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COMPATIBILITY OF BLENDS OF POLY(BUTYLENE TEREPHTHALATE) AND LIQUID CRYSTAL POLYMERS: A DSC STUDY

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ABSTRACT

A calorimetric study of blends of poly(butylene terephthalate) (PBT) with two liquid crystal polyesters, one aliphatic-aromatic poly(biphenyl-4,4'-ylene sebacate) (PB8) and the other wholly aromatic (Vectra B 950), has been made for the prime purpose of obtaining information on the interphase. The dependence of the transition temperatures and enthalpies on blend composition, together with examination of the chemical interactions occurring at high temperature at the interface, showed that the compatibility between PBT and Vectra is much lower than that between PBT and PB8. Electron scanning microscopy confirmed this conclusion.

INTRODUCTION

The discovery of high-modulus, high-strength liquid crystal polymers (LCP) [1] has opened new interesting possibilities to the practice of polymer blending. Marked improvements in the thermomechanical properties of several commercial polymers have been obtained by blending them with 5-30% LCP and processing the blends by injection moulding or extrusion [2-5]. The dispersed LCP phase can be highly oriented, with the domains assuming the

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geometry of elongated fibrils.

In many respects, these blends resemble the composites prepared by adding short glass or carbon fibers to a polymer, but they have the added advantage of being processed much more easily. In principle, the higher the LCP dispersion (e.g. the smaller the fibril dimensions) the stronger the reinforcing effect should be [6].

The results published so far [2-5] seem to indicate that, if the LCP fibrils are sufficiently long, interphase adhesion is not so important. However, with usual processing techniques, it cannot be always guaranteed that the LCP domains have a sufficiently elongated geometry. In this case, improvement of the compatibility between matrix and LCP may be essential for the attainment of a satisfactory property profile.

Of the many definitions of polymer compatibility, we will use the least restrictive, according to which two polymers are compatible if their blend does not exhibit gross symptoms of phase segregation, and if they give rise to at least some mixing of polymer segments at the interface, so as to display sufficient mutual adhesion. It is known that compatibility may be improved by the addition of compatibilizers (e.g. block or graft copolymers containing chain segments miscible with either components) or by inducing chemical reactions at the interface [7].

Several methods for studying polymer compatibility are available [8]. Differential scanning calorimetry (DSC) has been mainly used for proving the complete miscibility of two polymers on a molecular scale. In this case, a single glass transition, intermediate between those of the components, is expected for the blend. However, if one or both polymers are crystallizable, DSC will hardly provide direct and reliable information on the polymer T_g.

Indirect information on compatibility can be drawn, in the latter case, by the study of the melting and crystallization transitions, since both the degree of crystallinity and the melting point of the crystallizable polymer are expected to decrease with increasing content of the second component if there is miscibility in the melt. This has been observed, in fact, in a number of cases [9,10].

The situation can be further complicated for blends containing LCP, because the latter gives rise, above the melting point, to a phase of intermediate order, which is almost certainly immiscible with the other component even if the two polymers are wholly miscible in the isotropic state. In a previous paper [11] some of us have shown that the compatibility between poly(butylene terephthalate) (PBT) and an aliphatic-aromatic liquid crystal polyester poly-(biphenyl-4,4'-ylene sebacate) (PB8) can be satisfactorily studied by DSC.

In the present paper, we discuss the calorimetric data for blends of PBT with

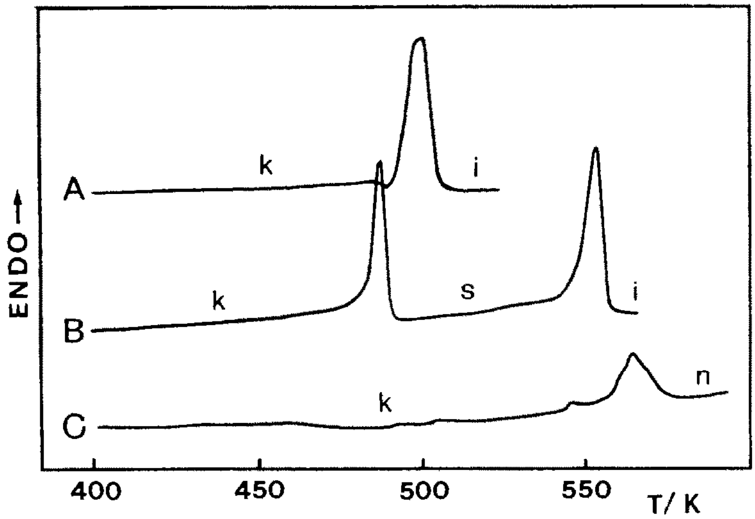

Fig. 1. DSC heating traces of PBT (A), PB8 (B) and Vectra B950 (C); (k=crystalline, s=smectic, n=nematic, i=isotropic).

a commercial wholly aromatic liquid crystal polyester (Vectra B 950) and compare them with old and new data on the PBT/PB8 blends.

EXPERIMENTAL

PB8 was prepared by the procedure of Asrar *et al.* [12] from 4,4'-diacetoxybiphenyl and sebacic acid. The crude polymer was dissolved in 60:40 (w/w) phenol-tetrachloroethane mixture, precipitated into excess methanol, extracted with boiling chloroform in a Kumagawa apparatus for 6 hours and dried in vacuo.

Vectra B 950 is a commercial copolyester synthesized from hydroxynaphthoic acid (60%), aminophenol (20%) and terephthalic acid (20%) [13]. A 5 Kg sample of this LCP was bought from Celanese Limited, Watford, England. It was dried in vacuo at 400 K for 12 hours before use.

A commercial PBT sample (Valox, General Electric Co.) was used in this study. It was dried under vacuum at 380 K for 12 hours before use.

The blends were prepared in the melt at 560 K with a Plastograph PL 3S Brabender mixer. For the investigation of the ester exchange reactions occurring in PBT/PB8 blends, the latter were prepared by coprecipitation from solutions in 60:40 (w/w) phenol-tetrachloroethane mixture.

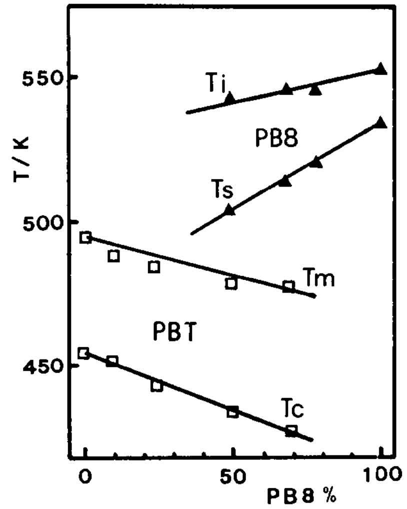

Fig. 2. Temperatures of the s → i (T_i) and i → s (T_s) transition of the PB8 phase, and of the k → i (T_m) and i → k (T_c) transition of the PBT phase in PBT/PB8 blends.

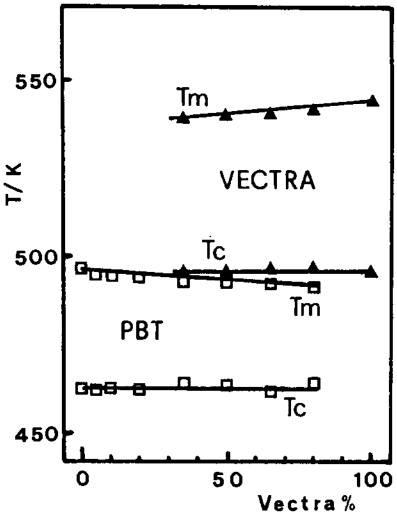

Fig. 3. Temperatures of fusion (T_m) and crystallization (T_c) of PBT phase and of the k → n (T_m) and n → k (T_c) transition of Vectra phase in PBT/Vectra blends.

The calorimetric analysis was carried out on a Perkin Elmer DSC-4 apparatus. Unless otherwise stated, the measurements were made at a rate of 20 K min^{-1}.

The scanning electron micrographs were taken on a Jeol T 300 SEM.

RESULTS AND DISCUSSION

The DSC heating traces of PBT, PB8 and Vectra B 950 are shown in Fig. 1. It can be observed that all three polymers are crystalline in the low temperature range. On melting, an isotropic phase is obtained from PBT, whereas the two other polyesters give rise to mesophases. The smectic mesophase of PB8 [12] is stable up to about 550 K, where it transforms into an isotropic liquid. The mesophase formed by Vectra B 950 at ~560 K is nematic and its range of stability extends up to the decomposition temperature [13].

From the thermal properties of the three polymers it may be concluded that, during blending, PBT and PB8 were isotropic liquids whereas Vectra B 950 was in the nematic liquid crystal state.

The transition temperatures of the PBT/PB8 and PBT/Vectra blends are shown in Figs. 2 and 3, respectively. In order to have comparable data, the DSC

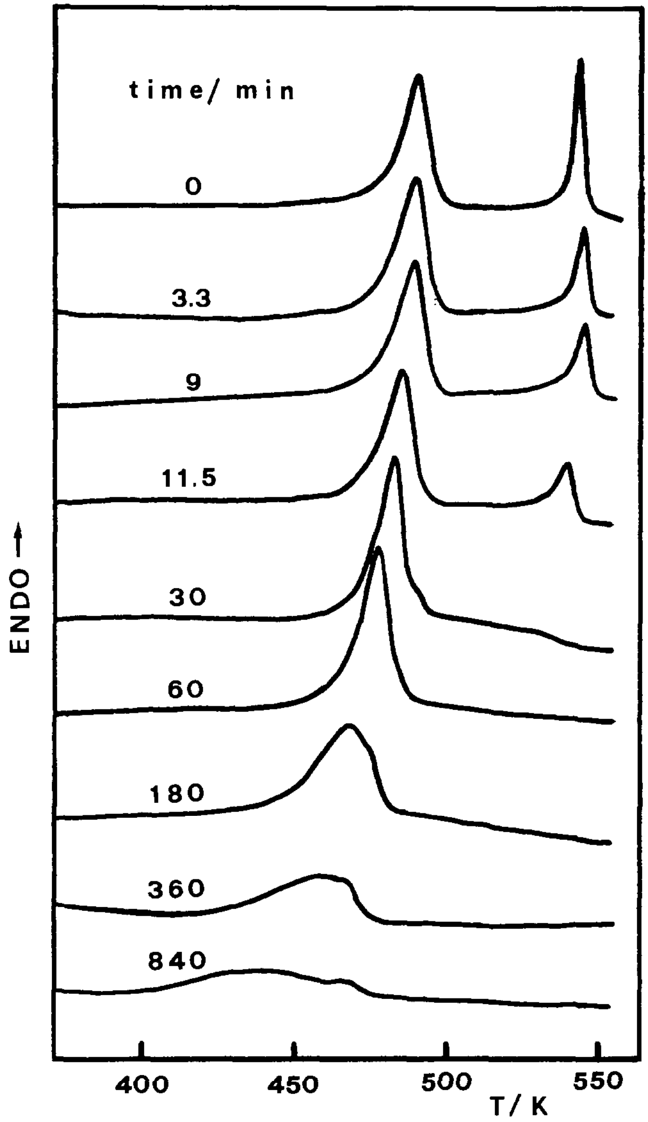

Fig. 4. DSC heating traces of 65:35 (w/w) PBT/PB8 blends after thermal treatment at 560 K for the indicated times.

heating traces of samples having the same thermal history (2 min at 563 K) were considered. The temperatures of mesophase formation (T_S) and crystallization (T_C) were recorded on the first cooling runs, carried out at 20 K min^{-1}, whereas the melting (T_m) and isotropization (T_i) temperatures were obtained on the subsequent heating cycle from room temperature. The data in Fig. 2 are in fair

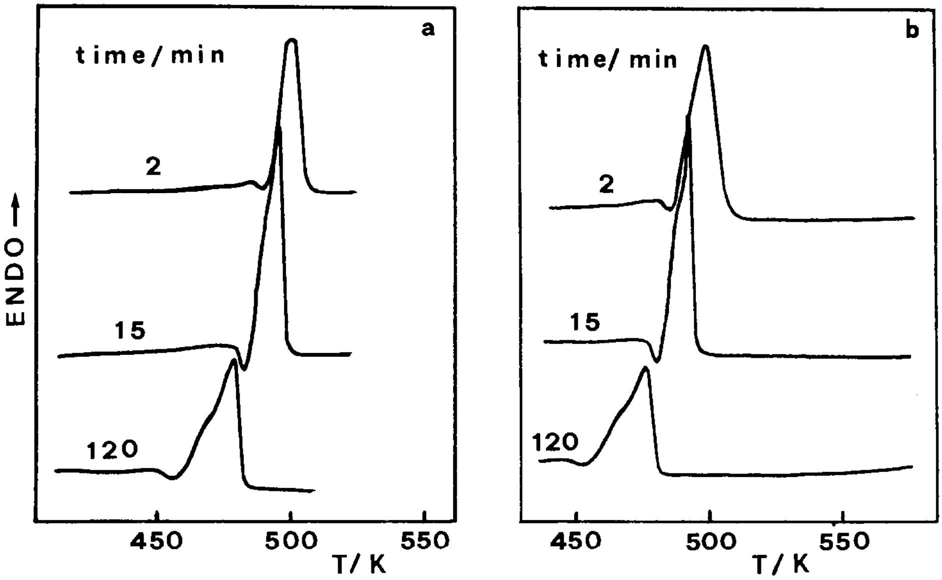

Fig. 5. DSC heating traces of pure PBT (a) and PBT/ Vectra 95:5 (b) samples after thermal treatment at 573 K for the indicated times.

agreement with those previously obtained for PBT/PB8 blends prepared by coprecipitation [11]. It is readily observed that both the PB8 T_s and the PBT T_c decrease markedly on increasing the amount of the other component. This shows that PBT and PB8 are at least partially miscible in the isotropic state and that a liquid, mixed PBT/PB8 phase is present, together with the smectic PB8 phase at temperatures between T_s and T_c. The effect on T_m and T_i is much less marked, the difference being due to kinetic effects of diffusion of the components to and from the liquid mixed phase.

As compared with Fig. 2, the data of Fig. 3 indicate that the transition temperatures of PBT and Vectra remain almost uninfluenced by blending. Since the isotropic state of Vectra is not accessible, T_i being higher than the decomposition temperature, it is not possible to guess whether PBT and Vectra are at least partially miscible in the amorphous. However, their compatibility, if any, must be very scant, judging from the plots of Fig. 3.

It is well known that compatibility between the phases of a blend can be increased if the two polymers can chemically react with each other to form block or graft copolymers at the interface. Thus, for example, Pillon and Utracki [7] added a catalyst during melt processing of polyester-polyamide blends in order to speed up the ester-amide interchange reactions, leading to

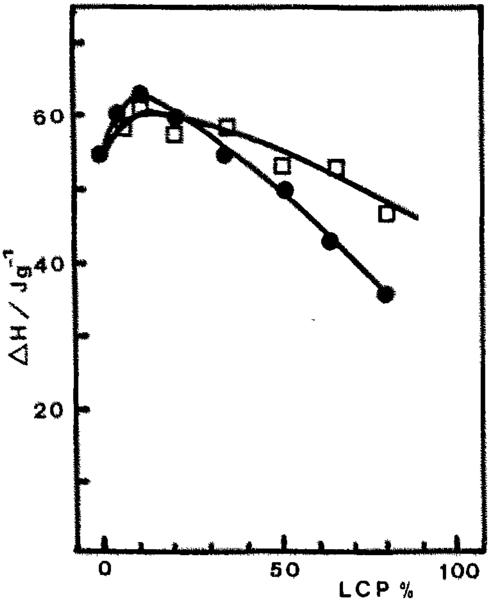

Fig. 6. Enthalpy changes associated with the fusion of PBT in PBT/PB8 (●) and PBT/Vectra (□) blends as a function of blend composition.

improved compatibilization. Ester exchange reactions taking place between polyesters in the melt have received much attention and the matter has been recently reviewed by Kotliar [14]. As for the PBT/PB8 blends, it has already been reported by some of us [11] that ester exchange reactions do occur in the melt at 560 K. The effect of holding coprecipitated PBT/PB8 blends (65:35) (w/w) for different time intervals at 560 K is illustrated in Fig. 4, where the DSC heating traces obtained after cooling to room temperature at 20 K min^{-1} are shown. It can be observed that the isotropization transition almost disappears within 30 min, showing that the periodicity of the PB8 macromolecules, which characterizes the smectic mesophase of this polymer, is nearly destroyed. Thermal degradation of PB8 has been reported to occur, starting from temperatures sufficiently higher than T_i [12], but measurements carried out by us on PB8 samples held at 560 K under nitrogen for a sufficiently long time (20÷60 min) have shown that the position and intensity of the isotropization peak undergo changes indicative of progressive losts of order of the mesophase. However, this is much slower than the process illustrated in Fig.4. Therefore, though no quantitative data on the kinetics of the transesterification can be drawn from the change in area of the isotropization peak, this change is certainly to be mainly related to this chemical process. By

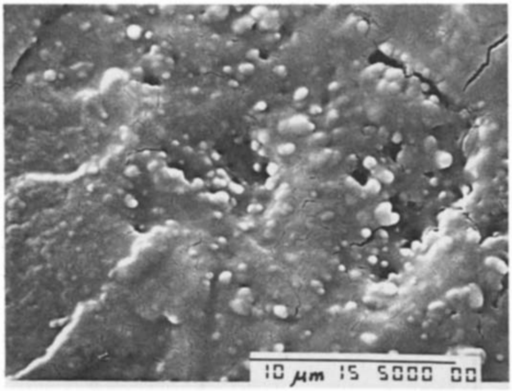

Fig.7. Fracture surface of a PBT/PB8 (80:20) blend.

contrast, no direct evidence on the course of transesterification can be drawn from the behaviour of the lower temperature peak because this is, in fact, the sum of two effects associated with the fusion of both crystalline phases of PBT and PB8.

An attempt at similar investigation of possible ester exchange reactions occurring between PBT and Vectra has been made. In this case, however, the only DSC peak that can be chosen for this analysis is that of melting of the PBT phase. A PBT/Vectra blend (95:5) was held at 573 K for different time intervals, cooled to room temperature at 20 K min^{-1} and analyzed in the DSC apparatus. The results are compared in Fig.5 with those obtained for pure PBT samples subjected to the same thermal treatments. It is apparent that the changes in the slope and the position of the melting peak of PBT are to be associated to the degradation of this polymer, rather than to its chemical interaction with Vectra. This result shows that in PBT/Vectra blends, the ester exchange reactions, if any, must be very much slower than in PBT/PB8 blends.

This is another piece of circumstantial evidence that very poor mixing of PBT and Vectra polymer segments takes place at the interface.

It had already been found that, in PBT/PB8 blends, the degree of crystallinity of the PBT phase appears to be higher than that of the pure polymer, for PB8 contents up to about 35% by weight [11]. The reasons for such behaviour, also observed for other systems [15,16], are not completely clear; however, it may be inferred that they should be found in interactions of some kind between the two phases. The dependence of the enthalpy of fusion of the PBT phase on blend composition, for PBT/PB8 and PBT/Vectra blends, is shown in Fig. 6. It is apparent that the variations of the normalized enthalpy of fusion of the PBT phase with blend composition are much less marked for the PBT/Vectra blend.

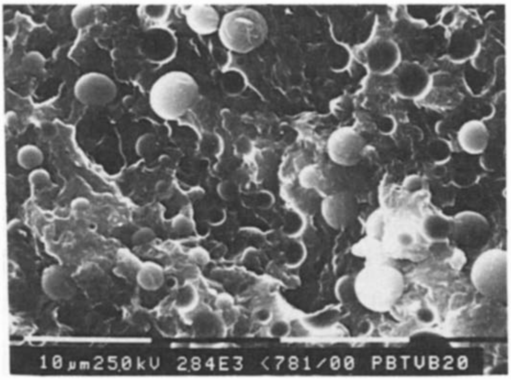

Fig. 8. Fracture surface of a PBT/Vectra (80:20) blend.

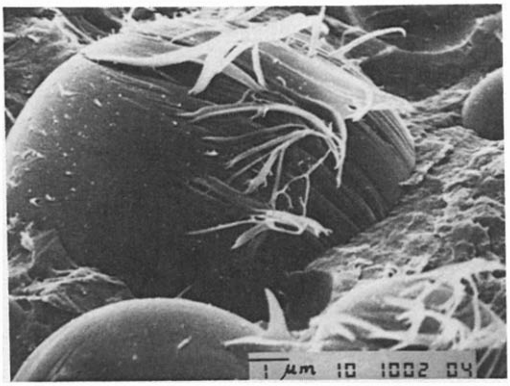

Fig. 9. Fracture surface of a PBT/Vectra (65:35) blend.

This finding also points to a far smaller compatibility between PBT and Vectra with respect to that observed between PBT and PB8.

Lastly a scanning electron microscope examination of the fracture surface of samples of PBT/PB8 and PBT/Vectra blends (Figs. 7 and 8) has shown that the segregation of the microspheres of Vectra (1÷5 µm diameter) is much more pronounced than that of PB8 microspheres (0.2÷1 µm diameter). It can be concluded, therefore, that the morphology examination confirms the results obtained from the calorimetric study and indicates that very low compatibility exists between PBT and Vectra.

Closer examination of the microsphere of Vectra remaining on the fracture surface (Fig. 9) demonstrated the fibrillar nature of the LCP: the microspheres, in fact, seem to be monodomains of macromolecules with a sufficiently uniform orientation.

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