

# Blends of PBT with Rigid Thermotropic LCP having Flexible Side Groups: Comparison of Their Tensile Properties with Semirigid Main-Chain TLCP Blends

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## SYNOPSIS

Two new thermotropic liquid crystalline polymers (LCPs) were synthesized. One is a dimesogenic LCP having a flexible hexamethylene spacer in the main chain, the other is a rigid-type main-chain LCP having alkoxy side groups on the terephthaloyl moiety of the polymer. Blends of LCP with poly(butylene) terephthalate were melt-spun at different LCP contents and different draw ratios to produce a monofilament. Maximum enhancement in the ultimate tensile strength was observed for the blends containing 5% LCP at any draw ratio, and decreased with further increase in LCP content. The initial modulus monotonically increased with increasing LCP content. The tensile properties of the rigid-type LCP blends were higher than those of the flexible main-chain LCP blends. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Thermotropic liquid crystalline polymers (LCPs) have been the subject of considerable research due to their specific chemical structures, high strength, high modulus, low viscosities, and other good mechanical properties.<sup>1-4</sup> In the molten state, LCP shows the increased mechanical strength and stiffness of a thermoplastic matrix polymer. Moreover, even relatively small amounts of LCP may induce a reduction in the melt viscosity, and thus improve processability. LCP may also improve other properties of thermoplastics, such as dimensional and thermal stability.<sup>5</sup>

Blending conventional thermoplastic polymers with LCPs can lead to easier processing and reinforcement of the matrix. Much work has been done in the area of blending LCPs with engineering thermoplastics.<sup>4-8</sup> It has been shown for some pairs of polymers that one can obtain so-called self-reinforced composites in which LCP phase *in situ* forms

reinforcing fibers in a matrix of an engineering thermoplastic.<sup>2,9-11</sup>

Recent literature has shown that flexible spacers or flexible side-groups in the rigid backbone of the LCPs may have a positive influence on the adhesion, and mechanical properties of the LCP blends may be improved.<sup>12-15</sup> Rodlike LCPs, e.g., the fully aromatic polyesters (Vectra, etc.), will therefore probably be replaced in many cases by LCPs containing flexible elements, designed to fit just one matrix polymer.

This paper deals with the physical and mechanical properties of two new thermotropic LCP blends. A structural main-chain LCP with a flexible spacer (Main-LCP) was prepared from 1,6-dibromohexane, hydroquinone and *p*-hydroxybenzoic acid; and a rigid LCP having dialkoxy side groups (Side-LCP) was synthesized from dialkoxyterephthalic acid and biphenol. The properties of the Main-LCP blends were compared with those of blends prepared from the Side-LCP and poly(butylene terephthalate) (PBT). We also describe the mechanical properties of the *in situ* composites obtained from the blends. To improve tensile properties, the optimum processing parameters such as draw ratio and the LCP content

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in the thermoplastic matrix were determined experimentally.

## EXPERIMENTAL

### Materials

The two LCPs used in this study were synthesized via a multiple-step route<sup>14,15</sup> described elsewhere.

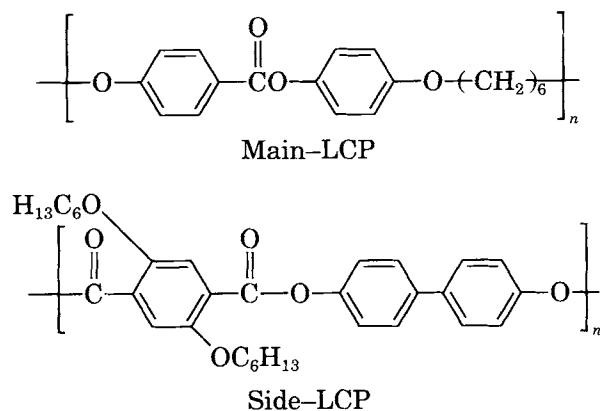
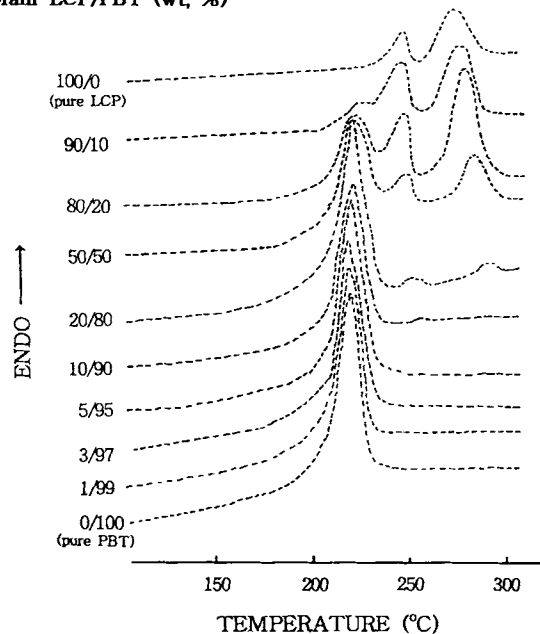


Table I summarizes the general properties of the LCPs and PBT. PBT for this work was purchased from Aldrich Chemicals in Milwaukee, USA.

### Blending

PBT, the thermoplastic matrix, and the LCP in the form of dry powder were dissolved in a mixed solvent. For the Main-LCP blends a phenol/*p*-chlorophenol/TCE(1,1,2,2-tetrachloroethane) 25/40/35 (wt/wt/wt) mixture was used. A mixed trifluoroacetic acid/chloroform (=50/50, wt/wt) solvent was used at room temperature for the Side-LCP blends. The concentrations of the solutions were less than 5% by weight to avoid aggregation of LCP itself in the solvent. The polymer solution was then coprecipitated in acetone drop by drop with vigorous agitation, and the white precipitates were washed with ethyl alcohol, H<sub>2</sub>O and acetone, repeatedly. The po-

Main-LCP/PBT (wt, %)



**Figure 1** DSC thermograms of pure PBT, Main-LCP, and their blends.

lyblends were dried in a vacuum oven at 110°C for 2–3 days.

For simplicity, the blends will be described as 0% LCP/PBT, 3% LCP/PBT, 10% LCP/PBT, and so on. Where LCP and PBT represent the polymer components used to prepare the blend, the numbers denote the amount of LCP in the blend in weight percent (wt %).

### Extrusion

The dried blends were pressed at 220°C, 2500 kg/cm<sup>2</sup> for a few minutes on a hot press. The film-type blends were dried in a vacuum oven at 110°C for 24 h, then the films were extruded through a capillary rheometer die. From the capillary rheometer, the hot extrudates were immediately drawn at different take-up speeds to form monofilaments with different diameters. The extrusion temperature for Main- and

**Table I** General Properties of LCPs and PBT

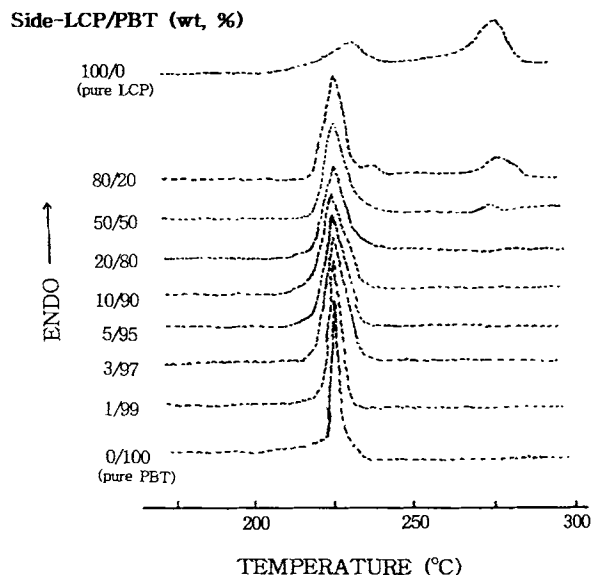
Polymer	$\eta_{inh}$	$T_g$ , °C	$T_m$ , °C	$T_i$ , °C <sup>a</sup>	$\overline{M}_n$
Main-LCP	0.59 <sup>b</sup>	—	248	275	—
Side-LCP	0.72 <sup>c</sup>	113	228	275	—
PBT <sup>d</sup>	—	40	223	—	30,000

<sup>a</sup> Isotropization temperatures.

<sup>b</sup> Inherent viscosity was measured at 30°C by using 0.1 g/dL solution in a phenol/*p*-chlorophenol/TCE = 25/40/35 (W/W/W).

<sup>c</sup> Inherent viscosity was measured at 30°C at a concentration of 0.5 g/dL in a *p*-chlorophenol/TCE = 60/40 (W/W) mixture.

<sup>d</sup> Aldrich Chemical.

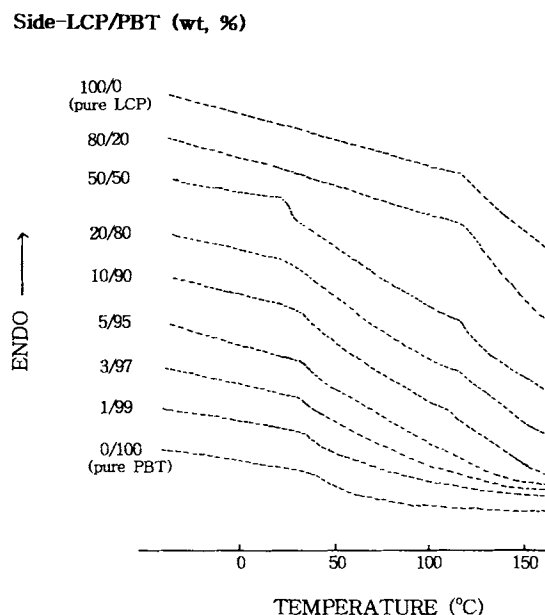


**Figure 2** DSC thermograms of pure PBT, Side-LCP, and their blends.

Side-LCP blends were 250°C and 245°C, respectively. The mean residence time in the capillary rheometer was 4–5 min.

### Characterization

Differential scanning calorimetry (DSC) measurements under N<sub>2</sub> atmosphere were carried out with DuPont 910 equipment. The temperature was raised and lowered at the rate of 20°C/min. The most thermograms of the polymers and their blends



**Figure 3** DSC thermograms of  $T_g$ 's of pure PBT, Side-LCP, and their blends after quenching samples from 240°C.

were obtained from the second heating runs with fast cooling thermal history to obtain more clear and distinct first- and second-order transitions on DSC thermograms. Thermal stability was examined on a DuPont 910 Thermogravimetric Analyzer at a heating rate of 20°C/min. A polarizing microscope equipped with a Mettler FP-5 hot stage was employed to examine the liquid crystalline behavior. The mechanical properties of the extrudate were

**Table II** Thermal Properties of Pure Polymers and LCP/PBT Blends

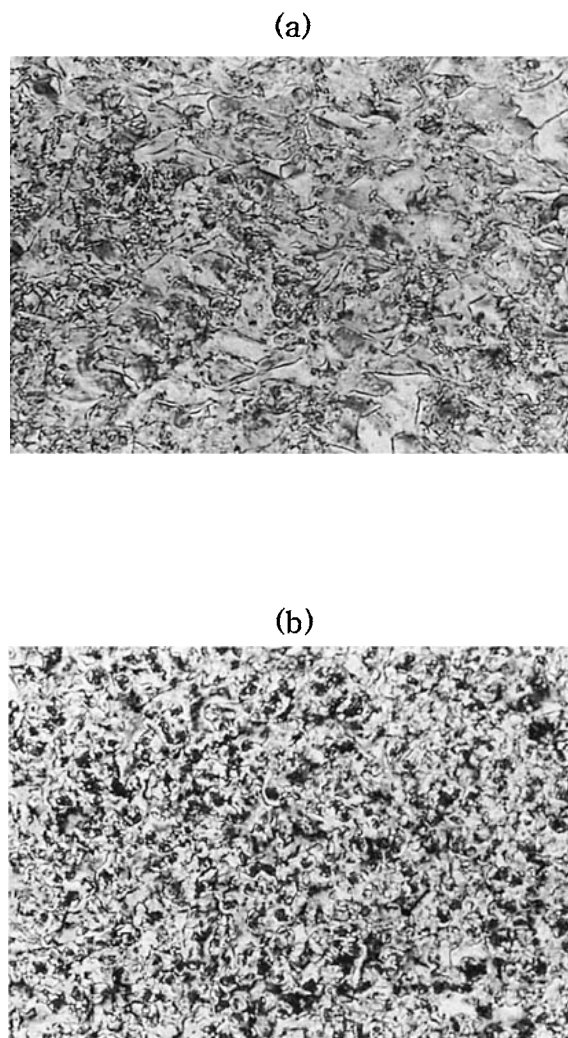
Blend (LCP/PBT)	Main-LCP					Side-LCP				
	$T_m$ , °C	$T_i$ , °C	L.C. <sup>a</sup>	D.C., % <sup>b</sup>	$T_g$ , °C	$T_m$ , °C	$T_i$ , °C	L.C.		
100/0 (pure LCP)	—	248	275	Nem. <sup>c</sup>	61	—	113	228	275	Nem.
80/20	226	249	280	Nem.	53	—	112	224	275	Nem.
50/50	223	249	284	Nem.	51	25	112	223	275	Nem.
20/80	223	252	290	Nem.	43	31	113	224	—	N.O.
10/90	224	257	—	N.O.	40	33	109	224	—	N.O.
5/95	223	—	—	N.O.	38	33	—	224	—	N.O.
3/97	224	—	—	N.O.	—	36	—	224	—	N.O.
1/99	223	—	—	N.O.	—	38	—	223	—	N.O.
0/100 (pure PBT)	223	—	—	—	30	40	—	223	—	—

N.O. = Not observed.

<sup>a</sup> Liquid crystalline texture.

<sup>b</sup> Degree of crystallinity.

<sup>c</sup> Nematic.



**Figure 4** Optical micrographs of the LCPs (magnification 200 $\times$ ). (a) pure Main-LCP; (b) pure Side-LCP.

measured on an Instron Mechanical Tester with a crosshead speed of 10 mm/min. Reported values are the average of 6 measurements.

Morphology of the fractured surfaces of the fiber samples was investigated with a Hitachi S-2400 scanning electron microscope (SEM). All samples were fractured perpendicular to the fiber direction in liquid  $N_2$  and the fractured surfaces were sputtered with gold using an SPI Sputter Coater for enhanced conductivity.

## RESULTS AND DISCUSSION

### Thermal Properties

DSC curves of the Main-LCP and its blends are shown in Figure 1. The thermograms of LCP obtained from the second heating runs show that an

endothermic peak appears at 248 $^{\circ}C$  which corresponds to the solid crystal-to-nematic melt transition ( $T_m$ ), while  $T_m$  of the PBT was observed at about 223 $^{\circ}C$ . DSC thermograms of the blends containing 1% to 5% Main-LCP in the PBT matrix are very similar to that of pure PBT. But on the blends in LCP content from 10 to 90 wt %, the transition points of all samples were around 224 $^{\circ}C$  and 250 $^{\circ}C$ , which were considered to be melting temperatures of PBT and Main-LCP, respectively. There is a small endotherm near 290 $^{\circ}C$  in 20% LCP/PBT which corresponds to mesophase-to-isotropic liquid transition ( $T_i$ ) of pure Main-LCP. With increasing LCP content, isotropic temperatures progressively shifted downward, as shown in Figure 1.

DSC thermograms of the blends of Side-LCP are shown in Figure 2. The nematic melt transition temperature ( $T_m$ ) of the pure Side-LCP was observed at about 228 $^{\circ}C$ . Each thermogram of the LCP/PBT blends is very similar to that of pure PBT. The isotropic transition of the pure Side-LCP was observed at 275 $^{\circ}C$ . An endothermic peak corresponding to mesophase-to-isotropic liquid transition is observed in the blends containing LCP contents higher than 50 wt %. The quenched samples from 240 $^{\circ}C$  in liquid nitrogen showed glass transition temperatures ( $T_g$ s) in the range of 25–40 $^{\circ}C$  and 109–113 $^{\circ}C$  separately, which were considered to be the  $T_g$ s of PBT and Side-LCP, respectively (see Table II). It is especially unusual to observe that the  $T_g$  decreases almost linearly from 40 $^{\circ}C$  to 25 $^{\circ}C$  with increasing LCP content. This behavior can probably be attributed to the mixing of PBT with the alkoxy side groups in the Side-LCP (Fig. 3). In the case of the Main-LCP blends, however, it was hard to identify the glass transitions on the DSC thermograms, even on the quenched second heating runs. But the degree of crystallinity of the PBT component in the Main-LCP blends decreases with decreasing LCP content in the matrix.

Figure 4 shows a threadlike nematic texture for pure LCPs. On the other hand, poorly developed nematic textures (not shown here) were observed for 80% LCP and 50% LCP on Polarized Optical Microscope. They, however, revealed strong stir opalescence above the melt transition temperature.

The thermal stability of the pure LCP polymers and their blends under an  $N_2$  atmosphere was studied by thermogravimetric analysis (TGA). Table III summarizes the experimental results of TGAs of the two-polyblends systems. Initial weight loss ( $T_D^i$ ) of Main- and Side-LCP blends was observed at 376–378 $^{\circ}C$  and 350–375 $^{\circ}C$ , respectively, depending on the LCP weight percent in the PBT matrix. Maximum rate of weight loss ( $T_D^{max}$ ) was observed in the

**Table III Thermogravimetric Analyses of LCP/PBT Blends**

Blend (LCP/PBT)	$T_D^i$ (°C) <sup>a</sup>		$T_D^{max}$ (°C) <sup>b</sup>		$W_i^R$ (%) <sup>c</sup>	
	Main <sup>d</sup>	Side <sup>e</sup>	Main	Side	Main	Side
100/0 (pure LCP)	378	350	477	463	17	26
10/90	377	369	436	432	6	7
5/95	378	373	435	431	7	7
3/97	378	373	431	432	6	8
1/99	376	375	438	429	6	8
0/100 (pure PBT)	382		429		8	

<sup>a</sup> Initial weight-loss temperature.  
<sup>b</sup> Maximum weight-loss temperature.  
<sup>c</sup> Weight percent of residue at 600°C.  
<sup>d</sup> Main-chain LCP.  
<sup>e</sup> LCP having alkoxy side groups.

temperature ranges of 438–477°C and 429–463°C. The Side-LCP blends showed lower temperatures in the initial weight loss and the maximum rate of weight loss than did the Main-LCP. It seems that the alkoxy side groups in Side-LCP are easily decomposed at high temperature. These TGA results

confirmed that all of the samples were thermally stable at the processing temperatures of 250°C and 245°C.

**Table IV Tensile Properties of LCP/PBT Extrudates<sup>a</sup>**

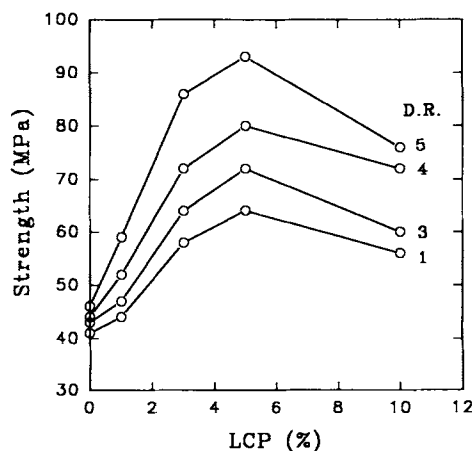
LCP Content, %	DR	Strength (MPa)		Modulus (GPa)	
		Main	Side	Main	Side
0 (pure PBT)	1	41		1.87	
	3	43		1.91	
	4	44		1.93	
	5	46		1.93	
1	1	44	45	1.91	2.01
	3	47	54	2.15	2.18
	4	52	60	2.30	2.43
	5	59	68	2.48	2.45
3	1	58	60	2.17	2.38
	3	64	65	2.40	2.79
	4	72	71	2.86	2.91
5	5	86	83	2.95	3.27
	1	64	67	2.29	2.84
	3	72	82	2.51	3.33
10	4	80	108	2.93	3.68
	5	93	124	3.09	3.92
	1	56	61	2.35	2.93
	3	60	65	2.57	3.45
	4	72	76	3.10	3.97
	5	76	79	3.19	4.21

<sup>a</sup> DR =  $D_i/D_f$  ( $D_i$  = Die diameter;  $D_f$  = Fiber diameter). L/D = 20. Extrusion temp. 250°C for Main-LCP; 245°C for Side-LCP.

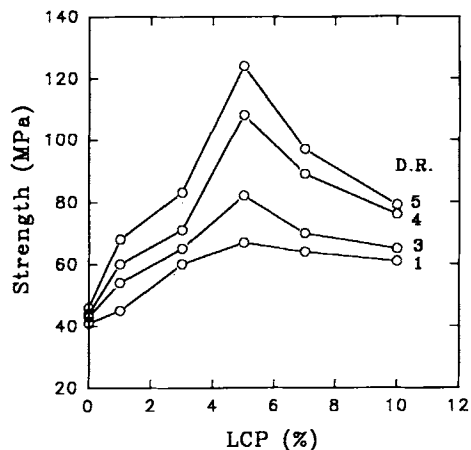
**Mechanical Properties**

The blends and pure PBT were extruded through a capillary die with various draw ratios (DRs) to examine the tensile strength and modulus of the extrudates. As shown in Table IV, the values of the strength and initial modulus of the blend fibers were enhanced remarkably with increasing DR. However, as expected in the case of a flexible coil polymer, the increase of the tensile strength and the modulus with DR was insignificant for pure PBT.

Addition of LCP to matrix polymer significantly increased tensile properties of the blends. The



**Figure 5** Ultimate strength of Main-LCP blends versus LCP content.

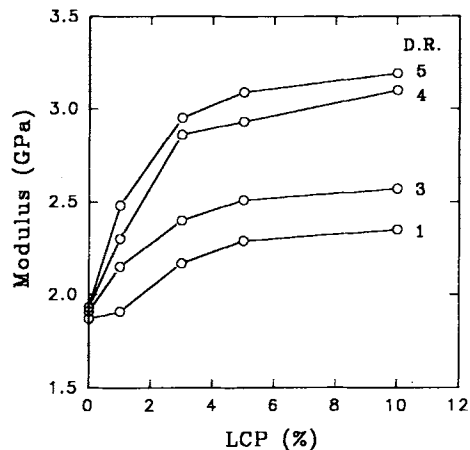


**Figure 6** Ultimate strength of Side-LCP blends versus LCP content.

strength of the blends containing even 1% of LCP content was higher than that of pure PBT. Particularly at  $DR = 5$ , in the 5% LCP/PBT of the two-polyblends systems, the ultimate strength achieved was more than twice that of PBT. At constant  $DR$ , the values in strength increased linearly with increasing LCP content up to 5 wt % and then decreased above 5% LCP content (see Figs. 5 and 6). For Side-LCP blends in Figure 6, the values of the ultimate strength increased from 46 to 124 MPa and then decreased to 79 MPa with increasing LCP content from 0 to 10 wt %. It is suggested that the LCP domains can agglomerate above 10% LCP content in the PBT matrix. This was cross checked by SEM. After all, in this blend system, the reinforcing effect did not obey a rule of mixtures. DeMeuse and Jaffe and others, have also reporting on their investigations of blends of LCPs,<sup>16-18</sup> have shown that the LCPs do not obey the rule of mixtures and their miscibility cannot, therefore, be predicted on the same basis. These investigators attribute this characteristic to the fact that LCPs are not simple rigid rods but instead can be characterized as semiflexible in nature.

The initial modulus increased with increasing amounts of LCP in PBT matrix. The effect of LCP content and  $DR$  on the modulus is shown in Figures 7 and 8. At  $DR = 5$ , the values of the initial moduli increased from 1.93 to 3.19 GPa for the Main-LCP and from 1.93 to 4.21 GPa for the Side-LCP, respectively, with increasing LCP content. This is possible because the well-dispersed LCP domains, especially in 5% LCP content, may induce orientation; therefore, the overall orientation may increase.<sup>19,20</sup>

In conclusion, the ultimate strength of the Side-LCP blends showed a significant improvement in

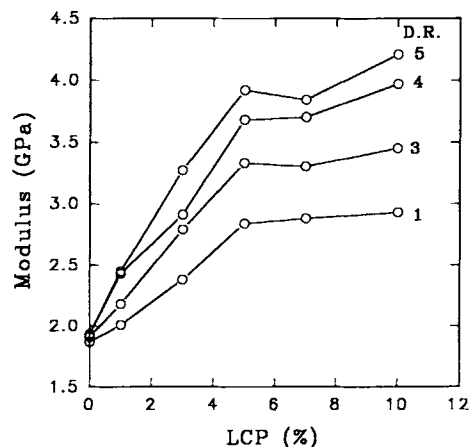


**Figure 7** Initial modulus of Main-LCP blends versus LCP content.

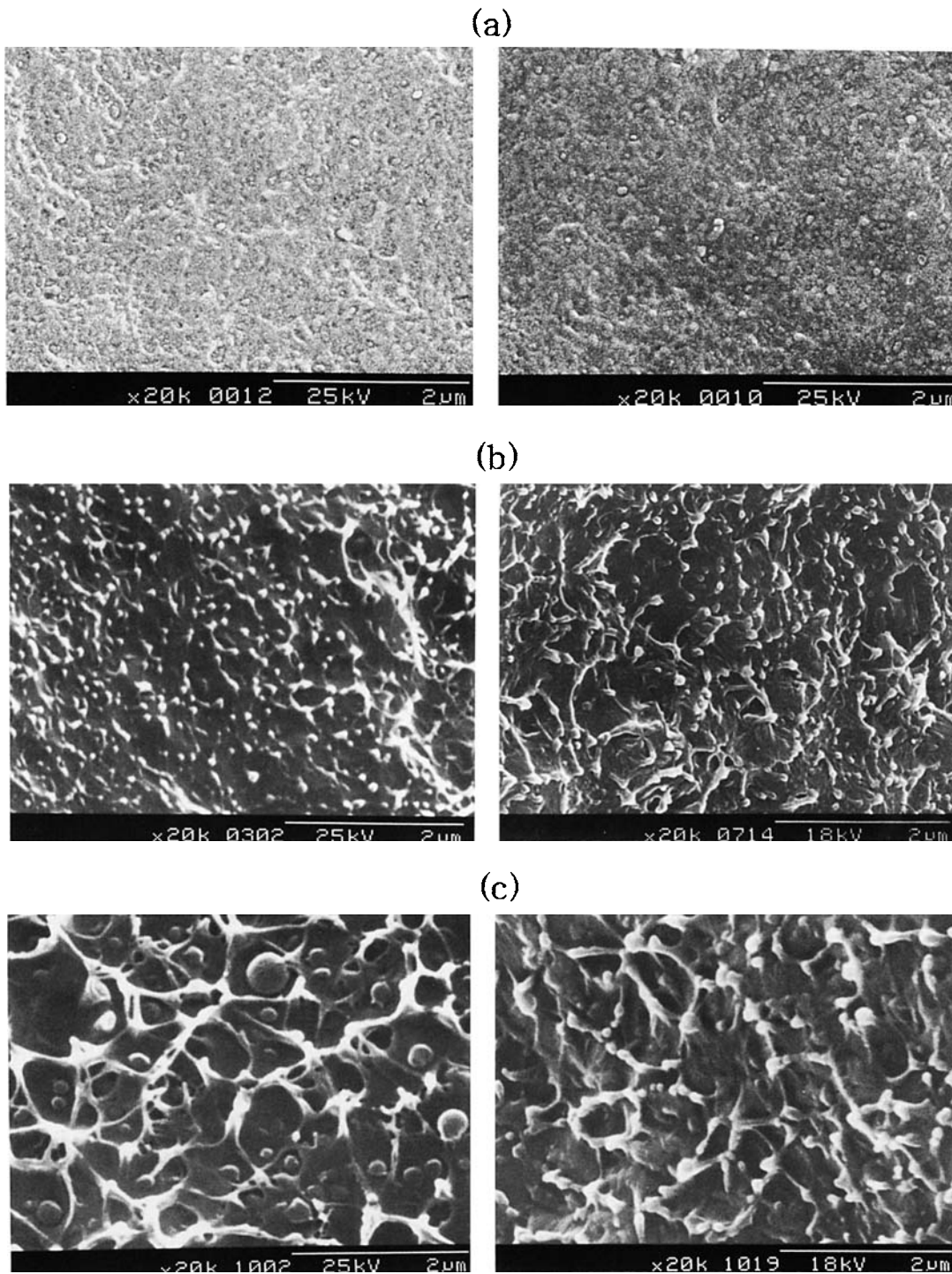
the 5% LCP/PBT blend fiber drawn at  $DR = 5$  with a strength of 124 MPa; the initial modulus was 4.21 GPa in the 10% LCP/PBT fiber. In contrast, those of Main-LCP blend fibers were 93 MPa and 3.19 GPa, respectively. It can be suggested that the alkoxy side-group LCP in the blends not only improved solubility and mixing of entropy between the two polymers, but also retained the rigidity of fibrillar structure.

### Morphology

SEM micrographs confirm the morphologies and tensile property changes of the blend fibers described above. The morphologies of the fracture surfaces of the extruded fibers containing 3–10 wt % LCP in PBT matrix is depicted in the micrographs in Figure 9.



**Figure 8** Initial modulus of Side-LCP blends versus LCP content.



**Figure 9** Scanning electron micrographs of as-spun fibers (20,000 $\times$ ). (a) 3% LCP/PBT for Main- (left) and Side-LCP (right); (b) 5% LCP/PBT for Main- (left) and Side-LCP (right); (c) 10% LCP/PBT for Main- (left) and Side-LCP (right).

Figure 9 shows that many fine spherical particles were formed in an undrawn blend fiber containing 3% and 5% Main-LCP. It is clearly seen that the particle size of the dispersed LCP phase increases with increasing LCP content. For 3% LCP/PBT

blend containing the smallest LCP particles, the LCP showed fine dispersion as spherical droplets of 50–70 nm in diameter. For 5% LCP/PBT the morphology consisted of spherical LCP domains, also finely dispersed, with 60–80 nm diameter in the PBT

matrix. It is conceivable that the well-dispersed LCP domain can increase the strength of the blend fibers, probably due to strong interfacial adhesion between LCP and PBT matrix.<sup>12</sup> Actually it was not found in the open circles around the LCP domains in the SEM micrographs. But in 10% Main-LCP/PBT, bigger spherical droplets were formed, caused by agglomeration of the LCP itself.

For the 3% Side-LCP blends, the morphology consisted of spherical LCP domains dispersed with a lack of fibrillation in the PBT continuous phase, very similar to that of Main-LCP blends. But above 3% LCP/PBT, more developed fibrillike structures were observed with diameters of 60–80 nm (see Fig. 9, right sides).

## CONCLUSIONS

Two new thermotropic LCPs were solution blended with an engineering thermoplastic; PBT was solution blended and extruded to examine the formation of an *in situ* composite.

One LCP (Main-LCP) has a flexible hexamethylene spacer in the main chain, and the other (Side-LCP) has bis-hexamethylene branches on a terephthaloyl group in an aromatic polyester.

The conclusion is summarized as follows:

1. Two new thermotropic LCPs showed nematic behavior.
2. LCPs highly dispersed in the PBT matrix and showed fine fibrillar structures in Side-LCP blends.
3. For two-polyblend systems, the maximum ultimate strength was obtained in the blend containing 5% LCP/PBT at any draw ratio, but the initial moduli increased with increasing amounts of LCP content.
4. The tensile properties of Side-LCP blends were higher than those of Main-LCP blends.

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