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Thermal Properties and Morphology of Liquid Crystalline Copolyester and Polyester Elastomer Blends

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THERMAL PROPERTIES AND MORPHOLOGY OF LIQUID CRYSTALLINE COPOLYESTER AND POLYESTER ELASTOMER BLENDS

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ABSTRACT

Polyester elastomer (PEL) blends having a hard segment of polyester (PBT), soft segment of polyether (PTMG), and a liquid crystalline copolyester (LCP), poly(benzoate-naphthoate) were prepared with a twin-screw extruder. Test specimens for thermal properties were prepared by injection molding. Rheological properties and morphology were investigated by Instron capillary rheometer (ICR) and scanning electron microscopy (SEM). Thermal properties of the LCP/PEL blends were investigated by DSC, dilatometer, heat deflection temperature tester, and a Rheovibron viscometer. DSC study revealed a partial miscibility between LCP and PEL. It was found that the LCP acted as a nucleating agent for the crystallization of PEL in the LCP/PEL

blends. The dimensional and thermal stability of the blends were increased by increasing the LCP content. The storage modulus (E') was improved by increasing the LCP content. The blend viscosity showed a minimum value at 5 wt% of LCP which increased by increasing the LCP content above 5 wt% of LCP. The morphology of the LCP/PEL blends showed poor interfacial adhesion between the two phases, and the fibrillar structure of LCP phase in the matrix was affected by the LCP content, shear rate, and extrusion temperature. The morphology of the blends was found to be affected by their compositions and processing conditions.

INTRODUCTION

The invention of kevlar, a high modulus lyotropic aromatic polyamide opened new areas of application leading to the replacement of inorganic fibers [1,2]. However, kevlar is not melt processable, Melt processable thermotropic liquid crystalline polymers (LCP) have found tremendous application in the polymer market.

Usually these thermotropic liquid crystalline polymers exhibit much lower shear viscosities than the flexible chain polymers making them easily melt processable.

It is well known that fiber reinforced composite produces outstanding mechanical properties [3]. The principle of fiber reinforcement is that hard and strong rods or fibers in the matrix polymer transfer the applied force. In order to improve the strength and modulus of the composite materials, several conditions are essential: a large aspect ratio of fibers, and strong adherence at the interface of fiber and matrix. Recently, fibers with diameter of 1-10 μm were widely used in fiber reinforced materials. It is easy to find fibers satisfying the condition of aspect ratio, but it is difficult to satisfy the condition of strong adhesion. There have been many studies which attempted to improve the interfacial adhesion between fiber and polymer matrix [4,5]. Currently, both lyotropic and thermotropic liquid crystalline polymers (LLCP and TLCP) are used for reinforcement. Thermotropic polymers have attracted much attention due to their good processability and many other advantages mentioned in earlier literature [6-8].

Blending of polymers to obtain a blend of superior mechanical property and thermal stability has been used by the polymer industry for a long time. Blends of LCP's with engineering thermoplastics are fast gaining popularity and are the focus of much attention [9,10]. The LCP phase in these blends forms fibers in the matrix of the thermoplastic material, leading to the formation of the so called self-reinforced or *in-situ* composites [11-16]. Blends of LCPs and thermoplastics consist of two phases since the two polymers are generally immiscible. The properties of the

blends are determined by the relationship between the different polymeric phases. Many researchers have studied polymer blends in which one component is liquid crystalline in nature [17,18]. In general, these researchers have elucidated the mechanical and morphological characteristics of such blends. However, the systematic studies on thermal and dynamic mechanical properties have not been carried out.

In this work, we focus on twin screw extruder blended and injection molded blends of a thermotropic liquid crystalline copolyester with polyester elastomer. The studies on the compatibility between two polymers, the dimensional stability of the blends, and the effect on the crystallization of PEL in the blend will be carried out. We also will study the conditions necessary for the development of a fibrillar morphology of the liquid crystalline copolyester. An attempt will be made to correlate the structure of the blends from SEM with the observed rheology. The thermal stability of the blends and the effect on the crystallization of PEL in the blends will also be explained. Furthermore, the relationship of the process conditions and morphology for the LCP/PEL blends will be also discussed.

EXPERIMENTAL

Materials

A matrix polymer of polyester elastomer (PEL) that consists of a hard segment of polyester (PBT) and soft segment of polyether (PTMG) was KOPEL KP 3355 (IV=2.5: inherent viscosity of a solution in *o*-chlorophenol at 25°C) manufactured by Kolon, Ltd. The weight ratio of hard segment to soft segment in the polyester elastomer was 1.33. A liquid crystalline copolyester (LCP) was Vectra A950 manufactured by Celanese Corp. The LCP was used as reinforcing agent of the PEL matrix.

Blends and Specimen Preparation

Materials were carefully dried at 100°C under vacuum for 8 hours, blended by using a twin-screw extruder (Automatic ZCM 32/36), immediately quenched in a water bath, and finally pelletized. The blends were carefully redried at 100°C under vacuum for 8 hours. The barrel was maintained at either 230, 290, 285, and 290°C. The rotor speed was fixed at 240 rpm. The contents of LCP in the blends were varied from 1 to 50 wt%. Molding was performed by using an Engel Es-1 injection machine and an appropriate mold producing ASTM test specimens. The blend was injected at 290°C (above the melting temperature of the LCP) into a mold which was kept at a constant temperature of 40°C.

Instruments and Measurement

The rheological behavior of the resins and their blends was studied by using an Instron 4201 capillary rheometer attached to the Instron testing machine. Measurements were done at 260°C and 290°C. A capillary with $L/D=33$ and $D=0.0762$ cm was used. For the morphology studies, the extrudates manufactured by capillary with $L/D=16$ were quenched with liquid nitrogen and fractured at cryogenic temperature. The fractured surfaces were coated with gold palladium for microscopy and observed with a Jeol JSM-35CF scanning electron microscopy. Thermal analyses of the blends were performed by Perkin Elmer DSC-7 thermal analyzer. All runs were done under nitrogen atmosphere at a heating or cooling rate of 20°C/minute and a temperature scan range from 0°C to 290°C. The isothermal crystallization data were obtained by heating the dried sample up to 290°C under nitrogen atmosphere, after holding it for 7 minutes, and then cooling at 100°C/minute to a predetermined crystallization temperature. Dynamic mechanical properties were obtained by a Toyo model DDV-II Rheovibron viscoelastometer. All the measurements were carried out at a frequency of 110HZ with a heating rate of 3°C/minute and a temperature scan range of -150°C to 200°C. The dimension of test bars was 0.3 x 0.3 x 7 cm. The dimensional stability of the blends was determined by the measurement of linear thermal expansion coefficient. The thermal expansion coefficient of the blends was measured by a Toyoseiki A-402330050 dilatometer in the temperature range from 30°C to 70°C. The measurements were made in the flow direction of the injection molded specimens. Heat deflection temperature (MDT) was determined according to ASTM D648 using a Tinius Olsen model 66-5 heat deflection temperature tester. The measurements were performed by using a load of 1.82MPa and raising the temperature by 2°C/minute. The dimension of the test bars was 0.635 x 1.27 x 12.7 cm.

RESULTS AND DISCUSSION

Thermal Properties

The thermal properties of LCP/PEL blends was studied by various instrumental methods. In order to erase all various thermal history, the samples were heated up to 290°C at 20°C/minute in the DSC and quickly quenched. Then the sample heating experiment was performed. Table 1 shows the thermal properties of quenched LCP/PEL blends. The T_g of LCP/PEL blends increased from -43°C (PEL) as the LCP content increased. This means that the LCP is partially compatible with PEL because of their chemical similarity [17-20]. The secondary crystall-

TABLE 1. Thermal Properties of LCP/PEL Blends.

Composition LCP/PEL	T_g^a (°C)	T_{sc}^b (°C)	T_m^c (°C)	$(T_m - T_g)^c$ (°C)	T_c^d (°C)	ΔT_c^e (°C)
0/100	-43	-8	195	238	154	33
5/95	-38	-10	194	232	165	25
10/90	-38	-10	194	232	165	22
20/80	-37	-10	193	230	165	22
30/70	-36	-10	193	229	165	17
50/50	—	-11	193	—	164	14
100/0	—	—	278	—	—	—

^aGlass transition temperature of PEL in the blend.

^bSecondary crystallization temperature of the blends.

^cMelting temperature of the blends.

^dCrystallization temperature of the blends.

^eDegree of super cooling of the blends.

ization temperature (T_{sc}) of the blends slightly decreased as the LCP content increased. The lowering of T_{sc} in the blends may be explained by considering the crystallization of pure PEL component. For a given polymer, $(T_m - T_g)$ can be viewed as the "window for crystallization". Pure PEL has a $(T_m - T_g)$ value of approximately 238°C. The $(T_m - T_g)$ of the blends decreased as the LCP content increased. This observation in conjunction with the lowering of T_{sc} suggests that the LCP component in the blend may possibly be acting as a nucleating agent for the crystallization of PEL. Also supporting this concept are the value for apparent supercooling ($\Delta T_c = T_m - T_o$; T_m is the melting peak temperature and T_o is the onset temperature of crystallization), which represent the width of the crystallization temperature region. The apparent supercooling (ΔT_c) required for initiating crystallization decreased from 33°C to 14°C as the LCP content increased from 0 wt% to 50 wt%, respectively. This indicates that as the level of possible nucleating LCP species increased, the crystallization rate was apparently enhanced and hence a narrow (ΔT_c) was observed. This speculation is somewhat similar to other's results [21-28]. The maximum melting peak of the blends decreased as the LCP content increased. This is due to a partially solubility effect of the LCP. Double melting points of PEL were observed at 195°C and 207°C. This is originated from the block copolymer of polyester elastomer. The melting point of LCP was 278°C, but

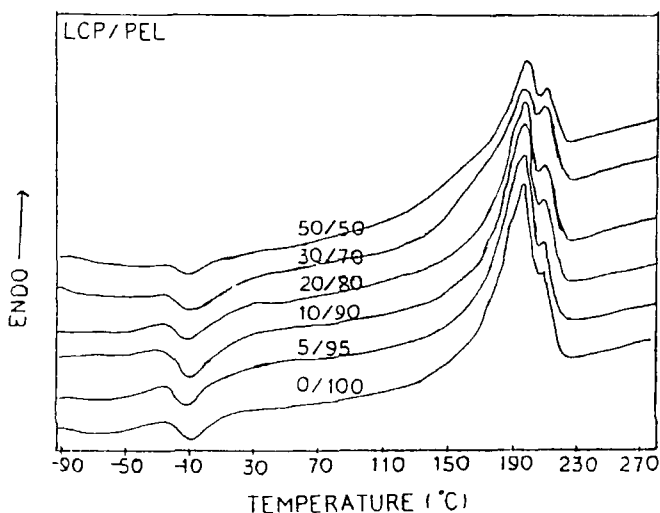


Figure 1. Differential scanning calorimetry scans of the LCP/PEL blends during heating the quenched sample. Heating rate: 20°C/min.

its T_g was not apparent. The DSC thermograms of the LCP/PEL blends are shown in Figure 1. These results on the thermal behavior were in a fair agreement with Joseph's results [21], which showed a lowering of T_{sc} and T_m in the LCP/PET blends. Joseph found that the melting point depression of PET is due to a partial diluent effect caused by the LCP and the lowering of T_{sc} in the blends may be explained by considering the crystallization of PET. The crystallization peak temperature of the LCP/PEL blends slightly increased with increasing LCP content (Figure 2). It was found that the LCP acts as a nucleating agent for the crystallization of PEL. It is suggested that LCP has a favorable effect on the crystallization of PEL in the blend. These results agreed well with the results for the LCP/PC blends by Jung and Kim [19].

Figure 3 shows the half time of crystallization ($t_{1/2}$) as a function of the isothermal crystallization temperature for the LCP/PEL blends. The half time of crystallization data was obtained by heating the dried sample up to 290°C under nitrogen atmosphere, holding it for 7 minutes, cooling at 100°C/minute up to the crystallization temperature, and then measuring the time at which the extent of crystallization is 50% complete. From Figure 3, like other semicrystalline polymers, the half time of crystallization of the blends increased with increasing the isothermal crystallization temperature. The LCP component dramatically decreased the half

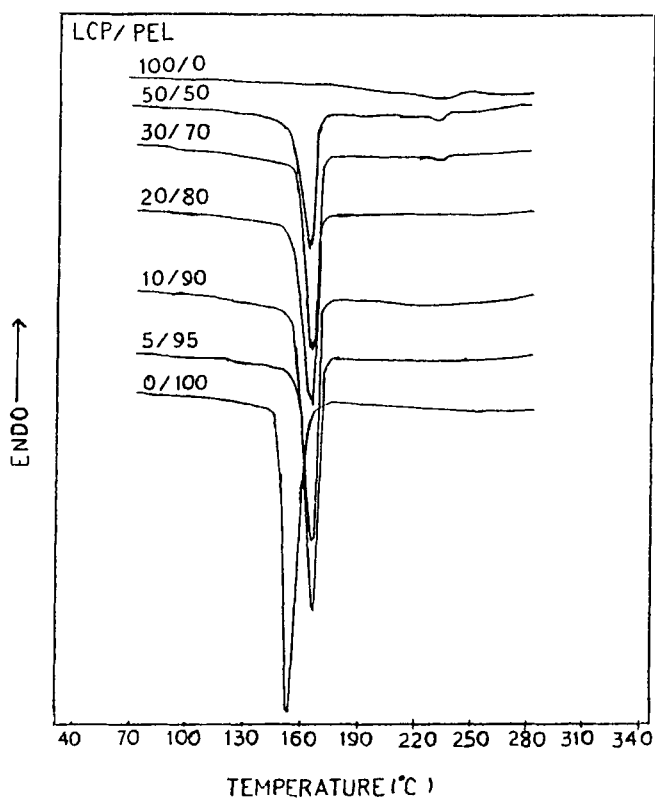


Figure 2. Differential scanning calorimetry curves of crystallization for the LCP/PEL blends. Cooling rate: 20°C/min.

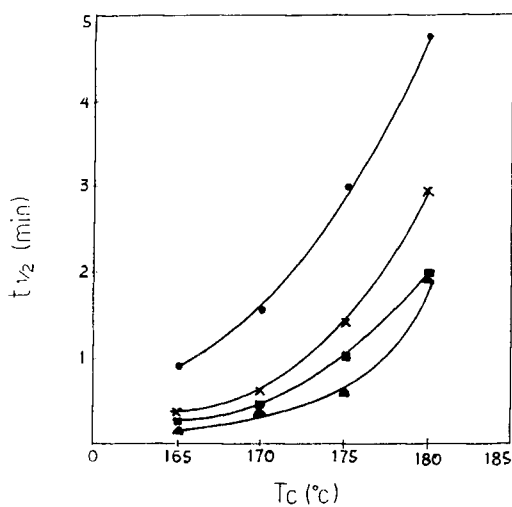


Figure 3. Plot of crystallization half time versus isothermal crystallization temperature for the LCP/PEL (0/100) blend (●), LCP/PEL (5/95) blend (▲), LCP/PEL (10/90) blend (■), LCP/PEL (30/70) blend (×).

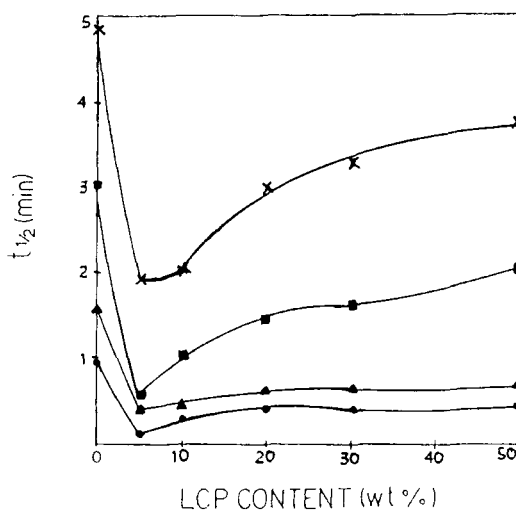


Figure 4. Plots of crystallization half time versus LCP content for the LCP/PEL blends at different crystallization temperature. (●) 165°C, (▲) 170°C, (■) 175°C, and (×) 180°C.

time of crystallization of LCP/PEL blends. It was found that this accelerating effect of the LCP is related to the heterogeneous nucleation. Nadkarni et al, [22-24] reported that the crystallization of PPS is accelerated by glass fiber due to the heterogeneous nucleation.

Figure 4 shows the half time of crystallization as a function of LCP content for the LCP/PEL blends. The half time of crystallization decreased with increasing LCP content and showed a minimum value at 5 wt% of LCP. This is due to the nucleating effect.

The dimensional and thermal stabilities of the blends were determined by the measurement of linear thermal expansion coefficient and heat deflection temperature (HDT). Figure 5 shows the linear thermal expansion coefficient as a function of LCP content for the LCP/PEL blends. The pure LCP exhibited a very low thermal expansion coefficient and also caused an abrupt reduction in the thermal expansion coefficient of the blends. The linear thermal expansion coefficient of the blends decreased with increasing LCP content. This is due to the orientation of the rigid units in the LCP molecules. It was also found that the addition of LCP enhanced the dimensional stability of the PEL.

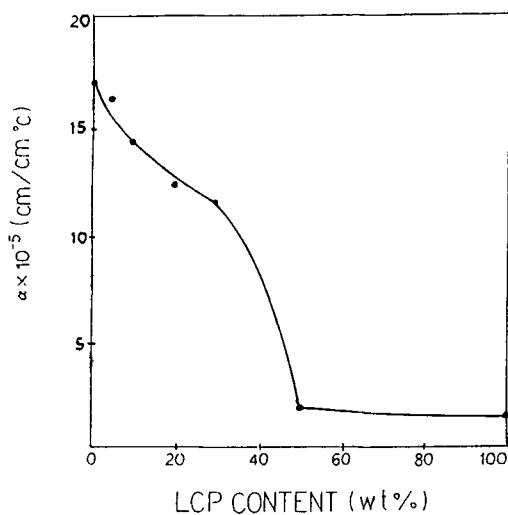


Figure 5. Plot of linear thermal expansion coefficient versus LCP content for the LCP/PEL blends from 30°C to 70°C.

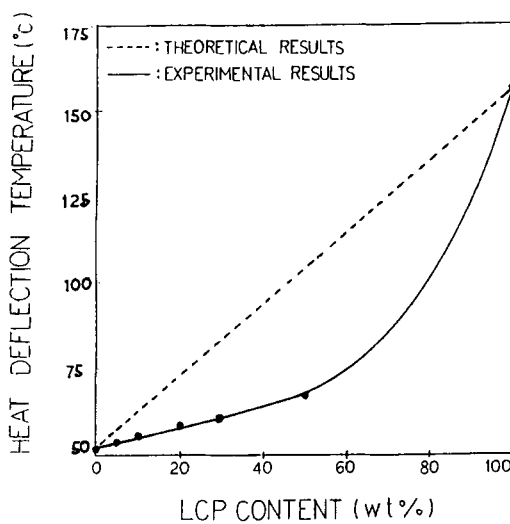


Figure 6. Plot of heat deflection temperature versus LCP content for the LCP/Pel blends.

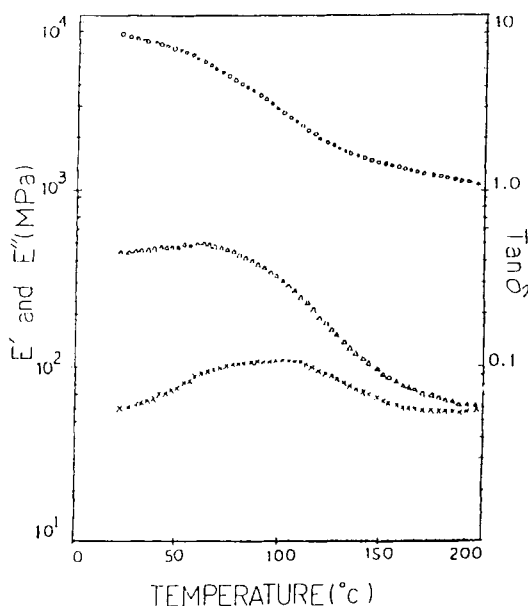


Figure 7. Plots of storage modulus (○), $\tan \delta$ (×), loss modulus (▲) versus the temperature for LCP.

Figure 6 shows the heat deflection temperature as a function of LCP content for the LCP/PEL blends. The heat deflection temperature of the LCP/PEL blends increased with increasing LCP content. This means that LCP enhance the thermal stability of PEL. This is due to the existence of the rigid unit of LCP in these blends. The heat deflection temperature of pure LCP was 157°C. These results showed that the LCP enhanced the dimensional and thermal stabilities of the PEL.

Figures 7-10 show the storage modulus (E'), $\tan \delta$ and loss modulus (E''), respectively as a function of temperature for LCP, PEL, and their blends. In Figure 7, the α relaxation temperature of the LCP at about 104°C is associated with the onset of cooperative motions along the main chain [27-29]. The storage and loss moduli of LCP decreased very slowly with increasing the temperature. It is presumed that the chain alignment was still maintained in the liquid crystalline polymers above the α relaxation temperature.

Figure 8 shows the storage modulus (E') as a function of temperature for the LCP/PEL blends. The storage modulus of the blends at 30°C increased with increasing LCP content. It was found that the LCP reinforced the PEL matrix. The storage modulus decreased remarkably with increasing temperature. Figure 9 shows

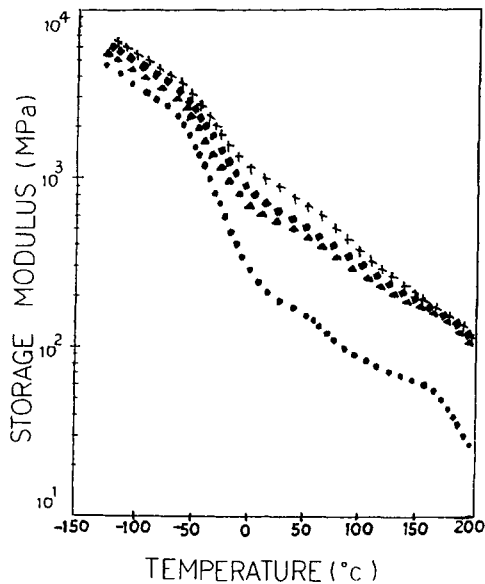


Figure 8. Plots of storage modulus (E') versus the temperature for the LCP/PEL blends: (1) 0/100 (●), (2) 10/90 (▲), (3) 30/70 (■), and (4) 50/50 (×).

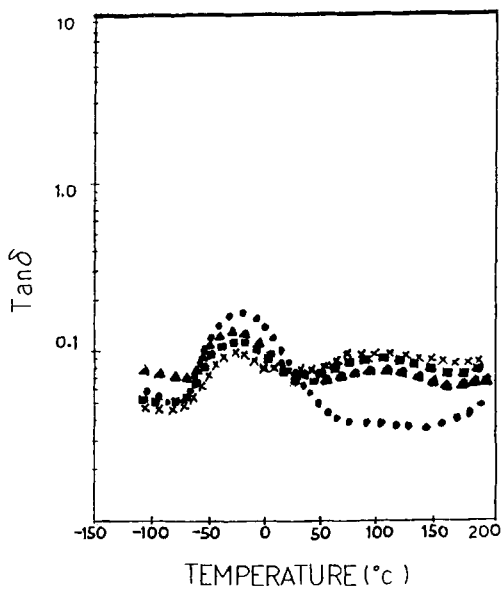


Figure 9. Plots of $\tan \delta$ versus the temperature for the LCP/PEL blends: (1) 0/100 (●), (2) 10/90 (▲), (3) 30/70 (■), and (4) 50/50 (×).

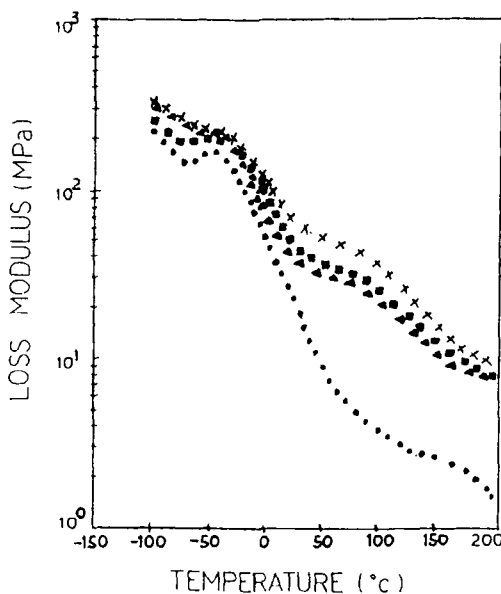


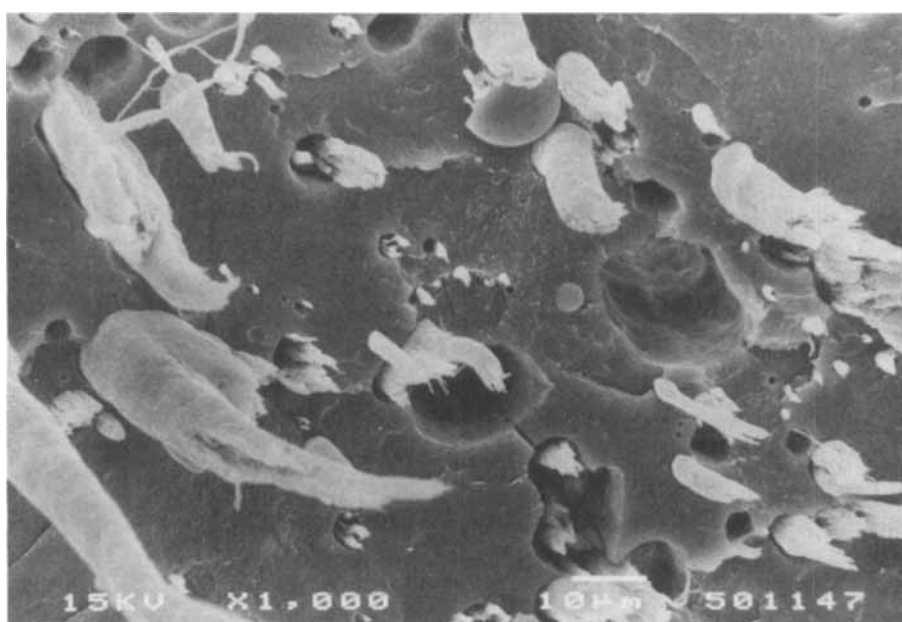
Figure 10. Plots of loss modulus (E'') versus the temperature for the LCP/PEL blends: (1) 0/100 (\bullet), (2) 10/90 (\blacktriangle), (3) 30/70 (\blacksquare), and (4) 50/50 (\times).

the $\tan \delta$ as a function of temperature for the LCP/PEL blends. The $\tan \delta$ of PEL showed a maximum at around -25°C . This is believed to be the α relaxation of the PEL. At this temperature, the storage modulus decreased remarkably, while the loss modulus showed a maximum value. The height of the $\tan \delta$ peak decreased with increasing LCP content as shown in Figure 9.

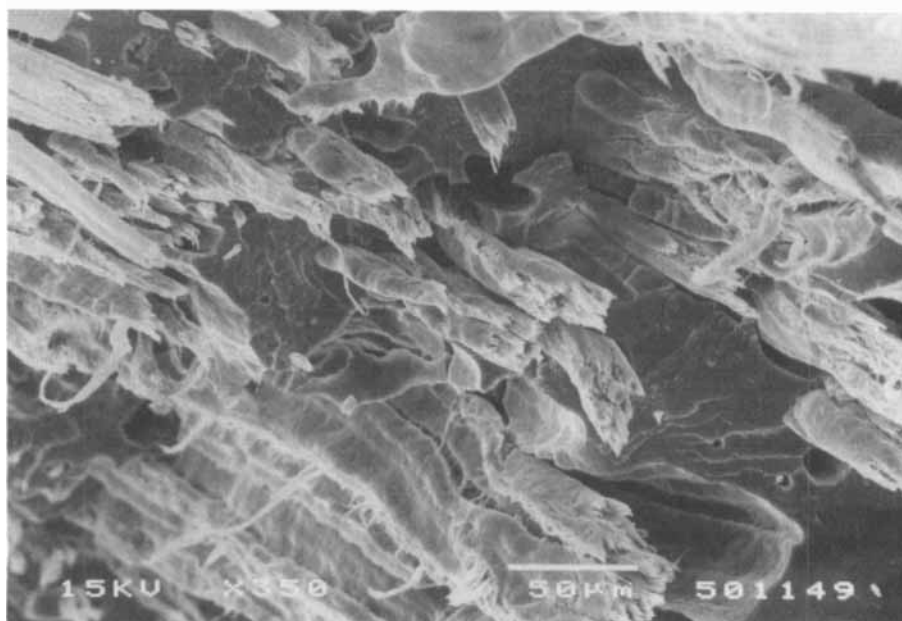
Figure 10 shows the loss modulus (E'') as a function of temperature for the LCP/PEL blends. The loss modulus of the blends increased with increasing LCP content at 30°C , but the height of the loss modulus peak at a temperature where showed a maximum $\tan \delta$ peak decreased with increasing LCP content. This means that the relative decrease in the height of $\tan \delta$ peak and E'' are related to increase the extent of crystallinity in the polymers because the transition behavior is associated with the local mobility of the polymer chains in the amorphous region of the polymer.

Morphology

Figure 11 shows the fractured surfaces of the extrudates formed by extrusion at 290°C and 5000s^{-1} . It was found that the blend morphology was fibrous and similar to that of the pure LCP above 30 wt% of LCP. In Figure 11, holes were left in the matrix because some of the particles and fibrils were pulled out of the matrix

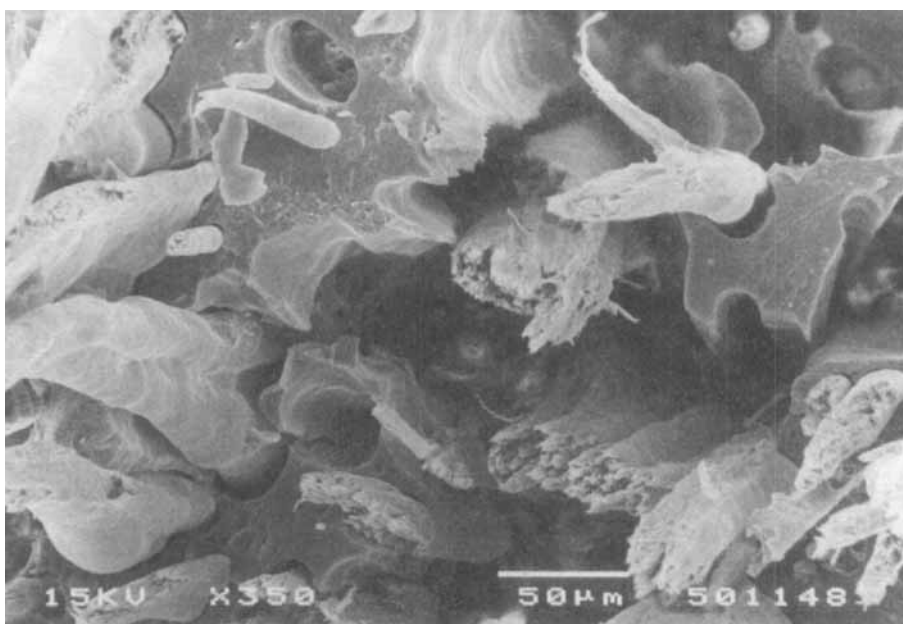


(a)

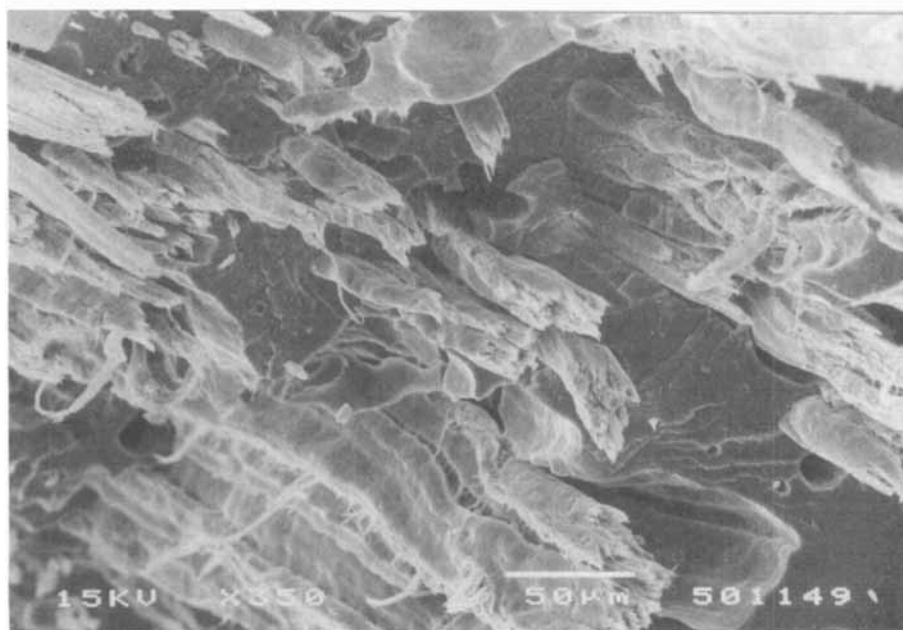


(b)

Figure 11. Scanning electron micrographs of the fractured surfaces of (a) LCP/PEL (30/70) blend and LCP/PEL (50/50) blend. All samples were extruded in a capillary viscometer ($L/D=16$) at $5000s^{-1}$ and $290^{\circ}C$ (X3500).



(a)



(b)

Figure 12. Scanning electron micrographs of the fractured surfaces of the LCP/PEL (30/70) blend and LCP/PEL (50/50) blend. All samples were extruded in a capillary viscometer ($L/D=16$) at (a) $1000s^{-1}$ and $5000s^{-1}$ (X3500).

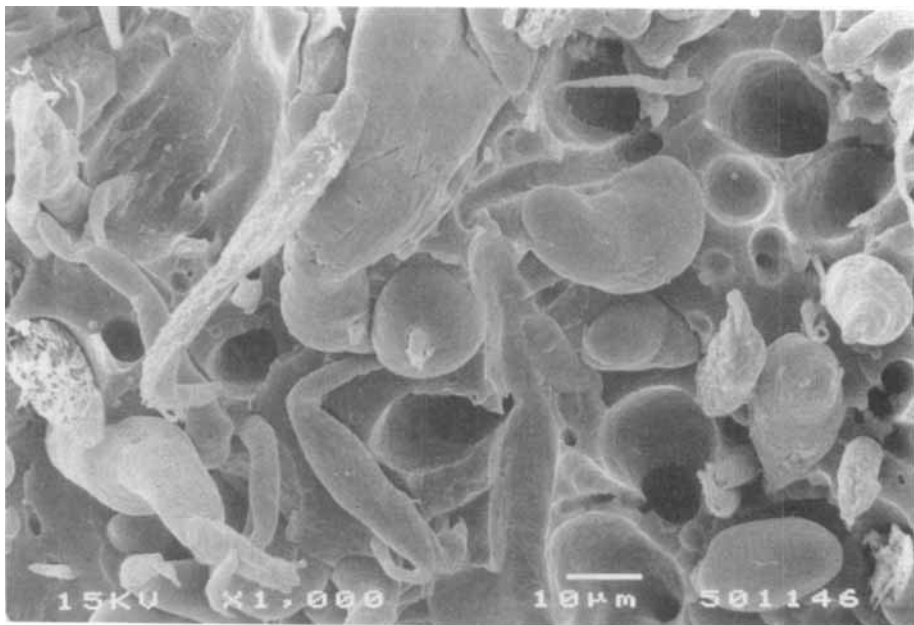
during the fracture. This means that the interfacial adhesion between two polymers is poor. The T_g of LCP/PEL blends was increased with increasing LCP content, This means that the LCP is partially compatible with PEL because of the chemical similarity of two polymers, But the interfacial adhesion between two polymers was poor as shown in Figure 11. This is due to the limited compatibility of two polymers.

Figure 12 shows the morphology of LCP/PEL (50/50) blend resulted from shear melt flow in order to observe the effect of shear rate (deformation rate) on the morphology of the LCP/PEL blends. The blend morphology at shear rate $5000s^{-1}$ was more fibrous than the blend morphology at shear rate $1000s^{-1}$. The domain size was reduced and the phase was deformed with increasing the shear rate. Above the shear rate $5000s^{-1}$, the blend morphology was fibrous and similar to that of the pure LCP. This is due to the increase in the shear thinning behavior of the LCP component. From Figure 12, the LCP domains become more elongated with a preferential orientation parallel to the machine direction with increasing deformation rate. It was found that the effect of increasing deformation rate was to elongate more effectively the LCP phase in the entrance region. Figure 13 shows the morphology of the LCP/PEL (50/50) blend resulting from different melt temperature in order to observe the effect of processing temperature on the morphology of the blends. Since the melting point of the LCP is $278^{\circ}C$, the measurements of rheology were carried out to observe the effect of processing temperature on the morphology of the LCP/PEL blends at two temperatures, $260^{\circ}C$, and $290^{\circ}C$. Extrudates extruded at $260^{\circ}C$, resulted in a fibrillar LCP domain, and extrudates extruded at $290^{\circ}C$, produced more effectively a fibrillar LCP domain as shown in Figure 13. From these morphologies, it was found that a desired fibrillar morphology of LCP can be obtained by controlling processing temperature. It was found that a fibrillar morphology of LCP can be obtained more effectively by controlling the processing temperature and shear rate.

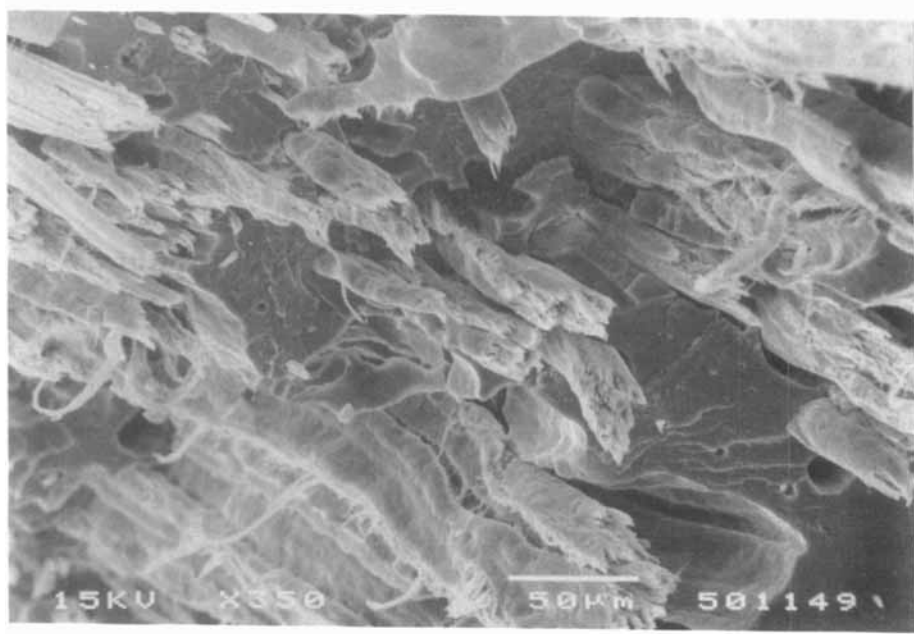
It can be concluded that the ultimate structure of the LCP phase is closely related to the processing conditions (temperature and shear rate) and their compositions.

Rheological Properties

Figure 14 shows the shear rate dependence on the melt viscosity of LCP, PEL, and LCP/PEL blends. The viscosities of LCP and LCP/PEL (50/50) blend showed a continuous shear thinning behavior. This is due to the structural changes in the melt, the melting of the residual crystallites, and the destruction of the domains of intermediate order. The viscosity of LCP/PEL (5/95) blend did not



(a)



(b)

Figure 13. Scanning electron micrographs of the fractured surfaces of the LCP/PEL (50/50) blend extruded at $5000s^{-1}$ in a capillary viscometer ($L/D=16$) at (a) $260^{\circ}C$ and (b) $290^{\circ}C$ (X3500).

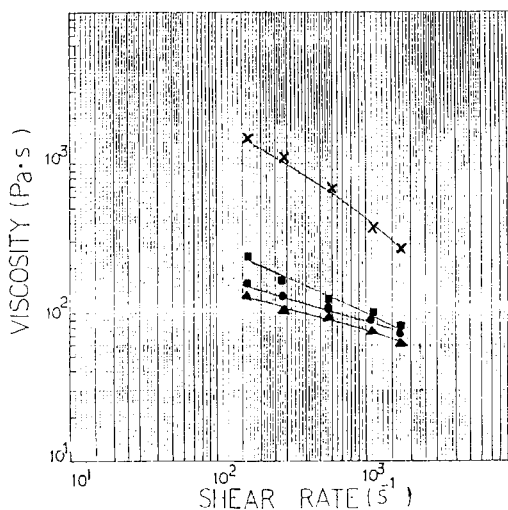


Figure 14. Plots of viscosity versus shear rate for LCP (×), PEL (●), LCP/PEL (5/95) blend (▲), and LCP/PEL (50/50) blend (■) at 260°C.

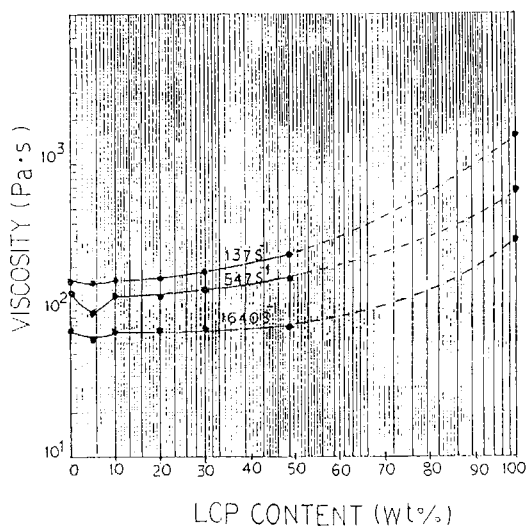


Figure 15. Plots of viscosity versus LCP content for the LCP/PEL blends as a function of shear rate at 260°C.

appear to shear thinning behavior. This originated from the addition of small amounts of LCP. The viscosity of the LCP/PEL blends decreased with increasing the shear rate. This is due to the increase of the shear thinning behavior of the LCP component. The viscosity of LCP/PEL (5/95) blend was much lower than that of parent polymer in the shear rate range studied. Figure 15 shows the viscosity of the LCP/PEL blends at constant shear rate as a function of LCP content. The viscosity of the LCP/PEL blends reached a minimum at 5 wt% of LCP, while the blend viscosity increased with increasing LCP content above 5 wt% of LCP. This is due to the incompatibility between two polymers and coarse morphology. The morphology of the LCP/PEL blends revealed that the interfacial adhesion between two polymers was poor. Therefore, the morphology obtained for the LCP/PEL blends was much coarser than that for the parent polymers. The thermal analysis of the LCP/PEL blends revealed a partial compatibility between LCP and PEL. It is presumed that these two properties in two directions, i.e., morphology will decrease the complex viscosity (poor interactions and adhesion). It was found that the LCP domains in the melt state possibly migrate toward the capillary surface and act as a lubricating layer over the capillary surface since the LCP/PEL blends are partially compatible. This results in a reduced blend viscosity.

CONCLUSIONS

The thermal properties of the LCP/PEL blends revealed a partial compatibility between the two polymers and a favorable effect on the crystallization of PEL in the blends. The linear thermal expansion coefficient and heat deflection temperature of the LCP/PEL blends revealed that the addition of LCP enhanced the dimensional and thermal stability of the LCP/PEL blends. The studies of dynamic mechanical properties of the LCP/PEL blends revealed that storage modulus (E') improved with increasing the LCP content. The morphology of the LCP/PEL blends revealed that the blend morphology was fibrous and similar to that of the pure LCP and the interfacial adhesion between the two polymers was poor. The ultimate fibrillar structure of LCP phase appeared to be closely related to the processing temperature and shear rate. The rheology of the LCP/PEL blends revealed a minimum viscosity in the blends of only 5 wt% LCP.

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