Polymer (Korea) Vol. 16, No. 2, pp 166－174 (1992)

전 방향족 액정코폴리에스테르(LCP)와 PBT 블렌드의 형태학 및 기계적 성질

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(1991년 9월 27일 접수)

Morphology and Mechanical Properties of Wholly Aromatic Liquid Crystalline Copolyester and Poly(butyleneterephthalate) Blends

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(Received September 27, 1991)

요 약 : PBT와 액정성 고분자 즉 전방향족 액정코폴리에스테르(LCP-1) 및 전방향족 액정코폴리에스테르아미드(LCP-2) 블렌딩은 이축압출기(twin screw extruder)에서 조성별로 행하여졌다. 사출성형 시편은 사출성형기로 제조하였으며, 블렌드의 열적, 기계적 및 형태학적 성질은 DSC, 인장시험기 및 SEM으로 조사하였다.

DSC를 이용하여 열적성질을 조사한 결과 PBT/LCP-1 블렌드의 경우 부분적인 상용성이 있음을 알았다. SEM을 사용하여 블렌드의 형태학을 관찰한 결과 두 수지간의 계면 접착력이 불량한 것으로 나타났다. 매트릭스내의 LCP 피브릴구조는 사출온도에 따라 변하였으며, 기계적 성질의 이방성은 LCP 함량과 시편두께에 크게 의존하는 것으로 나타났다.

Abstract : Blends of poly(butyleneterephthalate)(PBT) and liquid crystalline polymers, wholly aromatic copolyester(LCP-1) and wholly aromatic copolyesteramide(LCP-2), were prepared in a twin-screw extruder. Specimens for mechanical test were prepared by injection molding. Thermal, mechanical and morphological properties of the blends were investigated by differential scanning calorimetry(DSC), tensile tester and scanning electron microscopy(SEM), respectively. DSC study revealed a partial miscibility between PBT and LCP-1. The morphology of the blends showed a poor interfacial adhesion between the two phases, and the fibrillar structure of LCP resulted in the matrix which was controlled by injection conditions. The anisotropy of mechanical properties was greatly dependent on the LCP contents.

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INTRODUCTION

There has been a considerable interest in liquid crystalline polymers(LCP's), especially after the development of high modulus and high strength fibers prepared from the lyotropic aromatic polyamides(aramids) by Du Pont.[1,2] Thermotropic liquid crystalline polymers(TLCP's) are attractive because of their potential application as ultra-high strength fibers and molded articles.

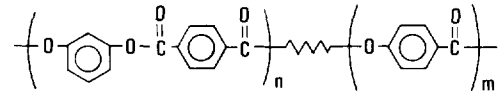
The blends of LCP's with other engineering plastics to enhance the mechanical properties were also of interest.[3] The ease of melt processing combined with high performance characteristics makes the thermotropic LCP blend with engineeringplastics very attractive.[3,4]

It is well known that fiber reinforced composite produces outstanding mechanical properties.[5] The principle of fiber reinforcement is that hard and strong rods or fibers in the matrix polymer transfer the applied force. To improve the strength and modulus of the composite materials, several conditions are prerequisite : a large aspect ratio(ratio of the length of fiber to its diameter) of fibers, a good orientation and strong adherence at the interface of fiber and matrix. Recently, fibers with diameter 1~10μm are widely used in fiber reinforced materials. It is easy to supply fibers satisfying the condition of aspect ratio but it is difficult to satisfy the condition of strong adhesion. There are many researchers who have tried to improve the interfacial adhesion between fiber and matrix polymer.[6,7] Nowadays, lyotropic and thermotropic liquid crystalline polymers(LLCP and TLCP) were used as a reinforcement. Many interesting studies for the blends of LLCP[8,9] and TLCP[10~12] and ductile polymers have been published. Specially thermotropic polymers have attracted much attention because of good processability and many other advantages mentioned by earlier researchers.[10~12]

This study investigates the improvement of mechanical properties of PBT by adding LCPs and the effect of LCP contents and the thickness of injected bar on the mechanical properties and morphology.

EXPERIMENTAL

A matrix polymer of PBT(I. V.=0.98 : intrinsic viscosity of a solution in ortho-chlorophenol at 30 ℃) was supplied by KOLON, Ltd. Two thermotropic liquid crystalline polymers were RD 66(I. V.= 1.21 : inherent viscosity of a solution in p-chlorophenol/pentafluorophenol/chloroform(30/30/40) mixture by volume at concentration 0.1g/dL at 30 ℃) manufactured by KOLON, Ltd.(LCP-1) and Vectra B950 manufactured by Celanese(LCP-2). The chemical structure of LCP-1 is as follows.



Materials were carefully dried at 120℃ under vacuum for at least 8hrs, and then blended, using a twin-screw extruder(Automatik ZCM 32/36), and immediately quenched in a water bath and finally pelletized. Two thermal profiles were used for all the investigated materials as follows.

(LCP-1/PBT blends) 200, 240, 250, 255 and 260 ℃.

(LCP-2/PBT blends) 230, 260, 265, 280 and 290 ℃.

The rotor speed was fixed at 200rpm. The contents of LCPS in the blends were varied 1 to 100 wt%. The blends were carefully redried at 120℃ under vacuum for at least 8hrs. Molding was performed using an Engel ES-1 injection mechine and an appropriate mold producing ASTM testing specimens. The LCP-1/PBT blend was injected at 265℃(above the melting point of the LCP-1) into a mold which was kept at a constant temperature of 60℃. The LCP-2/PBT blend was injected at 275 ℃ and 295℃(below and above the melting point of the LCP-2) into a mold which was kept at a constant temperature of 60℃. Test specimen of tensile and flexural measurements was prepared by

the screw type injection machine(Engel ES-1) with dog-bon(ASTM D-638) and flexural(ASTM D790) bars.

Thermal analyses of the blends were performed by Perkin Elmer DSC-4 thermal analyzer. All the runs were under nitrogen atmosphere with a heating or cooling rate of 20℃/min and a temperature scan range from 0℃ to 300℃.

Tensile properties were determined with an Instron model 1123 tensile tester operated at 5mm/min cross-head speed and a gauge length of 70mm at room temperature. The average values of at least ten measurements were taken as results. To study the morphology of the blends, the tensile specimen was quenched with a liquid nitrogen and fractured at cryogenic temperature. These fractured surfaces were coated with gold paradium for the microscopy and observed with a JOEL JSM-35 CF scanning electron microscope.

RESULTS AND DISCUSSION

Thermal Properties

The thermal properties of quenched LCP-1/PBT and LCP-2/PBT blends are shown in Table 1 and Table 2, respectively. LCP-1 exhibited glass transition at 128℃ but the Tg was not apparent in the blend system due to week peak. The Tg of PBT, 33℃, was increased as the LCP-1 content was increased due to partial miscibility of LCP-1 with PBT. It may be due to the existence of flexible units in the LCP-1 molecules.[13~15] However, the melting point of PBT was depressed by mixing with the LCP-1. There was depression of Tm especially in the blend of the highest LCP-1 content, probably due to a partial diluent effect of the LCP-1 polymer. The results are shown in Fig. 1. With this limited miscibility, the heat of fusion of PBT, as given in Table 1, was nearly constant even when the LCP content was increased.

Therefore PBT crystallization during heating was proceeded by excluding the LCP-1, and the mechanism of the crystallization was not affected by addition of LCP-1.

But with the blends of LCP-2/PBT, PBT exhibited constant Tg and Tm because of their immiscibility. Heat of fusion of PBT also remained constant. It may be due to the existence of rigid units in the LCP-2 molecules. The results are exhibited in Fig. 2.

Table 1. Thermal Properties of PBT/LCP-1 Blends.

Composition PBT/LCP-1	T_{g1} (℃)	T_{g2} (℃)	T_c (℃)	T_m (℃)	ΔH_f (cal/g)
100/0	33	–	42	222	13.19
97/3	34	–	44	222	13.21
95/5	35	–	46	222	12.96
90/10	36	–	48	221	12.61
80/20	37	–	49	220	11.42
70/30	41	–	54	220	10.31
50/50	43	126	58	218	7.62
20/80	45	127	84	217	2.79
0/100	–	128	–	216	–

ΔH_f : first heating run.
T_{g1} : glass transition temperature of PBT on cooling
T_{g2} : glass transition temperature of LCP-1 on cooling.
T_c : crystallization temperature of PBT on cooling.
T_m : melting temperature of PBT on cooling.

Mechanical Properties

Mechanical properties of LCP-1/PBT and LCP-2/PBT blends are summarized in Table 3 and 4, respectively. Tensile strength, flexural strength and modulus of LCP-1 are much lower than those

Table 2. Thermal Properties of PBT/LCP-2 Blends.

Composition PBT/LCP-2	T_g (℃)	T_c (℃)	T_m (℃)	ΔH_f (cal/g)
100/0	33	42	222	13.19
97/3	33	42	222	13.44
95/5	33	42	222	12.13
90/10	33	42	222	11.90
80/20	33	42	222	10.53
70/30	33	42	222	9.56
50/50	33	43	223	6.38
20/80	34	–	223	2.82
0/100	–	–	288	–

T_g, T_c, T_m(Quenching run), ΔH_f(First heating run)

of other typical thermotropic liquid crystalline polymers such as Vectra B950 and X7G.[13] For the blend with lower concentration of LCP(up to 30 wt%), tensile strength and flexural strength were decreased or remained constant due to the weak adhesion between two phases as the LCP content was increased. The elongational properties of the two blend systems were different from each other. As shown in Fig. 3, the decrement of elongation of LCP-1/PBT blend was smaller than that of LCP-2/PBT blend. This means that the adhesion of the former is better than the latter due to the partial miscibility as fore mentioned.

The effects of specimen thickness on the tensile properties are shown in Table 5 and Fig. 4 for LCP-1/PBT blends, and Table 6 and Fig. 5 for

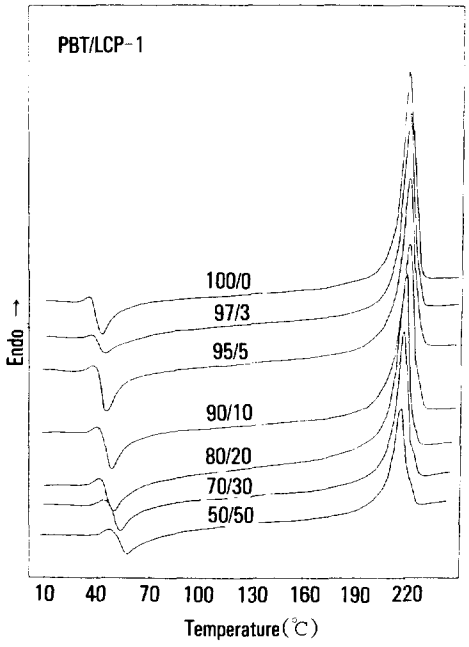


Fig. 1. Differential scanning calorimetry scans of the PBT/LCP-1 blends during the heating from the quenched sample. Heating rate : 20℃/min.

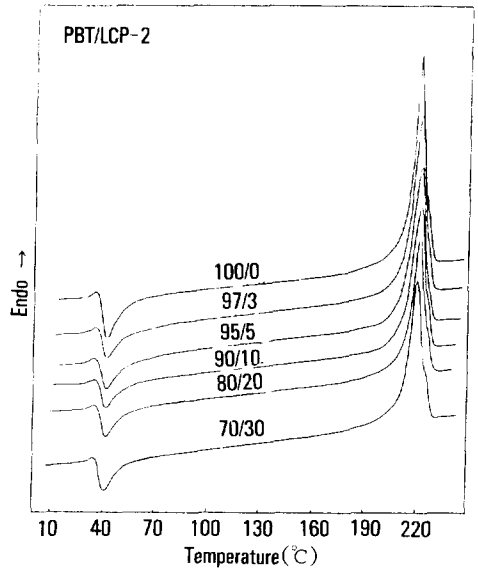


Fig. 2. Differential scanning calorimetry scans of the PBT/LCP-2 blends during the heating from the quenched sample. Heating rate : 20℃/min.

Table 3. Mechanical Properties of PBT/LCP-1 Blends.

Composition PBT/LCP-1	Tensile Strength (kg/cm^2)	Elongation (%)	Flexural Strength (kg/cm^2)	Flexural Modulus (kg/cm^2)	Impact Strength (kgcm/cm)
100/0	570	50.0	930	24,700	1.95
97/3	590	49.0	930	24,800	1.54
95/5	580	35.1	930	24,900	1.54
90/10	550	12.4	930	24,800	1.41
80/20	560	5.3	930	25,000	1.36
70/30	560	4.3	990	26,600	1.09
50/50	600	3.4	1120	30,000	1.09
20/80	650	5.7	1380	45,200	10.91
0/100	700	3.2	1460	46,100	15.07

Table 4. Mechanical Properties of PBT/LCP-2 Blends.

Composition PBT/LCP-2	Tensile Strength (kg/cm^2)	Elongation (%)	Flexural Strength (kg/cm^2)	Flexural Modulus (kg/cm^2)	Impact Strength (kgcm/cm)
100/0	570	50.0	930	24,700	1.95
97/3	560	49.2	1020	26,600	2.09
95/5	550	8.0	1020	26,600	1.91
90/10	530	4.6	1020	27,400	1.73
80/20	600	2.6	1030	29,500	1.32
70/30	640	2.0	1060	58,700	1.41
50/50	750	1.7	1070	78,100	1.68
20/80	1120	2.1	2100	121,500	10.90
0/100	1540	3.3	2950	186,400	13.07

Table 5. Tensile Properties with Specimen Thickness for PBT/LCP-1 Blends.

Thickness	1/8″ Specimen*		1/16″ Specimen*		1/32″ Specimen**	
Composition PBT/LCP-1	Tensile Strength (kg/cm^2)	Elongation (%)	Tensile Strength (kg/cm^2)	Elongation (%)	Tensile Strength (kg/cm^2)	Elongation (%)
100/0	570	50.0	580	200.0	520	200 ↑
97/3	590	49.0	570	103.5	550	200 ↑
95/5	580	35.1	580	32.5	540	200 ↑
90/10	550	12.4	530	25.4	480	93
80/20	560	5.3	540	9.5	470	4.0
70/30	560	4.3	550	9.4	450	3.3
50/50	600	3.4	770	8.8	370	2.0
20/80	650	5.7	870	5.2	—	—
0/100	700	3.2	930	4.3	470	4.0

* Flow direction : 1/8″, 1/16″, ** Transverse direction : 1/32″

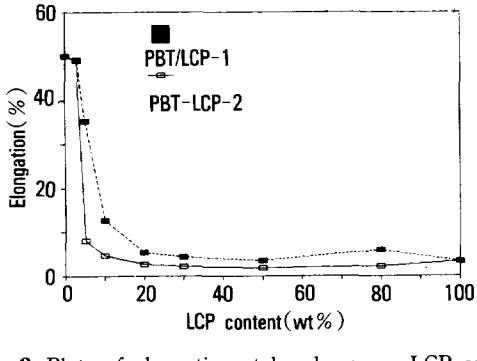


Fig. 3. Plots of elongation at break versus LCP content for PBT/LCP blends. Specimen thickness : 1/8″ dumbbell.

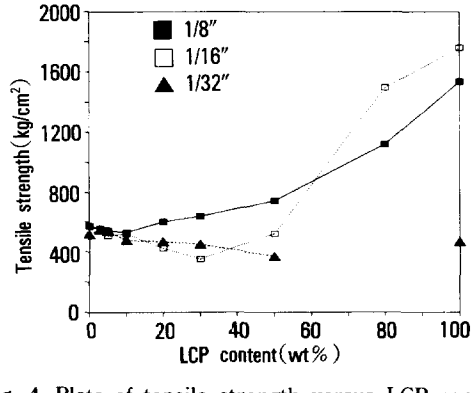


Fig. 4. Plots of tensile strength versus LCP content for PBT/LCP-1 blends. Flow direction : 1/8″, 1/16″. Transverse direction : 1/32″.

Table 6. Tensile Properties with Specimen Thickness for PBT/LCP-2 Blends.

Thickness	1/8″ Specimen		1/16″ Specimen	
Composition PBT/LCP-2	Tensile Strength (kg/cm^2)	Elongation (%)	Tensile Strength (kg/cm^2)	Elongation (%)
100/0	570	50.0	580	200↑
97/3	560	49.2	550	112.8
95/5	550	8.0	510	14.0
90/10	530	4.6	520	24.8
80/20	600	2.6	420	2.0
70/30	640	2.0	350	1.5
50/50	750	1.7	520	1.0
20/80	1120	2.1	1490	1.8
0/100	1540	3.3	1760	1.3

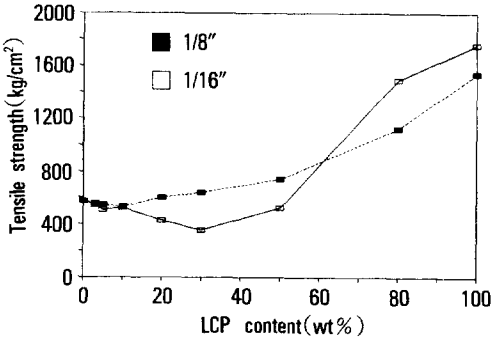


Fig. 5. Plots of tensile strength versus LCP content for PBT/LCP-2 blends.

LCP-2/PBT blend. The injection molded specimens used in this study were 1/8″, 1/16″ and 1/32″ in thickness. The tensile strength measurements were made both along the flow direction of 1/8″ bar and 1/16″ bar, and across the flow direction of 1/32″ bar on the LCP-1/PBT blend. As shown in Fig. 4, tensile strength was decreased as the thickness of test bar was decreased in the blend with lower concentration of LCP(up to 50wt%). But above 50wt% of LCP content, the increment of tensile strength of 1/16″ bar was larger than that of 1/8″ bar and the decrement of tensile strength of 1/32″ bar was larger than that of the blend with lower concentration of LCP. This may be accounted for mainly by higher orientation in the outer

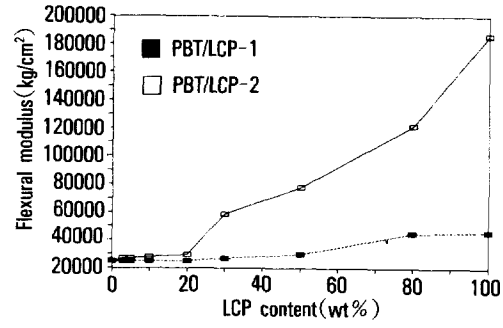


Fig. 6. Plots of flexural modulus versus LCP content for PBT/LCP blends. Specimen thickness : 1/8″.

layer due to the fountain flow phenomenon and by higher anisotropy at small thickness(e. g. 1/16″ bar and 1/32″ bar), with the anisotropy increasing as thickness was decreased and by the formation of LCP fibril above 50wt% of LCP. That is, LCP domain was changed from spherical droplets to fibrils with increasing LCP content(especially 50wt% of LCP)[12,15~17]. Further, the surface effect and the aspect ratio of LCP fibril in the 1/16″ bar may be larger than 1/8″ bar due to the different shear rate.[11] For the LCP-2/PBT blend, the tensile strength of 1/16″ bar was larger than that of 1/8″ bar at 80wt% of LCP-2 content. Compared with the result of LCP-1/PBT blend, the fibril formation is difficult for the LCP-2 because the viscosity ratio of LCP-2 to PBT is higher than the viscosity ratio of LCP-1 to PBT.

According to Jackson and Kuhfuss,[18] materials with high flexural modulus can be obtained when the pure LCP is injection molded. Flexural modulus of LCP-1/PBT and LCP-2/PBT blends is given in Fig. 6. As the LCP content was increased, flexural modulus of the LCP/PBT blend was increased. In fact, flexural modulus of the blend with 50wt% of LCP-2 was approximately three times of the value of PBT homopolymer because LCP-2 might act as a reinforcing agent of blends. However, this modulus value is 58% lower than the flexural modulus value obtained for the pure LCP-2 injection molded under similar conditions.

Morphology

The morphology of the blend was investigated

by the scanning electron microscopy(SEM) of the fractured surface prepared in liquid nitrogen. The fractured surface of pure PBT and pure LCP-1 are shown in Fig. 7(a) and Fig. 7(b). In Fig. 7(b), the morphology of pure LCP-1 appeared to be fibrillar in character and the degree of fibrillation was high due to the rigid nature of the LCP. It shows the similar structure of liquid crystalline polymer fiber as defined by Jaffe et al.[19] But in Fig. 7(a), the morphology of pure PBT appeared to be non-fibrillar in character.

The apparent interfacial adhesion could be determined generally from SEM micrograph.[11~14] Fig. 8 shows a fractured surface of LCP/PBT(10/90) blend. In Fig. 8, the fractured surface of LCP/PBT blend revealed ellipsoidal LCP domains embedded in the PBT matrix and LCP-1/PBT blend showed a somewhat better interfacial adhesion than LCP-2/PBT blend due to the partial miscibility. To observe the effect of processing temperature on the morphology of LCP-2/PBT(30/70) blend, the injection molding experiments were carried out at two temperature, 275℃ and 295℃, because the melting point of LCP-2 is 288℃. As shown in Fig. 9, injection bar molded below the melting point of LCP-2 produced a fibrillar LCP domain, whereas injection bar molded above the melting point of LCP-2 resulted in a spherical LCP particles. From these morphology, it is obvious that a desired fibrillar morphology of LCP can be obtained by cont-

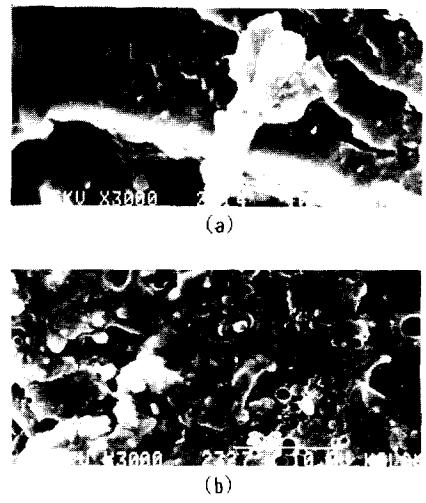


Fig. 8. Scanning electron micrographs of the fracture surfaces of (a) PBT/LCP-1(90/10) blend and (b) PBT/LCP-2(90/10) blend(X3000).

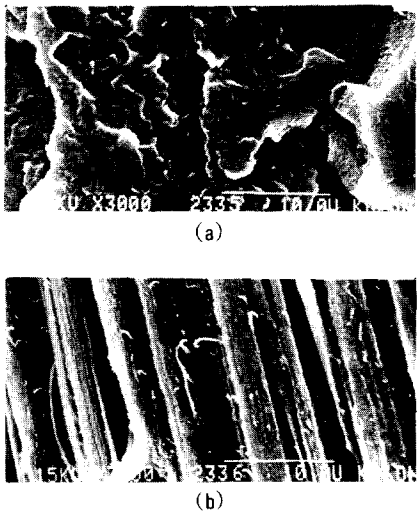


Fig. 7. Scanning electron micrographs of the fracture surfaces of (a) PBT and (b) LCP-1(X3000).

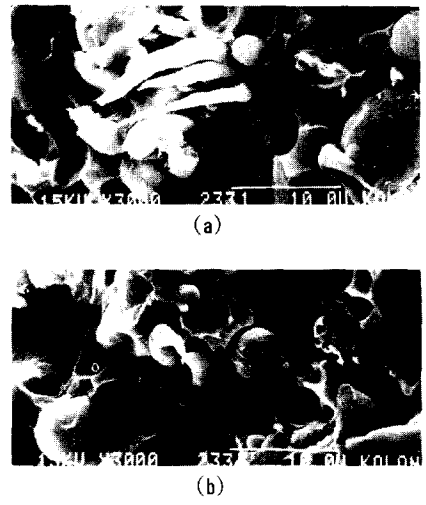


Fig. 9. Scanning electron micrographs of the fracture surfaces of PBT/LCP-2(70/30) blend. (a) molded at 275℃ and (b) molded at 295℃.

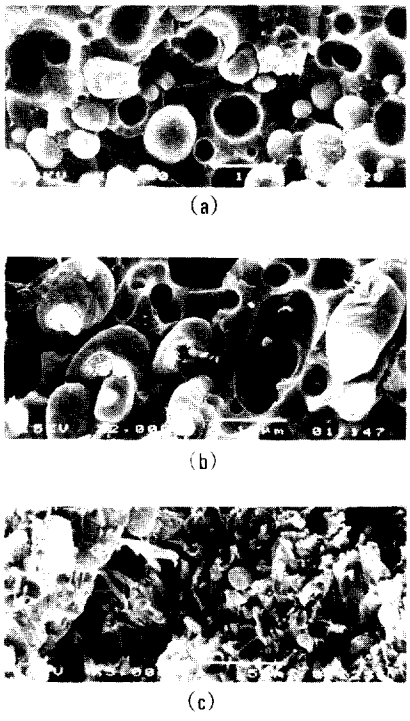


Fig. 10. Scanning electron micrographs of the fracture surface of 1/8″ bar of (a) PBT/LCP-2(70/30), (b) PBT/LCP-2(50/50) and (c) PBT/LCP-2(20/80) blend.

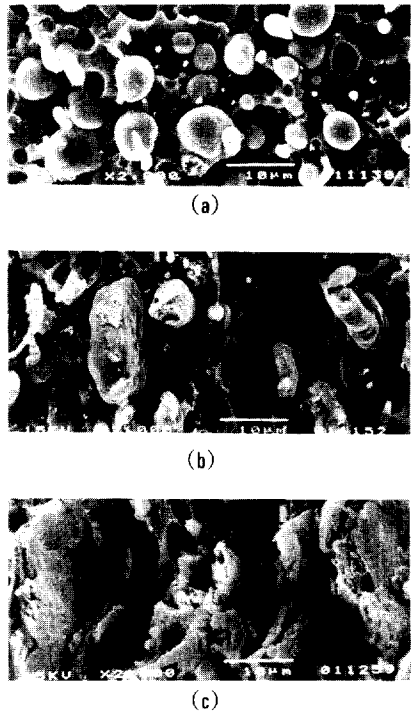


Fig. 11. Scanning electron micrographs of the fracture surface of 1/6″ bar of (a) PBT/LCP-2(70/30), (b) PBT/LCP-2(50/50) and (c) PBT/LCP-2(20/80) blend.

rolling processing temperature.

To investigate the effect of specimen thickness on the morphology for the LCP-2/PBT blend, 1/8″ bar and 1/16″ bar were fractured at cryogenic temperature. The fibril formation of LCP-2 is shown in the photograph of 1/8″ bar with 80wt% LCP-2 as shown in Fig. 10, while the photograph of 1/16″ bar with 50wt% LCP-2 shows some fibrillar LCP-2 domain as shown in Fig. 11. The fibril formation of 1/8″ bar seemed to be more difficult than that of 1/16″ bar due to the different shear rate.

CONCLUSIONS

1. In the wholly aromatic liquid crystalline copolyester/PBT blends, a partial compatibility was predicted whereas wholly aromatic liquid crystalline copolyesteramide proved to be incompatible with PBT.

2. At the high concentrations of LCP(above 50 wt%), tensile and flexural strengths and flexural modulus were increased with increasing LCP content.

3. The studies of the morphology of LCP/PBT blends revealed that LCP formed finely dispersed spherical domains in the PBT matrix and the interfacial adhesion between two polymers was poor.

4. The ultimate fibrillar structure of LCP domains appeared to be closely related to the injection molding temperature and the specimen thickness.

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