

The mechanical properties of ternary liquid-crystalline polymer blends

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The possibility of improving the compatibility of and the adhesion between liquid-crystalline poly(oxybenzoate-*co*-oxynaphthoate) (Vectra) and polycarbonate (PC) by adding a stable compatibilizer based upon the transesterification between liquid-crystalline poly(oxybenzoate-*co*-ethylene terephthalate) (POB/PET) (60/40) and polycarbonate was investigated. The goal was to provide a physical interaction between the matrix polymer and the liquid-crystalline polymer through a third polymer that contained similar chemical structural units to those in both polymers. It was found that at proper compositions the adhesion between Vectra and PC was greatly improved by the presence of the compatibilizer, as indicated by the morphological evidence. These ternary liquid-crystalline polymer blends displayed improved ultimate tensile stress (30% increase as compared to PC) and elongation at break (seven times as compared to binary blend) even under a nominal injection-moulding process. The impact property of the ternary liquid-crystalline polymer blend was also improved as compared to that of the binary liquid-crystalline polymer blends. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Thermotropic liquid-crystalline polymer (LCP) blends have attracted great attention in recent years^{1–4} because of their unique applications. The first advantage was that the low viscosity of the liquid-crystalline polymer can reduce the overall viscosity of the blend, and is a good processing aid. Secondly, at proper compositions and under shear or extensional flow, the LCP can form fibrillar structure in the host thermoplastic matrix *in situ*. Owing to the high modulus of LCP in the oriented direction, the *in situ* fibrous LCP morphology served as reinforcement for the host thermoplastics. A previous study⁵ has indicated that the morphology and the properties of *in situ* composites were affected by the interaction between the LCP and the matrix. Therefore, the compatibility or the adhesion between the LCP and the matrix has been a critical factor in developing LCP-reinforced composites.

A number of studies have been carried out to improve the compatibility of LCP and the matrix polymer. They included modification of the LCP fibre's geometry to have mechanical locking to the matrix⁶ and chemical grafting of flexible polymer to the LCP fibre surface⁷. Another study by DiBenedetto's group used a second LCP as a compatibilizer to improve the adhesion between incompatible LCP/thermoplastic phases⁸.

Our group has been studying the transesterification between a liquid-crystalline polyester such as poly(oxybenzoate-*co*-ethylene terephthalate) (POB/PET) or poly(oxybenzoate-*co*-phenylene isophthalate) (HIQ)

and polycarbonate (PC)^{9–11}. We have found that, for a binary LCP blend, the compatibility between the LCP and the PC increases with ester exchange. However, these binary LCP blends suffered the drawback of not having consistent material properties during further processing. Our goal is to achieve compatible LCP blends, and our approach is to develop a compatibilizer based upon the transesterification between the matrix polymer and a second LCP that contains the same liquid-crystalline (rigid-rod) chemical structure as that in the reinforcing LCP. Therefore, the compatibilizer can be a block copolymer exhibiting liquid-crystalline character. Since the compatibilizer consisted of both the matrix polymer unit and the rigid-rod unit, the physical interaction between the matrix polymer and the compatibilizer as well as that between the LCP and the compatibilizer would be enhanced. Therefore, the compatibility of the ternary system would increase. This brings about better adhesion between the matrix polymer and the LCP. Consequently, during the application of these blends, stress can be transferred better across the blends. This resulted in better mechanical properties for the blends.

EXPERIMENTAL

Materials

Liquid-crystalline poly(oxybenzoate-*co*-ethylene terephthalate) (POB/PET) (60/40), denoted as P64, was provided by Unitika Corp., Japan. Polycarbonate (PC) was purchased from General Electric. The trade name of the PC is Lexan 121, and its molecular weight is $M_w = 158\,900$. Liquid-crystalline copolyester Vectra

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A900 consisted of 73% oxybenzoate and 27% 2-oxy-6-naphthoate and was supplied by Hoechst Celanese Corp. The Vectra A900 is shortened as Vectra in this study.

Compatibilizer preparation

The pellets of liquid-crystalline P64 and PC were dried at 110°C under vacuum for 8 h prior to the mixing. The mixture of P64 and PC was put into a Brabender mixer. The speed of the roller blade was 50 rpm. Blends containing 50 and 60% P64 were prepared. One blending temperature, 290°C, was chosen. The samples were taken out from the Brabender mixer every 4 min, and quenched in water for further analysis. The thermal analysis of the blends was carried out with a DUPONT 2910 differential scanning calorimeter. The samples were heated from 30 to 270°C at a heating rate of 20°C min⁻¹, and then quenched in liquid nitrogen. The samples were heated again from 30 to 300°C at the same heating rate. The d.s.c. curves of the samples were taken the second time the samples were heated up at the heating rate of 20°C min⁻¹. To verify the transesterification between P64 and PC, nuclear magnetic resonance (n.m.r.) was employed to investigate the chemical structure of blends. The blends were dissolved in deuterated chloroform for 4 h; then, the undissolved particles were filtered with a syringe filter. Tetramethylsilane was added to the solution as an internal reference standard, and the liquid mixture was put in a n.m.r. tube. A Varian Fourier Transform NMR (Unity-300) was used for this measurement. In the scanning electron microscopy (SEM) study, the samples were quenched in liquid nitrogen, and then were fractured. The fractured surface was coated with 10 nm thick gold for observation in a Hitachi S-2500 SEM.

Ternary blend preparation

The three-component LCP blends were mixed at 300°C in a twin-screw compounder attached to the Brabender. The speed of the twin screw was 80 rpm. The blend compositions of Vectra/PC/compatibilizer were 10/90/5 and 20/80/5. For comparison with the mechanical properties of blends without compatibilizer, two blends containing Vectra PC at 20/80 and 10/90 were also prepared. These blends were moulded with a Toshiba IS55EPN injection-moulding machine. The melt temperature was 300°C, and the cycle time was 30 s during the moulding process. Tensile tests were performed according to ASTM D638 at 23°C using a Testometric Micro 500 machine. Data reported were obtained at a crosshead speed of 1.3 mm min⁻¹. Unnotched Izod tests were performed according to ASTM D256 specification. For each data point, six specimens were tested, and the average value was taken.

RESULTS AND DISCUSSION

The thermal analysis curves of P64, Vectra and PC are shown in *Figure 1*. In *Figure 1*, the glass transition temperatures (T_g) of P64 and PC are 62.91°C and 150.28°C, respectively. There is a melting peak at 193.10°C for P64, and the melting point for Vectra is 285.88°C. The d.s.c. curves of the binary P64/PC blend at composition 50/50 for different blending times are displayed in *Figure 2*. There is only one T_g apparent. The T_g of the 50% P64 blend gradually decreases with

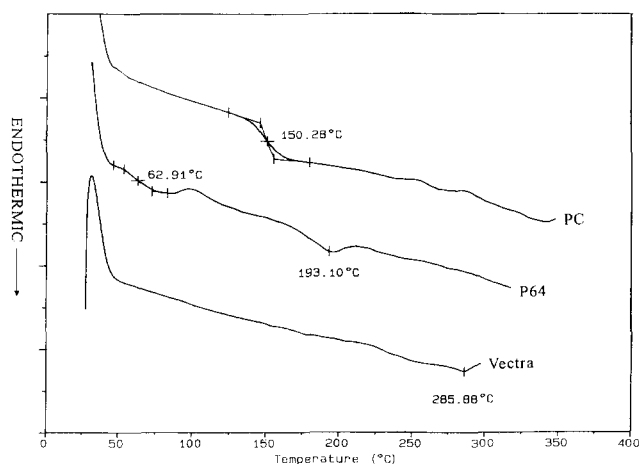


Figure 1 The d.s.c. curves of PC, P64 and Vectra A900

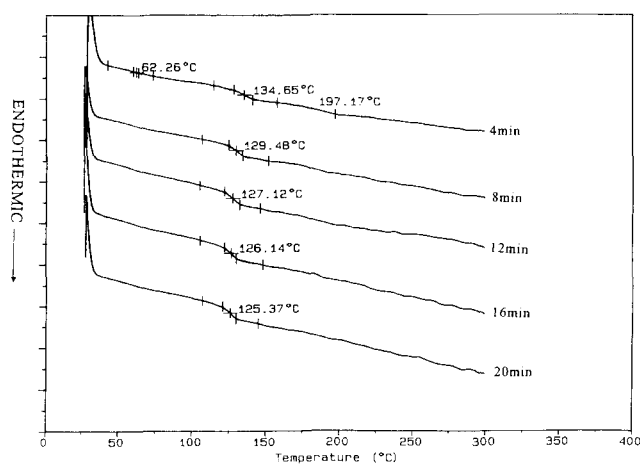


Figure 2 The d.s.c. curves of 50/50 P64/PC blends mixed at 290°C for different times

increasing blending time, from 134.65°C after 4 min to 125.37°C after 20 min, as shown in *Figure 2*. Additionally, the melting peak of P64 disappeared after 8 min blending time. This indicated that there was a change in chemical structure in the blend.

As the concentration of the P64 increased to 60% in

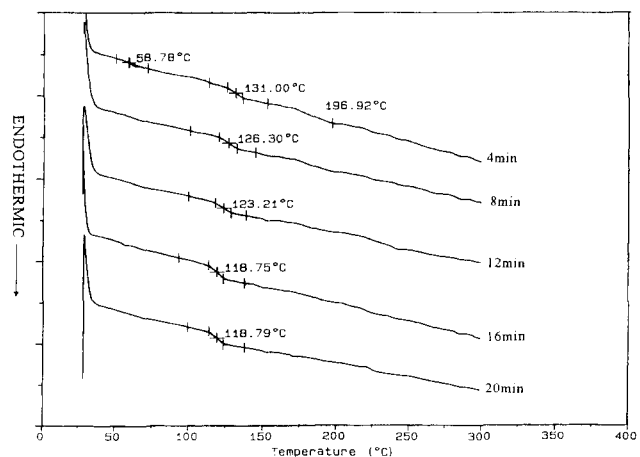


Figure 3 The d.s.c. curves of 60/40 P64/PC blends mixed at 290°C for different times

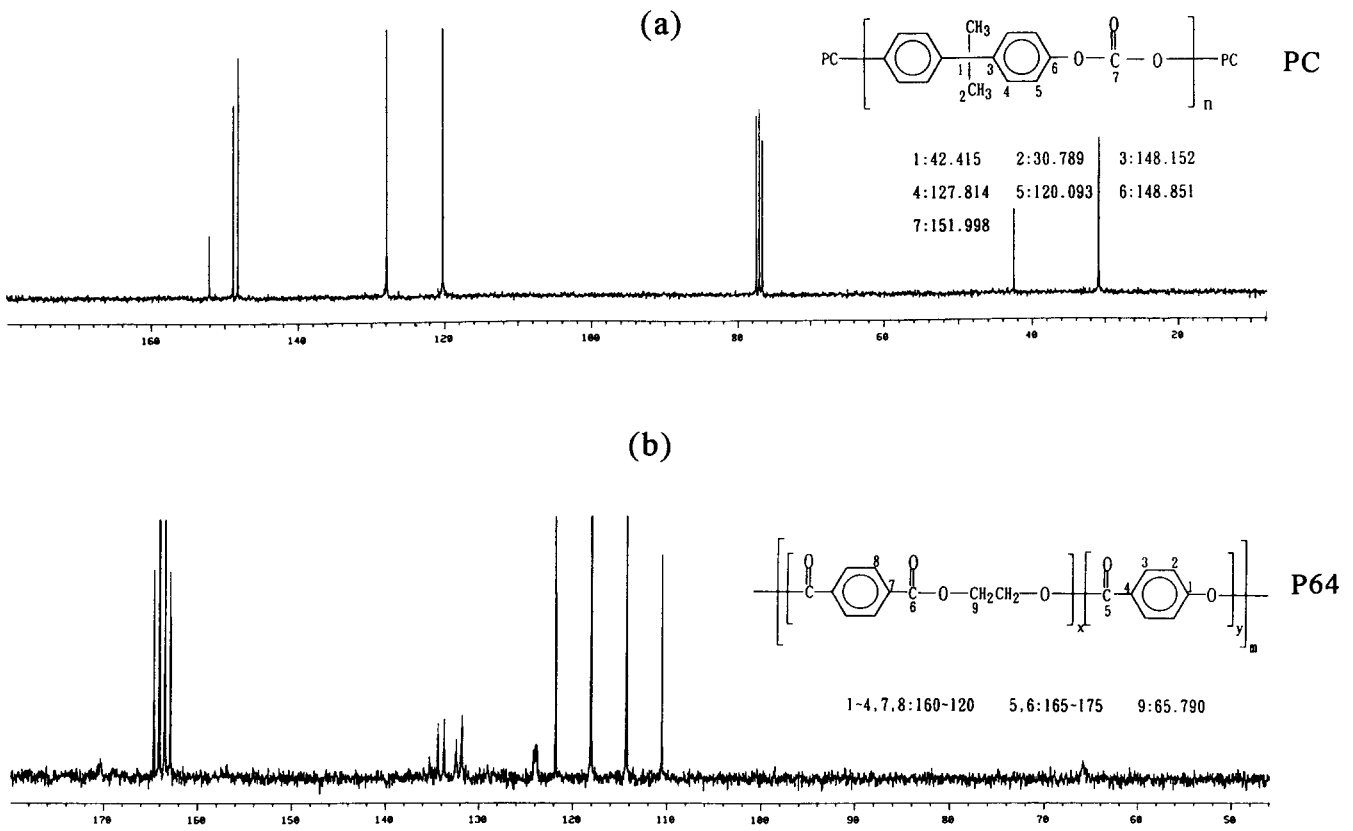


Figure 4 The n.m.r. spectra of (a) PC dissolved in deuterated chloroform and (b) P64 dissolved in deuterated trifluoroacetic acid

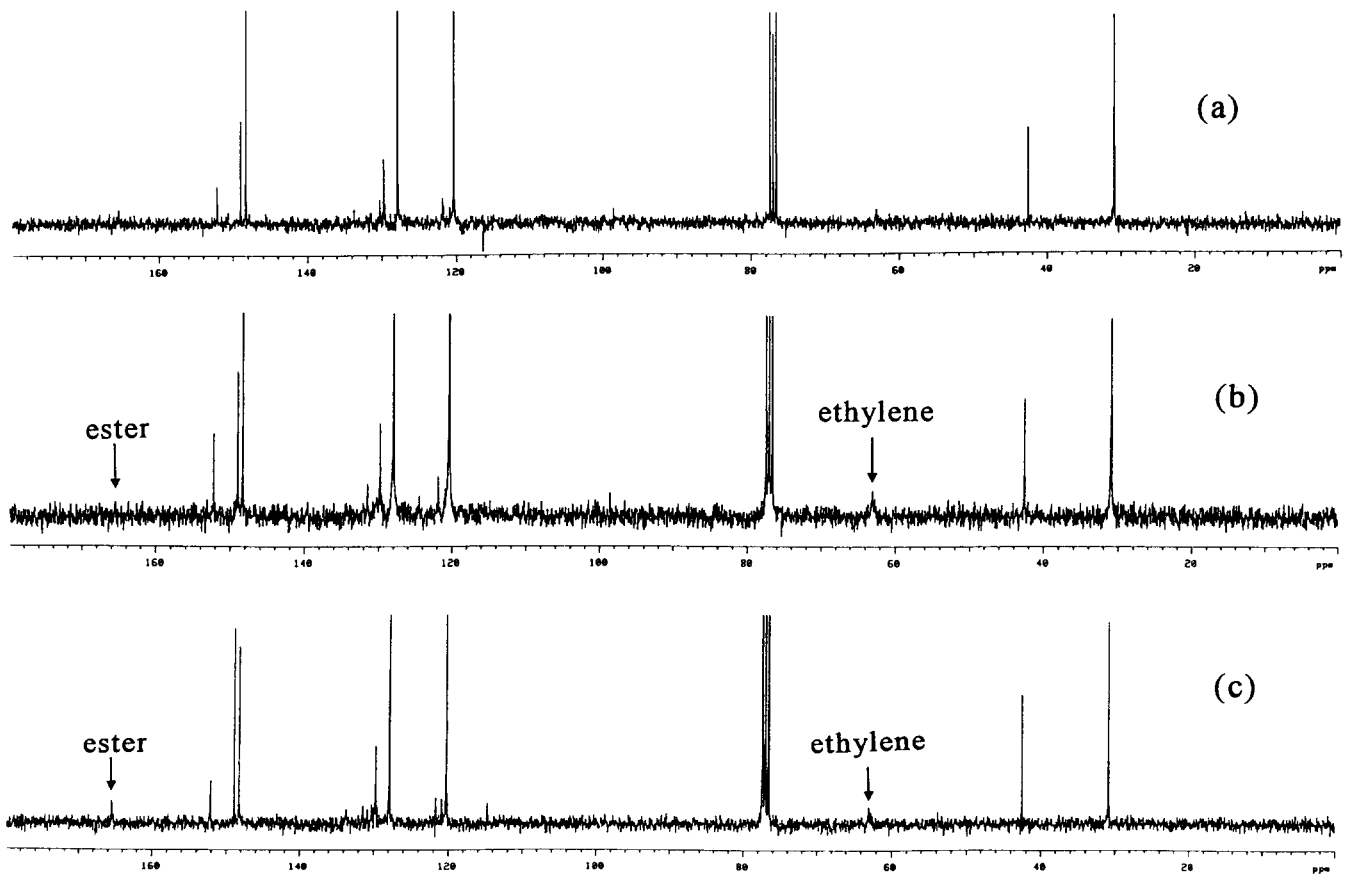


Figure 5 The transient n.m.r. spectra of extracted 60/40 P64/PC blend mixed at 290°C for (a) 4 min, (b) 12 min and (c) 20 min

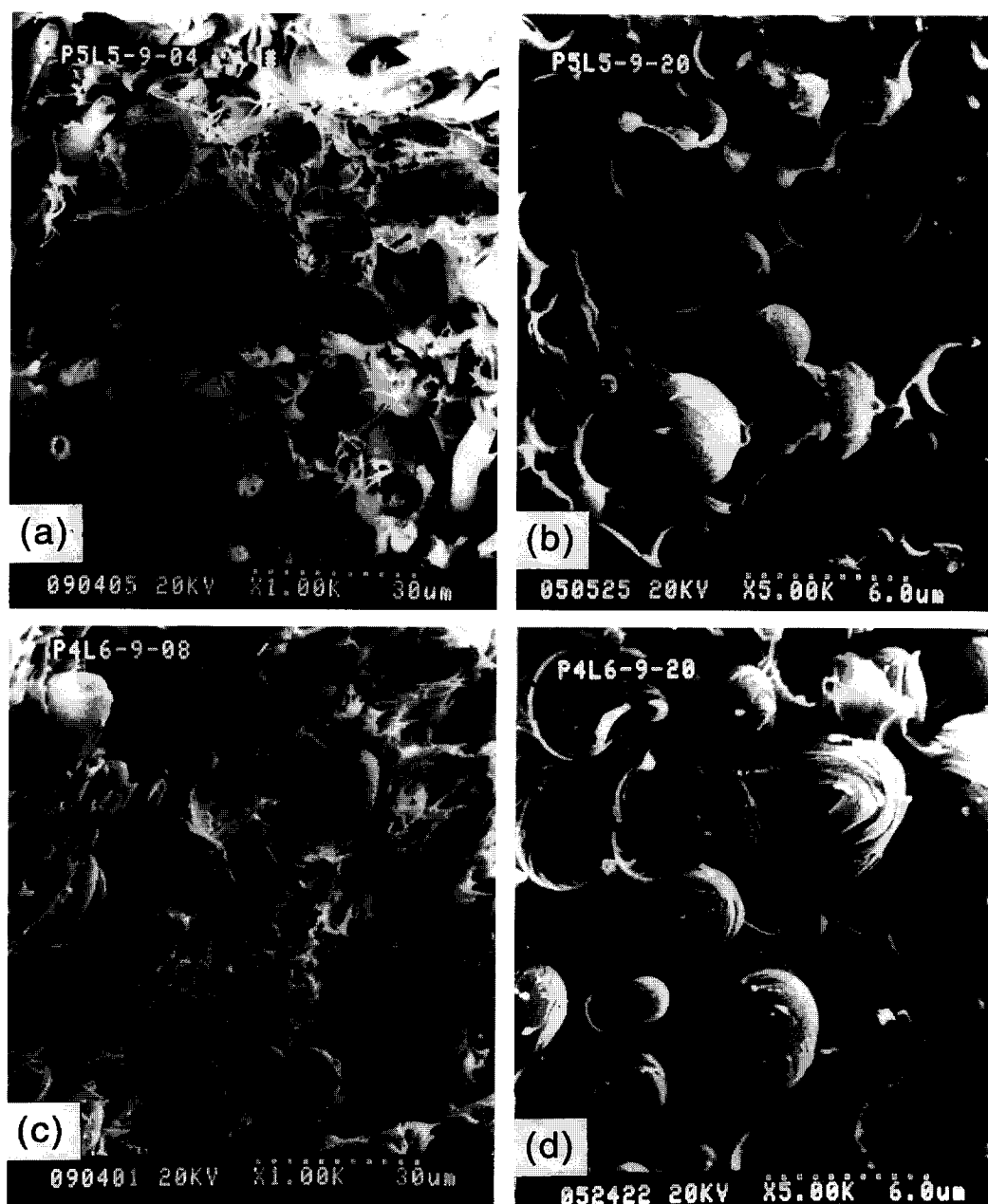


Figure 6 The SEM micrographs of (a) 50/50 P64/PC mixed at 290° for 4 min, (b) 50/50 P64/PC mixed at 290°C for 20 min, (c) 60/40 P64/PC mixed at 290°C for 8 min and (d) 60/40 P64/PC mixed at 290°C for 20 min

P64/PC blend, the decrease in T_g of the blend with blending time became more dramatic, from 131.00°C after 4 min to 118.79°C after 20 min (Figure 3). The melting peak of P64 also disappeared after 8 min blending time. The trend in both blends can be explained by the fact that transesterification (ester exchange) between P64 and PC took place. Ester exchange between polyester and PC has been documented in the literature⁹. Owing to the transesterification, chain scission often took place in the P64 blends, resulting in lower molecular weight and T_g .

Further evidence on the ester exchange can be found in the n.m.r. spectra of the 60% P64 blend. The ^{13}C resonance peaks of PC dissolved in deuterated chloroform and P64 dissolved in deuterated trifluoroacetic acid are shown in Figures 4a and 4b, respectively. Since only PC dissolved in chloroform, the portion of the 60% P64 blend extracted by deuterated chloroform would contain

only PC molecules and its derivatives. In Figure 4a, the resonance peaks resulting from the different carbons in PC are listed. In Figure 4b, there is an ester peak and an ethylene peak at 165 and 65.79 ppm, respectively, for P64. The transient ^{13}C n.m.r. spectra of the extracted 60% P64 blends are presented in Figure 5. As compared to the spectrum of pure PC in Figure 4a, all n.m.r. spectra of the extracted blend displayed distinctive PC peaks in Figure 5. Additionally, ester and ethylene peaks showed up for blending times more than 12 min, as shown in Figures 5b and 5c. This is direct evidence that transesterification between P64 and PC took place at this composition and in this blending condition. Secondly, the extent of ester exchange increased with the blending time, judging from the peaks in Figure 5.

The SEM micrographs also exhibited morphological differences for P64 blends taken at different blending times, as shown in Figure 6. Comparing Figures 6a and

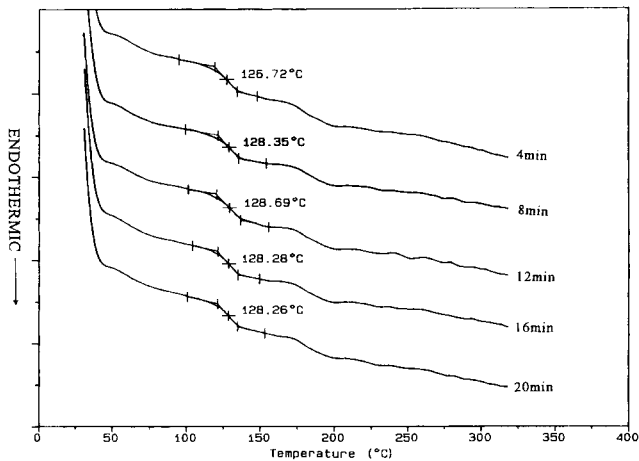


Figure 7 The d.s.c. curves of inhibited 60/40 P64/PC blend mixed at 290°C for different times

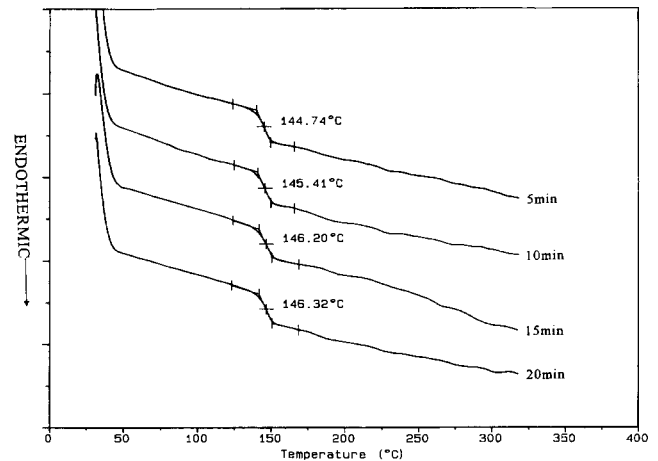


Figure 8 The d.s.c. curves of 20/80 Vectra/PC blend mixed at 300°C for different times

6b, one found that the interface between the P64 and PC was less apparent after 20 min blending, indicating the occurrence of ester exchange at the interface. A similar phenomenon can be observed in *Figures 6c* and *6d* for 60% P64 blend, though there might be a phase inversion between blends after 8 and 20 min blending time.

As the ester exchange between PC and P64 continued, the chemical structure of the polymers became more random. Moreover, the molecular weight of the polymers decreased with the ester exchange. These two facts make the transesterified compatibilizer less effective in terms of interacting with both PC and P64. Therefore, it is necessary to control the ester exchange by adding inhibitor, which had been carried out by our group in a previous study¹⁰. In this case, 0.05% triphenylphosphate was added to the 60% P64 blend after 4 min blending time.

In *Figure 7*, the T_g of the inhibited 60% P64 blend stayed at around 128°C throughout a 20 min span. It indicated that the ester exchange between P64 and PC has been effectively stopped by the inhibitor. This inhibited compatibilizer, Vectra and PC were mixed in the Brabender mixer at 300°C as described in the prior section. To ensure the ester exchange did not happen between Vectra and PC, the thermal analysis of a blend of Vectra/PC at composition 20/80 was carried out. The analysis result is presented in *Figure 8*. In *Figure 8*, the T_g of the 20% Vectra blend was between 144.74 and 146.32°C during 20 min blending time, indicating little change in physical property.

The stress-strain curves of injection-moulded bars from 10/90 Vectra/PC blend as well as from 10/90/5 Vectra/PC/compatibilizer blend are shown in *Figure 9*. In *Figure 9*, the tensile modulus of the 10/90 Vectra/PC blend was about the same as that of pure PC. The failure behaviour of PC is typically yielding, whereas the failure behaviour of 10/90 Vectra/PC is brittle failure. In *Figure 10*, in comparing with 20/80 Vectra/PC blend, the tensile modulus and elongation at break increased substantially for the blend of Vectra/PC/compatibilizer (20/80/5). The ultimate stress for the Vectra/PC/compatibilizer (20/80/5) blend increased by 30% as compared to that of pure PC. Also, the elongation at break for the compatibilized blend increased to 5.5% as compared to 0.6% for the uncompatibilized blend. This indicated that the stress

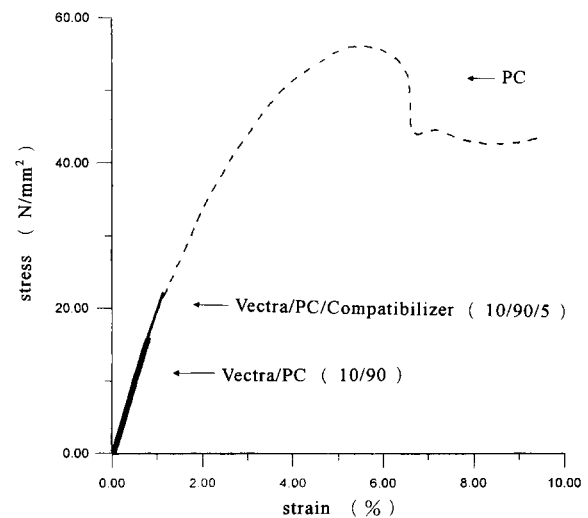


Figure 9 The stress-strain curves of PC, Vectra/PC (10/90) and Vectra/PC/compatibilizer (10/90/5)

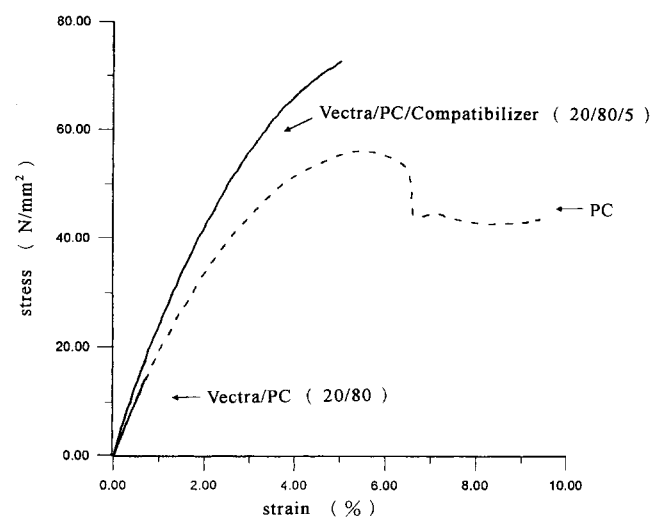


Figure 10 The stress-strain curves of PC, Vectra/PC (20/80) and Vectra/PC/compatibilizer (20/80/5)

was transferred in a broader cross-sectional area of the specimen.

It is well documented in the literature that elongation at break is very sensitive to phase adhesion or partial miscibility at the interface of blend components in a phase-separated system^{12,13}. This can be interpreted as the adhesion between Vectra and PC being improved by the presence of the compatibilizer.

The improved interface interaction for the case of added compatibilizer was manifested in the SEM micrographs of the fractured surface, as displayed in *Figures 11* and *12*. *Figures 11* and *12* show the centre region and the side region of the fractured surface of injection-moulded tensile bars respectively both with and without the addition of 5 phr compatibilizer. Comparing *Figures 11c* and *11d*, the observed interfaces were different in the sense that the LCP droplet

and PC interfaces were not distinctive for the compatibilized case, especially for the compatibilized 20% Vectra case. On the other hand, clear interfaces were observed for the case without compatibilizer. Another point was that the side and the centre morphology of the 20% Vectra blend without compatibilizer exhibited the well known skin-core morphology in LCP blend moulded parts, as shown in *Figures 11a* and *12a*. On the contrary, as in *Figures 11b* and *12b*, the compatibilized Vectra blend displayed more uniform morphology throughout the cross-sectional area.

Further improvement in the mechanical property of the compatibilized Vectra blend can be found in impact tests. The unnotched Izod impact test results are listed in *Table 1*. In *Table 1*, it can be seen that the impact property of the bar moulded from compatibilized 20/80 Vectra/PC blend has been greatly enhanced, as much as

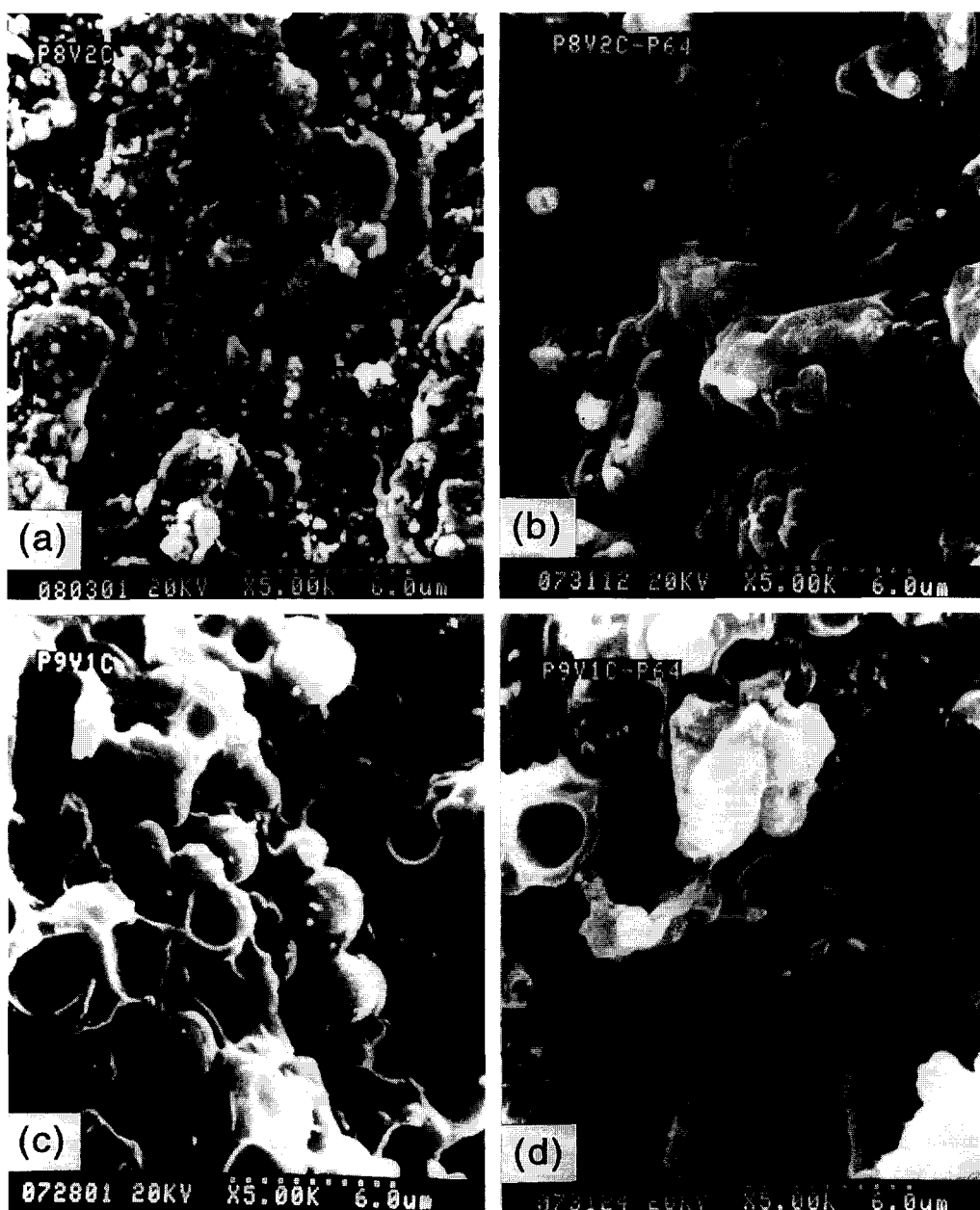


Figure 11 The SEM micrographs of the centre region of the fractured surfaces normal to the injection-moulded bars of blends: (a) Vectra/PC (20/80); (b) Vectra/PC/compatibilizer (20/80/5); (c) Vectra/PC (10/90); (d) Vectra/PC/compatibilizer (10/90/5)

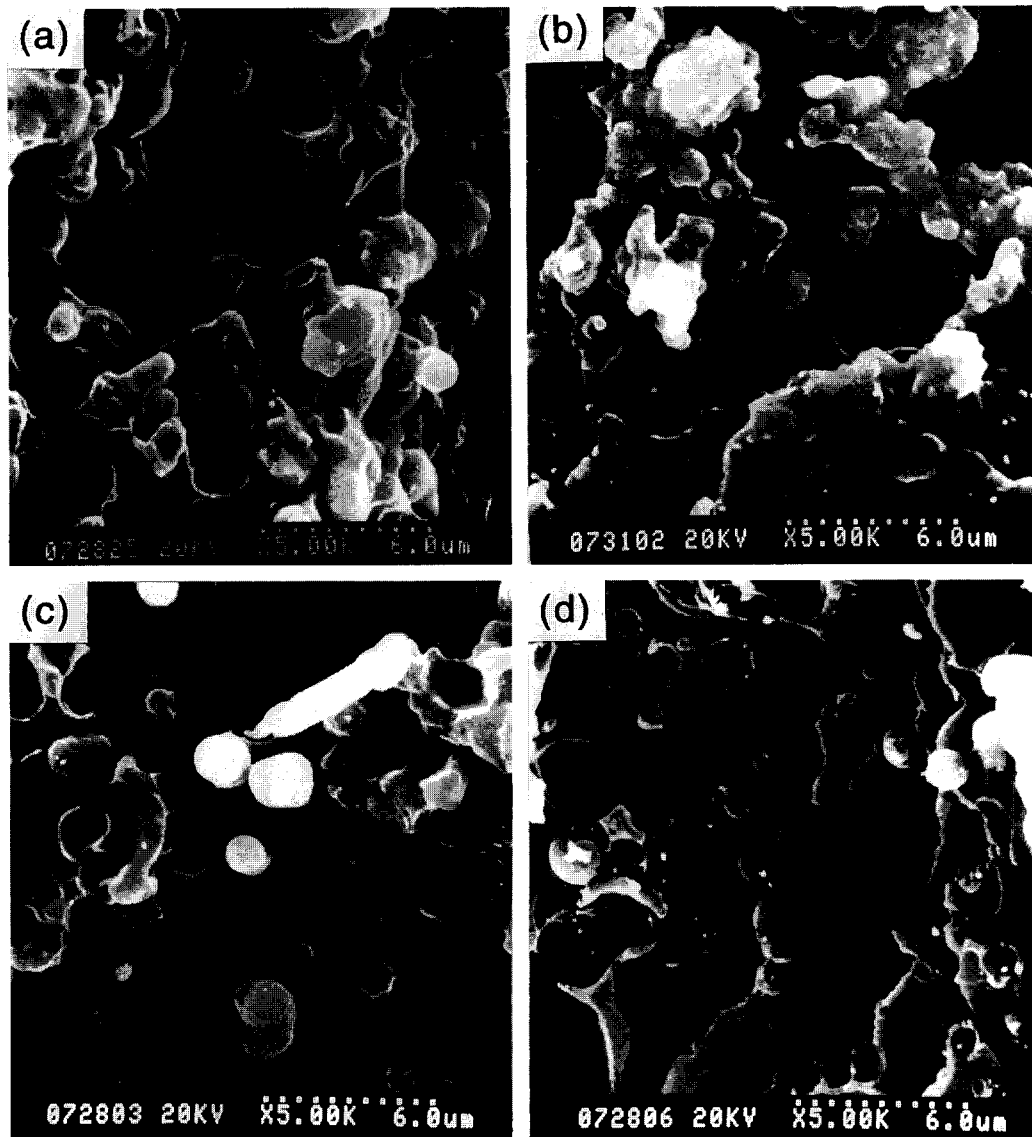


Figure 12 The SEM micrographs of the side region of the fractured surfaces normal to the injection-moulded bars of blends: (a) Vectra/PC (20/80); (b) Vectra/PC/compatibilizer (20/80/5); (c) Vectra/PC (10/90); (d) Vectra/PC/compatibilizer (10/90/5)

Table 1 The impact strength of unnotched injection-moulded bars

Blend composition	Impact strength (J m^{-1})
Vectra/PC (10/90)	178.89
Vectra/PC/Compatibilizer (10/90/5)	240.83
Vectra/PC (20/80)	50.20
Vectra/PC/Compatibilizer (20/80/5)	428.80

seven times as compared to that from the non-compatible blend.

CONCLUSIONS

A compatibilizer based upon the transesterification between liquid-crystalline poly(oxybenzoate-co-ethylene terephthalate) (POB/PET) (60/40) and polycarbonate has been developed. This compatibilizer can exhibit liquid-crystalline behaviour, and was effective in improving the adhesion between polycarbonate and incompatible liquid-crystalline polymer, Vectra (which

do not have ester exchange reaction). At proper composition, the enhanced adhesion in these ternary liquid-crystalline polymer blends resulted in greatly increased tensile properties such as elongation at break and ultimate stress in injection-moulded bars. The impact property of these ternary blends was also improved. An additional benefit was the more uniform morphology in the injection-moulded samples. This demonstrated the idea that, by providing enough physical interaction between matrix polymer and LCP through a third polymer, a compatible liquid-crystalline polymer blend can be formed. The third polymer contained similar chemical structural units to both matrix polymer and LCP through transesterification. These compatible LCP blends can have enhanced properties even when processed in very practical injection-moulding machines.

It is envisioned that further enhancement in mechanical properties of these ternary liquid-crystalline polymer blends can be achieved through an elongational flow process such as fibre spinning.

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