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Thermal properties of blends of poly(ethylene terephthalate) and a liquid crystalline copolyester

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Summary

A thermotropic liquid crystal copolyester (CHQ/BP/TA/IA; 40/10/40/10)(LCP),and melt blends of poly(ethylene terephthalate) (PET) with LCP have been studied for thermal transition and crystallization behaviour. The LCP has a mesophase transition (K ⟶ M) in the temperature range of 295-315°C. The endothermic peak showing mesophase to Isotropic (M ⟶ I) transition is observed around 420°C. These transitions are supported by hot stage polarizing microscopy. In blends of PET/LCP, the mesomorphic transition is observed at temperature around 314°C, along with the melting transition of PET around 274°C. The dynamic calorimetric measurements reveal that the two polymers are at least partially miscible.

Introduction

Liquid crystal compounds are useful materials for application because of their ability to show spontaneous anisotropy and readily induced orientation in the liquid crystal state. Blends of liquid crystalline polymers (LCP) with thermoplastic matrix materials have been studied by many researchers (1-6). These researchers have reported an improvement in mechanical properties of the matrix polymer due to the addition of LCP. Thermotropic LCP are composed of long chain rod-like molecules that exhibit an ordered structure in the melt. The molecules of these polymers are found to be associated in an ordered fashion and are known to form elongated domains (7). Thus, they are known to be "self-reinforcing" polymers (8).

The objective of this study is to determine phase transition in thermotropic liquid crystal (CHQ/BP/TA/IA) system. Blends of PET with LCP are investigated for compatibility of two components. DSC and optical microscopic studies have been used to achieve this objective. Preliminary data on this system have been reported elsewhere (9).

Experimental

The liquid crystalline polyester used in this study was provided by Du Pont Co. and composed of the copolymer of 40 mol% chlorohydroquinone (CHQ), 10 mol% 4,4'-dihydroxybiphenyl (BP), 40 mol% terephthalic acid (TA), and 10 mol% isophthalic acid (IA). The poly(ethylene terephthalate)(PET) was provided by J.K.Synthetics Ltd. To minimize moisture effects and hydrolysis all samples were dried in a vacuum oven at 90°C for approximately 24 hrs before blending. Blending was carried out using Brabender Plasti-coder equipment with twin screw compounder (DSK 42/5) at 300°C. Extruded strands of the blend were quenched in cold water, granulated and the granules were dried before further processing. Compression moulded films (approx. 100 μm thick) of PET, blend and LC copolyester at 300°C under 30 kg/cm^2 pressure was prepared and immediately quenched in ice-water mixture. Phase transition temperatures and enthalpies of LC copolyester, PET and the blends of LCP with PET were performed in a Perkin-Elmer differential scanning calorimeter (DSC) model-7 under nitrogen atmosphere. Measurements were made with a heating rate of 20°C/min from 50 to 325°C. The sample was held for two min at 325°C and cooled from 325 to 50°C with varying cooling rate 10-20°C/min followed by second heating run at 20°C/min to 325°C. For the evaluation of the transition enthalpies, an indium and tin samples were used as reference standards and automatic base line correction was used. The textures of the phases were observed between coverslips with a polarizing microscope (Leitz). For LC polyester which exhibit high clearing point, the mesophase textures were photographed from quenched samples. The polymer placed between two microscope cover glasses was rapidly heated slightly below its clearing point on a specially designed controlled metal bath apparatus. The upper cover glass was moved back and forth with a microspatula and at the temperature at which the polymer showed stir-opalescence, the sample was rapidly quenched by pouring the coverslips in ice-cold water.

Results and discussion

Polarized light photomicrographs investigation of LCP, obtained from quenched samples show readily identifiable nematic threaded-schlieren textures (Fig. 1a) around 310°C. However, there is some indication that this LCP may also form a smectic mesophase a straited texture with typical transition bars (Fig.1b & c) between crossed polarizers. The orientation variation of the platelets in this texture is sinusoidal about the shear direction with most of the misorientation within the shear plane. The photomicrograph of LCP (Fig. 1d) obtained by quenching from 420°C shows both the nematic phase and dark black spots, which marks the appearance of degradation. The DSC thermogram of as-received LCP as shown in Fig. 2 reveals several transitions. The first one at 110°C is associated

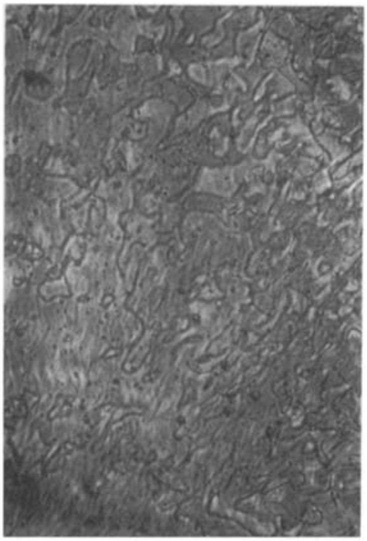

Fig.1a
threaded-schlieren texture at 305°C

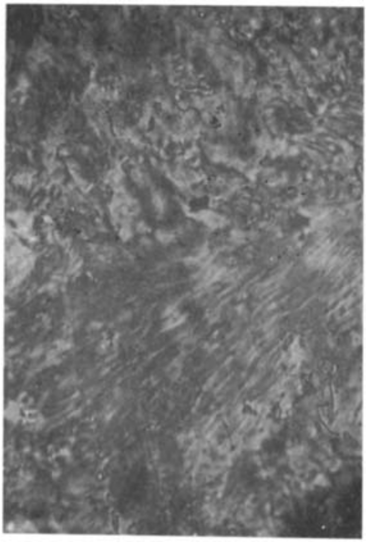

Fig.1b
Nematic texture at 315°C

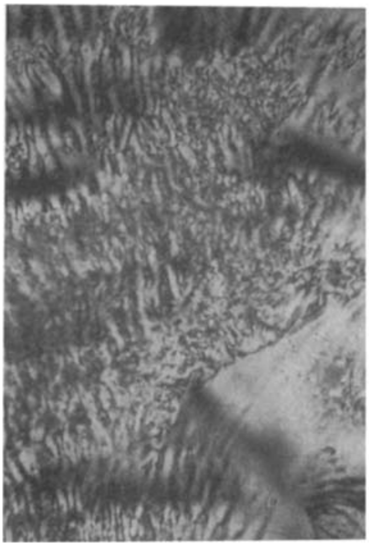

Fig.1c
Nematic/straited texture at 325°C

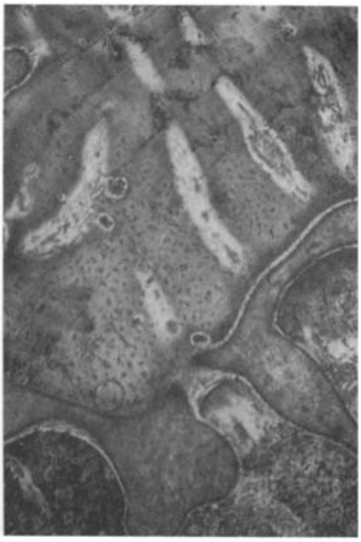

Fig.1d
Nematic mesophase with black spots at 420°C

with the glass transition (T_g). At increasing temperature, a small and broad endothermic peak appearing around 305°C is associated with the melting of small amounts of the crystalline phase, i.e. crystal (k) ⟶ mesophase (M) transition. The transition around 420°C is observed even with the heating rate of 40°C/min. Finally, a peak whose endothermic maximum at 421°C is ascribed to the isotropization of the material i.e. mesophase (M) ⟶ isotropic (I), accompanied by the thermal decomposition of the polymer. The transition at 421°C is supported by microscopic studies described earlier. These three transitions of the LCP, in general, correlate well with the reported literature on similar systems (10).

The DSC curve of an LCP sample cooled from the mesophase at 325°C exhibit the crystallization exotherm at 232°C. When the sample cooled from the isotropic state (430°C), no isotropic - mesophase transition is observed, because isotropic state is followed by the decomposition of the material. The melting enthalpy is 3.2 J/g and the isotropization enthalpy is 1.2 J/g.

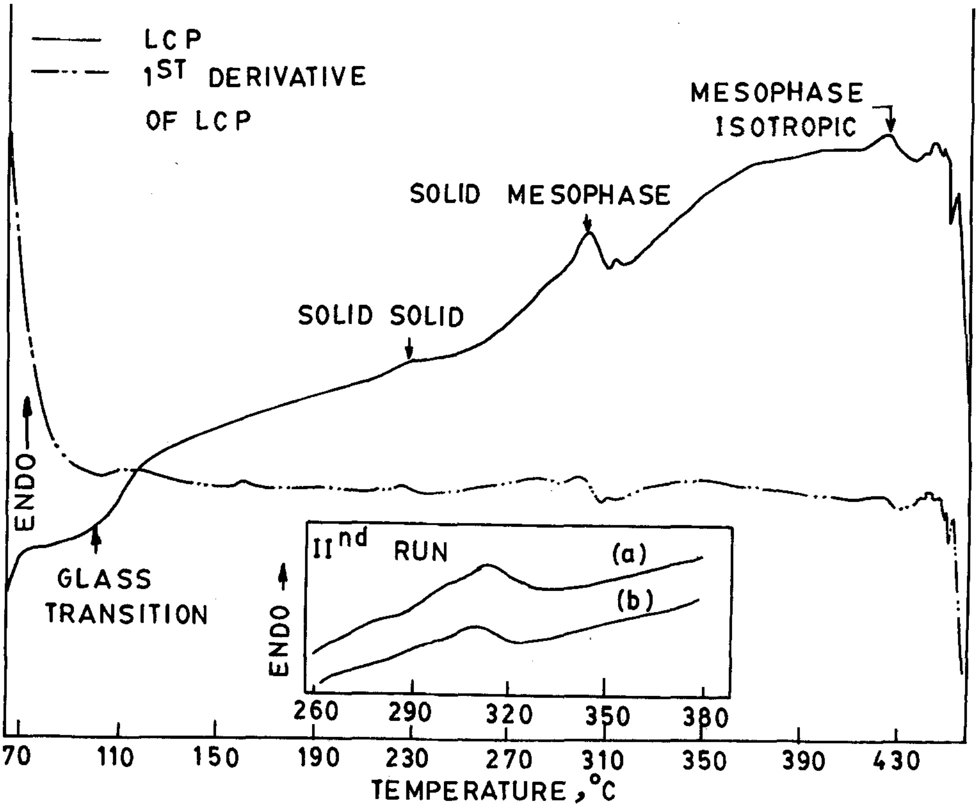

FIG.2 DSC PROFILE AT 20°C MIN^{-1} OF LC POLYESTER (LCP)
(a) COOLING RATE IN PRECEDING CYCLE--(10°C/min)
(b) COOLING RATE IN PRECEDING CYCLE--(20°C/min)

It is observed that, as the cooling rate increases from 10 to 20^{o}C/min, a decrease in both the heat of crystallization ($\triangle H_c$) and crystallization temperature (T_c) occurs. It is believed that as the cooling rate increases, the supercooled mesophase hinders the crystal growth and perfection of the material, as indicated by the $\triangle H_f$ value. The effect of cooling rate has been studied in the subsequent heating cycle (2nd run). Fig. 2 shows that T_m depends on the preceding thermal treatment and is shifted toward higher values for sample crystallized at slower rates.

TABLE 1

Thermal transitions of the LC polyester, PET and blends

Sample	Glass transition Tg (^{o}C)	Melting T_f (^{o}C)	$\triangle H_f$ (J/g)
PET	72	274.5	36.8
PET/LCP 5	72.5	273.5	44.5
PET/LCP 10	73.5	273	45.1
PET/LCP 15	75	274.5, 314	38.2
LCP	110	315	3.2

The transition temperatures and the enthalpies obtained for PET, LCP and blends are given in Table 1. The reported transition temperatures values correspond to the end temperature (T_f) of endotherm and exotherm minima of DSC curves. From the thermal behaviour of these systems, it is observed that during blending, PET is in the isotropic state whereas LCP is in the mesophase liquid crystal state. The heating traces of the polymers and the blends are shown in Fig. 3. PET is characterized by an endothermic end temperature (T_f) at 274.6^{o}, whereas LCP displays a well resolved endotherm T_f at 315^{o}C. With the LCP content of 10% in the blend, two distinct endotherms are observed. The first, at 270-275^{o}C is attributed to the melting of the PET phase, whereas the second at 305-310^{o}C is ascribed to the crystal-mesophase transition of the LCP phase. The other two changes involved along with the melting endotherm are glass transition (Tg) and cold crystallization temperature of PET. With the increasing LCP level, Tg shifts to a slightly higher temperature and only single glass transition (Tg) is obtained. This indicates at least partial miscibility of PET and LCP components.

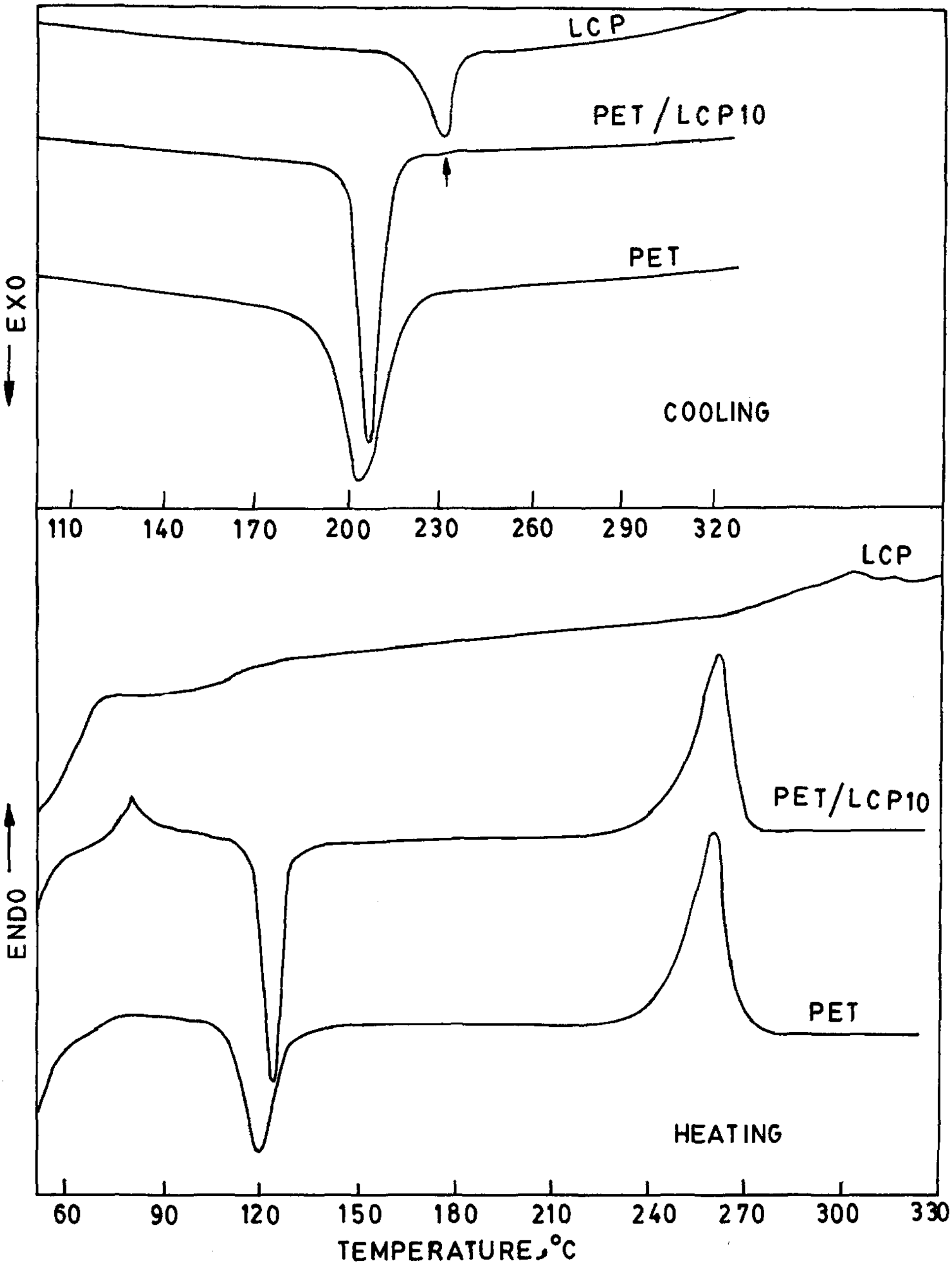

FIG-3 DSC HEATING AND COOLING TRACES OF PET/LCP BLEND FILMS.

From the cooling curves (Fig. 3), it can be seen that temperature of crystallization (T_C) for the blends is slightly higher as compared to that of PET. This indicates that LCP acts as nucleating agent for PET, due to the fact that 300°C for melting of film in DSC is below the crystal - mesophase transition temperature of LCP. It is seen that the T_C for PET chips is around 197°C, where as for extruded PET film, it is around 205°C, which suggests that while processing the film some degradation has occured.

TABLE 2

Effect of cooling conditions on crystallization

Sample	Cooling condition (°C/min)	Crystallization peak (°C) (T_C)	Heat of crystallization $\triangle H_C$ (J/g)
PET	10	205.5	39.6
	20	186.5	40.2
PET/LCP 5	10	207.5	46.8
	20	202	46.2
PET/LCP 10	10	208	41.4
	20	201.5	41.8
PET/LCP 15	10	205.5	35.1
	20	199	36.2
LCP	10	232	3.1
	20	228	2.9

Table 2 shows that the cooling rate influences the crystallization behaviour of PET, LCP and the blends. It is observed that the heat of crystallization ($\triangle H_C$) value for 5 and 10% blend is higher than the virgin PET in both the cooling conditions, whereas for 15% blend the $\triangle H_C$ value drops down from 40 J/g to 35 J/g. These results further suggest that LCP acts as a nucleating agent for the crystallization of PET and this effect probably reaches a maximum at an LCP level between 0-10 weight %. These results also indicate partial miscibility of the two components. At higher levels of LCP phase segregation takes place and thus resulting in a decrease in order which is responsible for decrease in $\triangle H_f$ and $\triangle H_C$ values.

Conclusion

(i) The LCP shows glass transition around 110°C, crystalline to mesophase transition in the range of 295 - 315°C and mesophase to isotropic transition around 420°C.

(ii) The single glass transition in the blends shows at least partial miscibility.
(iii) The crystallization temperature increases with the addition of LCP in PET. These observations also support the partial miscibility.

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References

1. A. I. Isayev and M. Modic, Polymer Composites **8**, 269 (1987).
2. A. I. Isayev and S. Swaminathan, in Advanced Composites III, Expanding Technology, ASM, (1987), p.259.
3. R. A. Weiss, W. Huh and L. Nicolais, Polym. Eng. Sci., **27**, 684 (1987).
4. G. Kiss, Polym. Eng. Sci., **27**, 410 (1987).
5. K.G. Blizard and D.G. Baird, Polym. Eng. Sci., **28**, 653 (1988).
6. P. Zhuang, J.L. White and T. Kyu, Polym. Eng. Sci., **28**, 1095 (1988).
7. Y. Onogi, J.L. White, and J.F. Fellers, J. Non. Newt. Fluid Mech., **7**, 121 (1980).
8. G. Menges and G. Hahn, Modern Plastics, p.56 (Oct. 1981).
9. S. Mehta and B.L. Deopura, Proceedings of 7th National Symposium on thermal analysis, India October (1989), p.249.
10. P. Meurisse, C. Noel, L. Monnerie and B. Fayolle, Brit. Polym. J. **13**, 55 (1981).

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