

Blends of Phenolphthalein Poly(ether ether ketone) and a Thermotropic Liquid Crystalline Copolyester

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Received 20 November 1996; accepted 8 July 1997

ABSTRACT: Blends of phenolphthalein poly(ether ether ketone) (PEK-C) and a thermotropic liquid crystalline copolyester (LCP), poly[(1-phenylethyl-*p*-phenylene terephthalate)-*co*-(1-cumyl-*p*-phenylene terephthalate)], was prepared via melt mixing. The studies of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) indicate that the PEK-C/LCP blends display two glass transition temperatures which correspond to those of PEK-C- and LCP-rich phases, respectively. The PEK-C/LCP blends were judged to be partially miscible. Scanning electron microscopy (SEM) was employed to examine the morphology of the blends, and it was observed that all the PEK-C/LCP blends displayed a phase-separated structure. The interface between the PEK-C- and LCP-rich phases is poor. The Young's modulus of the PEK-C/LCP blends was found to increase with LCP content due to the high modulus of the LCP. However, the tensile strength and the elongation at break of the blends greatly decreases with increase of LCP content, owing to the poor interfacial adhesion. From the thermogravimetry analysis (TGA), it was observed that all the blends exhibited a two-step weight loss mechanism, and the thermal degradation onset temperature of the blends was lowered with the addition of LCP content. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1923–1931, 1998

Key words: polymer blends; phenolphthalein poly(ether ether ketone); thermotropic LCP; mechanical properties

INTRODUCTION

Blends of thermotropic liquid crystalline polymers (LCP) with high-performance thermoplastics have attracted considerable attention in the

past decades due to the academic and technical importance of the materials. The main objective of such studies is to improve the mechanical properties and processability and to establish the balance between the properties and economic advantage through the synergistic contribution of LCP and high-performance polymers. The addition of LCP to a high-performance polymer cannot only improve the processability for LCP/thermoplastics blends, but also reinforce the mechanical properties due to the highly ordered fibrous structure of LCP formed during melt flow.^{1–4} To obtain the beneficiary combination of properties for the polymer blends, study of the miscibility and phase

Correspondence to: Q. Guo.

Contract grant sponsor: Hong Kong University of Science and Technology; contract grant number: 584/95P.

Contract grant sponsors: Presidential Fund of the Chinese Academy of Sciences; State Science and Technology Commission of China.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 59525307.

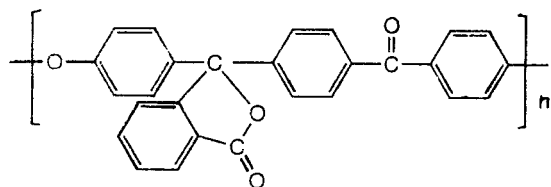
Journal of Applied Polymer Science, Vol. 69, 1923–1931 (1998)

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CCC 0021-8995/98/101923-09

structure is essential. In general, the interfacial adhesion between phases and the morphology have direct influences on the mechanical properties of the blends.⁵⁻⁷

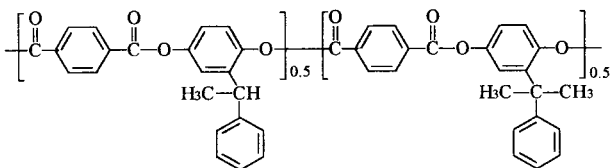
Phenolphthalein poly(ether ether ketone) (PEK-C) is a newly developed engineering thermoplastic,⁸ and it has shown excellent mechanical and thermal properties. The chemical formula of PEK-C is schemed as the following:



PEK-C is an amorphous poly(ether ether ketone); the rather bulky and polarizable phenolphthalein group in place of an aromatic ring makes the polymer amorphous in marked contrast to the poly(ether ether ketone) (PEEK) developed by Imperial Chemical Ind., Ltd.^{9,10} The phenolphthalein cardo group results in an increased rigidity of the molecular chain; thus, the higher glass transition temperature ($\sim 220^\circ\text{C}$) was displayed. Since PEK-C is relatively low in price compared to PEEK, considerable attention has been given to it as a high-performance thermoplastic as well as a matrix for advanced composites¹¹. PEK-C was also used to toughen epoxy resins.^{12,13}

Recently, many works have been done on blends of PEK-C with other polymers. They involve the miscibility and properties of blends of PEK-C with poly(hydroxether of bisphenol A) (phenoxy),^{12,14,15} polysulfone,¹⁴⁻¹⁶ poly(ethylene oxide),¹⁷ poly(*N*-vinyl-2-pyrrolidone),¹⁸ poly(2,6-dimethyl-1,4-phenylene oxide),¹⁹ PEEK,²⁰ and a poly(ether imide).²¹

In this contribution, we present the results of our study on the blends of PEK-C and a thermotropic LCP: poly[(1-phenylethyl-*p*-phenylene terephthalate)-*co*-(1-cumyl-*p*-phenylene terephthalate)]. The LCP consists of *p*-benzenedicarboxylic acid, 1-phenylethyl hydroquinone, and 1-cumyl hydroquinone (in a molar ratio of 50/25/25); its chemical formula is



The blends were prepared by melt mixing. The miscibility, morphology, and mechanical properties were studied. The techniques employed included differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The mechanical properties of the compression-molded specimens were investigated by tensile tests.

EXPERIMENTAL

Materials and Preparation of Samples

The phenolphthalein poly(ether ether ketone) (PEK-C) used in the study is a commercial product with a reduced solution viscosity of 0.68 dL/g when measured in a 0.5 wt % solution in chloroform at 25°C ; it was supplied by the Xuzhou Engineering Plastics Factory (Xuzhou, Jiangsu, China). The thermotropic LCP is poly[(1-phenylethyl-*p*-phenylene terephthalate)-*co*-(1-cumyl-*p*-phenylene terephthalate)] consisting of *p*-benzenedicarboxylic acid, 1-phenylethyl hydroquinone, and 1-cumyl hydroquinone (in a molar ratio of 50/25/25), which was kindly provided by Dr. H. H. Wu of Granmort Inc. (Granville, OH). According to the information obtained, the copolyester was synthesized via a direct condensation reaction of the three monomers in solution. To increase the molecular weight, solid-state polymerization was carried out after the precipitation and drying of the copolyester at 300°C for 24 h.

Prior to preparation of the blends, the materials were desiccated at 120°C under a vacuum for 12 h to remove the possible moisture. The two polymers were mixed using a Haake plasticoder mixer at 330°C for 15 min. PEK-C/LCP blends with weight ratios of 100/0, 95/5, 90/10, 75/25, 50/50, 25/75, and 0/100 were prepared. The samples were further compressed at 330°C into sheets with a thickness of ca. 1.0 mm. To investigate the tensile behavior, the sheets were machined into dumbbell specimens.

Differential Scanning Calorimetry

The calorimetric measurements were performed on a DuPont TA 2190 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with an indium standard. To obtain the glass transition temperature (T_g), the

samples (about 10 mg in weight) were heated at a heating rate of 20°C/min in all cases. The glass transition temperature (T_g) was taken as the midpoint of the heat-capacity change. The heat of fusion was calculated from the peak area; the maximum of the endotherm transition was taken as the melting temperature (T_m).

Dynamic Mechanical Analysis

The dynamic mechanical tests were carried out on a DuPont DMA 983 dynamic mechanical thermal analyzer at 1.0 Hz. The scan was performed at a heating rate of 3°C in a tensile mode from 20°C until the sample became too soft to be tested. The dimension of specimen was $1.5 \times 1.0 \times 0.1$ cm.

Tensile Tests

Tensile test specimens were prepared according to ASTM D638 type IV. The tests were performed on an Instron Model 5567 testing machine at room temperature, and a crosshead speed of 25 mm/min (corresponding to the strain rate of 0.5 min^{-1}) was used in all cases. Average values were obtained from at least five successful determinations. The standard deviation for the Young's modulus and tensile strength was typically 5%.

Thermogravimetric Analysis

A DuPont TGA 2950 thermogravimetric analyzer was used to investigate the thermal stability of the blends. The samples (about 10 mg) were heated under an air atmosphere from ambient temperature to 600°C and at a heating rate of 10°C/min in all cases. The thermal degradation temperature was taken as the onset temperature of the thermal decomposition.

Scanning Electron Microscopy (SEM)

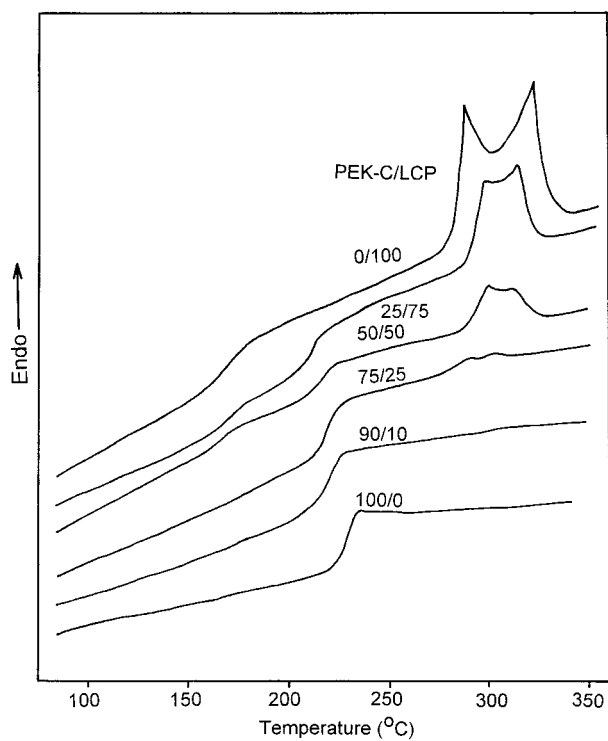
To investigate the morphology of the blends, the specimens were fractured under cryogenic conditions using liquid nitrogen. The surface of the fractured ends was examined using SEM. A JEOL 6300F scanning electron microscope was employed for this observation, before which the surfaces were coated with thin layers of gold of 100–150 Å.

RESULTS AND DISCUSSION

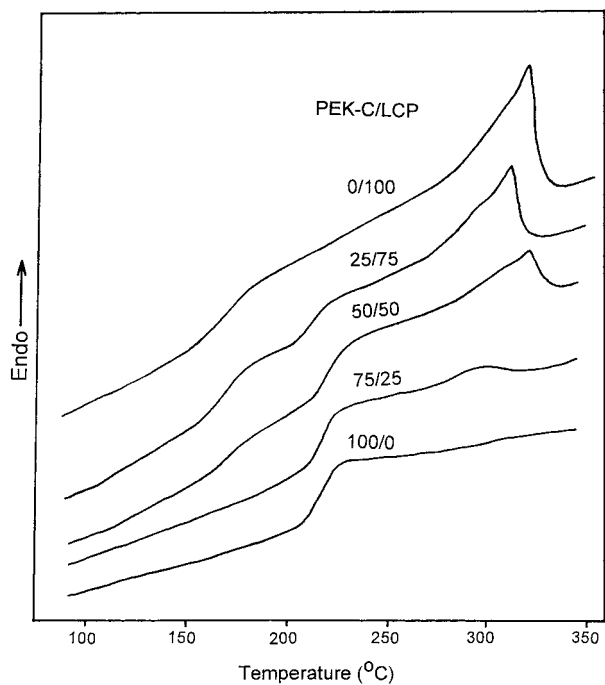
Thermal Properties

DSC thermograms of the first and the second scans for the PEK-C/LCP blends are shown in Figure 1(a) and (b), respectively. For the pure PEK-C and LCP, the thermograms of both scans show well-defined glass transitions centered at ca. 220 and 170°C, respectively. From Figure 1, it can be seen that the DSC thermograms of the PEK-C/LCP blends clearly exhibit two separate glass transition temperature (T_g 's), especially at the midcomposition range, and the T_g 's are close to those of pure PEK-C and LCP. The existence of two T_g 's indicates that the blends possessed a phase-separated structure. In addition, it was noted that the T_g of the PEK-C-rich phase substantially shifts to a lower temperature with increase of the LCP content, whereas the T_g of the LCP-rich phase remains almost unchanged with increasing PEK-C content. These results indicate that a considerable amount of LCP dissolves in the PEK-C-rich phase, but that the LCP-rich phase contains little PEK-C. The PEK-C/LCP blends are partially miscible. It should also be pointed out that the DSC thermograms of the blends containing 10 and 25 wt % LCP did not display an obvious glass transition for the LCP-rich phase owing to the low content of LCP.

Besides, the thermograms of LCP as well as the blends with higher LCP content also clearly show the melting and isotropic transitions. The DSC thermograms of the first scan can clearly give the melting and mesophase-to-isotropic liquid transitions [Fig. 1(a)]. In the case of pure LCP, the peak around 300°C was responsible for the crystalline melting transition temperature (T_m), whereas the peak centered at ca. 310°C was ascribed to the mesophase-to-isotropic liquid transition temperature (T_i). It is noticed that, in the second scans, the melting transition became the shoulders which overlap with the mesophase-to-isotropic liquid transition peaks to some extent, and the enthalpy of the transition also decreased, as shown in Figure 1(b). The samples were thermally treated at the temperature above T_i for 5 min and then quenched to room temperature before the second scans were recorded. In contrast to the melting transition, the change of the mesophase-to-isotropic liquid transition is quite small. These results indicate that the thermal history has a much stronger effect on the melting transition than on the mesophase-to-isotropic liquid



(a)



(b)

Figure 1 DSC thermograms of the PEK-C/LCP blends: (a) the first scan; (b) the second scan. For easy comparison, all curves are normalized to 1 mg of the sample.

transition.²² As well known, the mesophase-to-isotropic liquid transition occurs between the liquid states, and thus the transition process can easily be carried out due to the larger mobility of molecular chains in comparison with the melting transition. The LCP was difficult to crystallize during the quenching, and thus liquid crystalline glass of the LCP was obtained. Therefore, only the isotropization transition was clearly displayed on the DSC thermograms of the second scan after quenching.²² It is also noted that no obvious melting or isotropic transition was observed for the blends when the LCP content was less than 25 wt %, which suggests that the crystallization of LCP in these blends becomes more and more difficult with increase of LCP content, presumably due to the partial miscibility between the components. Therefore, the blends containing less than 25 wt % could be amorphous. Figure 2 shows the thermal transition temperatures of the first scans obtained from Figure 1(a) as functions of the LCP content. It can be seen that the T_i slightly decreases with increase of PEK-C in the blends, whereas the T_m almost remains invariant. By measuring the area under the melting peaks, it is possible to evaluate the enthalpy of fusion, ΔH_f , of LCP in the blends. The results thus obtained are listed in Table I, together with the other thermal properties. It is noted that both the heat of fusion, ΔH_f , and the crystallinity of LCP decrease

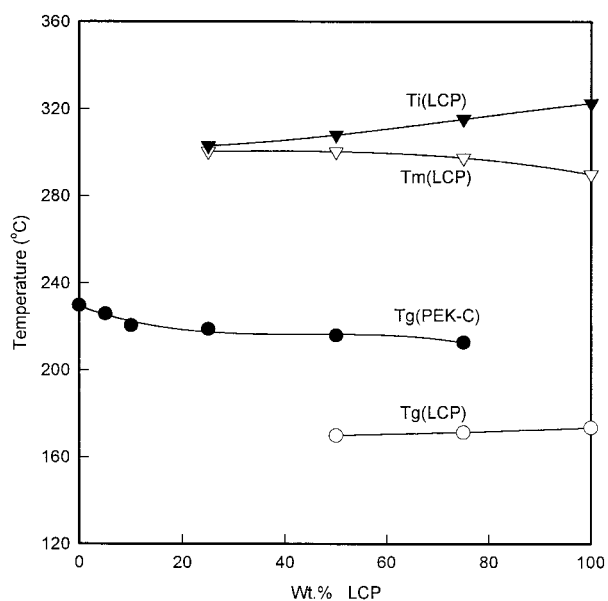


Figure 2 Thermal transition temperatures of the first scans versus blend composition for the PEK-C/LCP blends.

Table I Thermal Properties of PEK-C/LCP Blends

PEK-C/LCP	T_m (°C)	ΔH_f (J/g blend)	ΔH_f (J/g LCP)	T_i (°C)	T_g (°C)
0/100	290	15.3	15.3	323	173
25/75	297	5.75	7.68	315	213/171
50/50	300	2.96	5.85	306	216/170
75/25	300	1.04	4.2		218
90/10					220
95/5					226
100/0					229

From the DSC thermograms of the first scan as shown in Figure 1.

with increase of PEK-C content, which can be ascribed to both the higher T_g of PEK-C and partial miscibility of the two polymers.

Dynamic Mechanical Properties

For a further insight into the miscibility of the PEK-C/LCP blends, dynamic mechanical measurements were performed to evaluate the glass transition temperatures of the blends. Figure 3 shows the DMA spectra of the PEK-C/LCP blends. A single well-defined $\tan \delta$ peak centered

at ca. 230°C was identified for pure PEK-C, which was ascribed to its glass transition. In case of the PEK-C/LCP blends, two separate loss peaks can be observed especially for the LCP-rich blends, suggesting that the blends are phase-separated. This is in good agreement with the DSC results. It is noted that there appear to be only single $\tan \delta$ peaks on the DMA curves of the 95/5, 90/10, and 75/25 PEK-C/LCP blends, responsible for glass transition of the PEK-C-rich phase, but that of the LCP-rich phase is difficult to be discerned owing to the low content of LCP in these blends. However, this phenomenon does not suggest that the system is miscible in the region of these blend compositions.

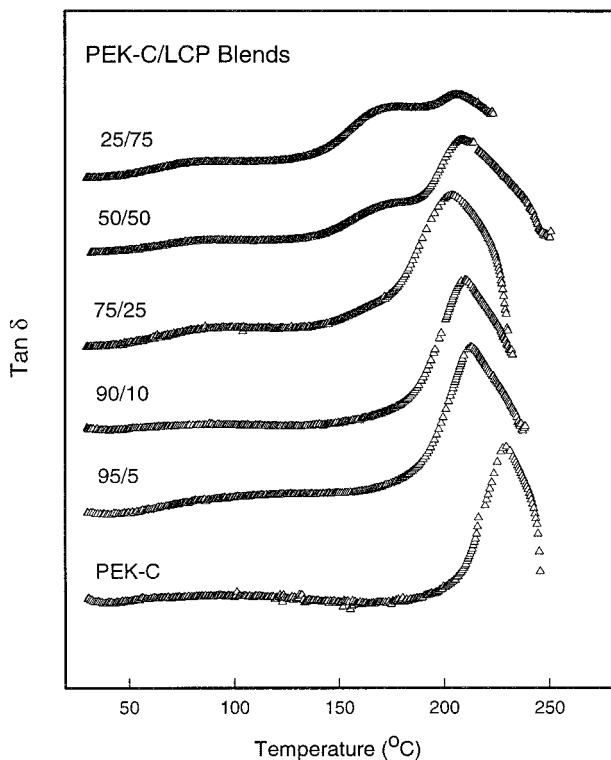


Figure 3 $\tan \delta$ versus temperature for the PEK-C/LCP blends.

Morphology

The morphology of the PEK-C/LCP blends was investigated by SEM. Figure 4(a)–(e) presents SEM micrographs of the fracture ends of the blend specimens frozen by liquid nitrogen. The heterogeneous morphology was observed for all the blends. For the blends containing 5 and 10 wt % LCP, the discrete thermoplastic particles with broadly distributed sizes ranging from 0.3 to 2 mm in diameter were dispersed in the continuous PEK-C matrix [Fig. 4(a, b)]. With increasing LCP content, the morphology of the blends changed dramatically. Inclusion of 25 wt % LCP gives rise to an obviously different morphology, that is, LCP spherical particles begin to coagulate and there appear some larger cavities on the fracture surface [Fig. 4(c)]. With LCP content up to 50 wt %, a typical complete phase-inverted morphology was formed, and the blends exhibited a phase-inverted morphology which consists of PEK-C domains wrapped in the LCP continuous phase as shown in Figure 5(d). Furthermore, it

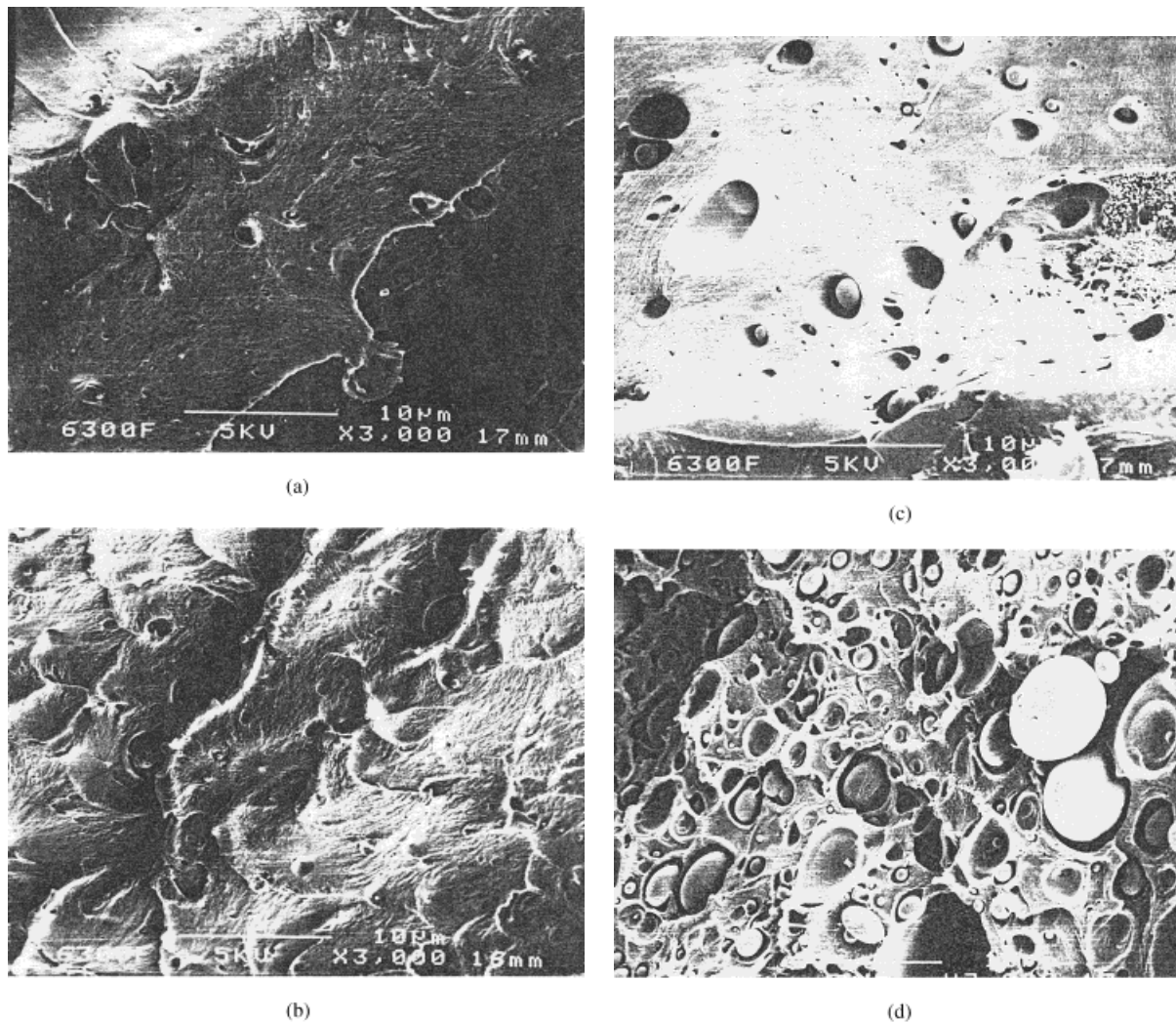


Figure 4 SEM micrographs of the PEK-C/LCP blends. PEK-C/LCP: (a) 95/5; (b) 90/10; (c) 75/25; (d) 50/50; (e) 25/75.

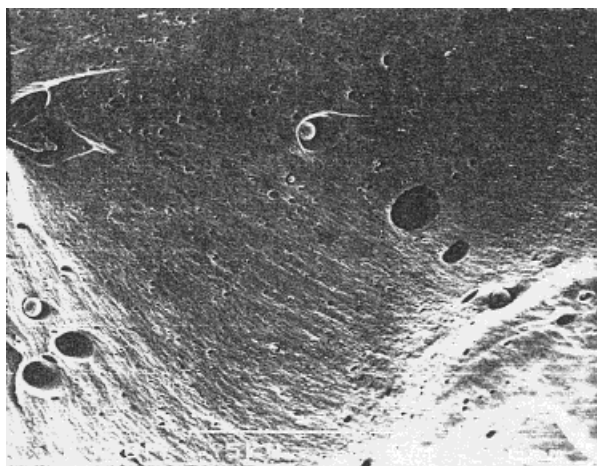
can be seen from Figure 5(e) that the SEM micrograph of the 25/75 PEK-C/LCP blend clearly displays spherical particles of the PEK-C-rich phase (0.3–3 μm in diameter) dispersed in the LCP continuous phase. This observation implies that the phase inversion occurred in the blend composition between 25 and 50 wt % LCP content. Besides, all the SEM micrographs clearly show that the interfacial adhesion between the phases is rather poor.

Tensile Properties

The tensile behavior of the blends was investigated at the strain rate of 0.5 min^{-1} at room temperature. In all cases, deformation occurred with-

out an observable yield phenomenon from the stress–strain curves, which shows that PEK-C and the PEK-C/LCP blends are basically brittle materials. However, the stress–strain curves of pure PEK-C displayed some characteristics of ductile fracture. From the initial slope, the Young's moduli of PEK-C and the PEK-C/LCP blends were calculated. Figure 5 shows the Young's moduli as a function of blend composition. It can be seen from the figure that the Young's moduli for the PEK-C/LCP blends tend to remarkably increase with increasing LCP content, which is responsible for the high modulus of the crystalline LCP.

The properties at high deformation are illustrated in Figures 6 and 7 by the tensile strength and the elongation at break, respectively. It can



(c)

Figure 4 (Continued)

be seen that both the tensile strength and the elongation at break decrease rapidly with increase of LCP content, which is typical for an essentially immiscible blend system.²³⁻²⁷ The result is indicative of the poor adhesion between the PEK-C- and LCP-rich phases. The poor interfacial adhesion resulted in decreases in both tensile strength and elongation at break. This is in accordance with the SEM observation.

Thermal Stability

Thermogravimetry analysis (TGA) was applied to investigate the thermal stability of the blends.

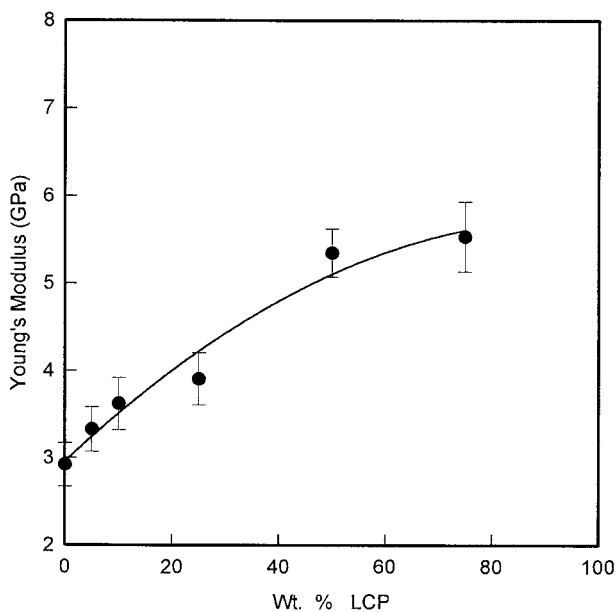


Figure 5 Composition dependence of Young's modulus at room temperature for the PEK-C/LCP blends.

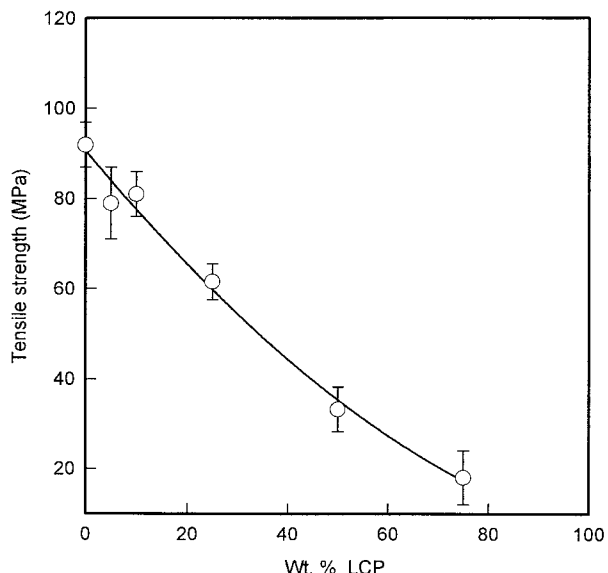


Figure 6 Composition dependence of tensile strength at room temperature for the PEK-C/LCP blends.

Figure 8 shows the TGA curves recorded in air, and the corresponding onset degradation temperature as a function of blend composition is presented in Figure 9. It can be seen that the pure LCP and LCP-rich blends exhibited a two-step weight-loss mechanism. However, no apparently separate weight-loss step was observed for the blends, corresponding to the initial degradation of the pure components, respectively. This phe-

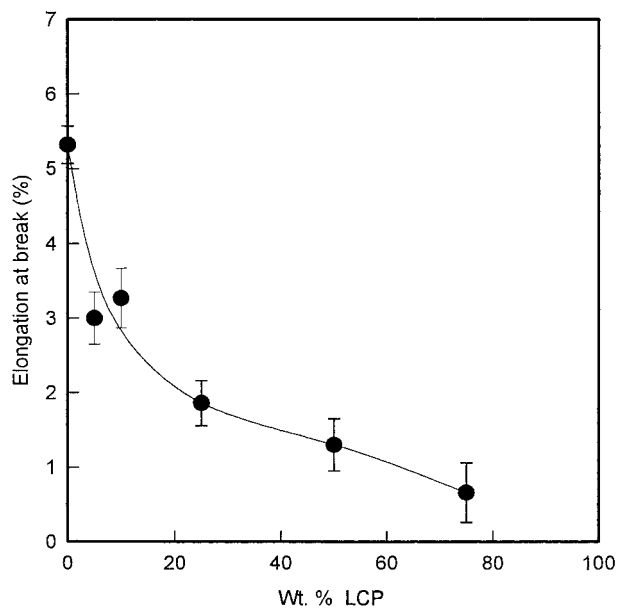


Figure 7 Composition dependence of elongation at break at room temperature for the PEK-C/LCP blends.

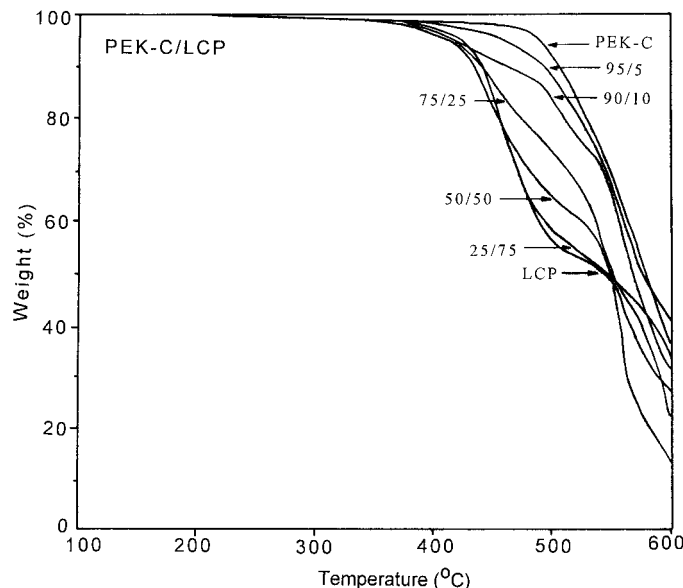


Figure 8 TGA curves for the PEK-C/LCP blends heated at 10°C/min in air.

nomenon could be attributed to the synergistic contribution of the two phases in energy transportation. If we compare the thermal stability of the two polymers, it is clear that PEK-C is more thermally stable than is LCP. It was observed that the thermal stability of the blends greatly decreases with increase of LCP content. However, the blends at the midcomposition (e.g., with 25 and 50 wt % LCP) exhibited lower thermal degradation temperatures, which were even lower than

that of the pure LCP (Fig. 9). This could result from the disadvantageous energy transportation between the PEK-C- and LCP-rich phases. Similar phenomena were also reported by Calahorra et al.²⁸ and Lee et al.²⁹ for polyarylate/poly(ethylene terephthalate) blends and for poly(ether imide)/thermotropic LCP blends, respectively.

CONCLUSIONS

From the above results, it can be concluded that

1. PEK-C and LCP are partially miscible. Their blends have two T_g 's corresponding to those of the PEK-C- and LCP-rich phases, respectively.
2. SEM observations revealed that the blends have a two-phase structure and the interfacial adhesion between the phases is rather poor.
3. The Young's modulus remarkably increases with increasing LCP content owing to the high modulus of the LCP. Adding LCP to PEK-C greatly decreased the system's tensile strength and elongation at break, as expected for an essentially immiscible system.
4. Adding LCP to PEK-C decreased the system's thermal degradation onset temperature.

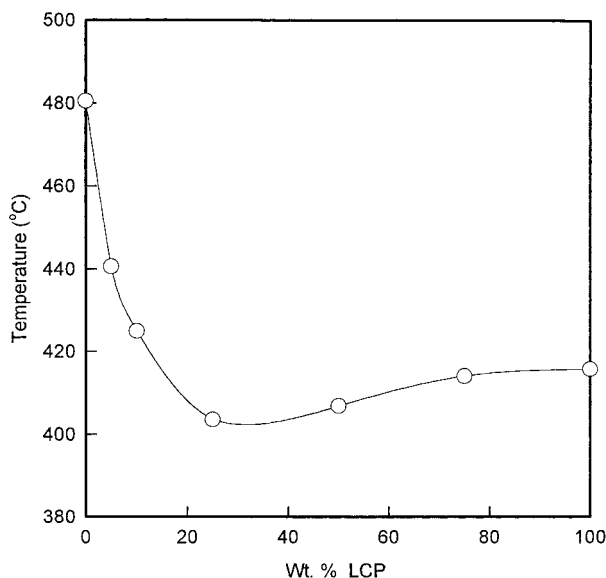


Figure 9 Plot of the onset degradation temperature for the PEK-C/LCP blends versus blend composition.

This work was supported by the RGC Earmarked Grant for Research (No. 584/95P), HKUST 95/96, the Hong

Kong University of Science and Technology. Also, the financial support of the Presidential Fund of the Chinese Academy of Sciences and the State Science and Technology Commission of China are also acknowledged. One of authors (Q. G.) wishes to express his appreciation to the National Natural Science Foundation of China for awarding a "Premier Grant" for Outstanding Young Scientists (No. 59525307).

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