and thus improving the orientation and (b) reinforcement of the matrix by LCP. In higher weight percent of LCP-drawn blend fibers, the mechanical properties are lower due to phase segregation.

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