

Ester exchange reactions in polyarylate/poly(ethylene terephthalate) blends

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Blends coagulated by a solution/precipitation procedure of a polyarylate (PAr) based on bisphenol A and tere/isophthalates with poly(ethylene terephthalate) (PET) have been studied by a variety of experimental methods. Differential scanning calorimetry experiments have shown that in blends containing more than 30% PET, conditioning of the blends at high temperatures required for calorimetric measurements resulted in progressive ester exchange reactions. The 10% and 20% PET mixtures, in which this extreme conditioning was not required, showed a single glass transition, contrary to the behaviour of the other PET compositions. These differences may be attributed to the shape of the spinodal curve, which has been simulated according to the McMaster model for polymer mixtures. The progression of the interchange reactions has been followed by solvent extraction of the resulting products and subsequent Fourier transform infra-red spectroscopy analysis. A parallel decrease in the PET heat and temperature of fusion in the insoluble fractions was observed. In our opinion this was due to the incorporation of PAr units in the PET chains, which caused a decrease in their crystallizable segment length.

(Keywords: polyarylate; poly(ethylene terephthalate); miscibility; thermal transitions; transesterification)

INTRODUCTION

There is an increasing interest in the understanding of the interchange reactions that take place in polymer blends between the different functional groups involved in mixtures of some polycondensation polymers, such as polyamides and polyesters. Consequently, significant progress has been made in the last few years given the industrial applications and the academic interest in the subject. In fact, the control of the interchange reactions may provide a new route in preparing new materials directly during processing. The complicated processes involved and the variety of experimental conditions could result in a wide range of microstructures. On the other hand, and mainly in crystalline polymers, its tendency to react in the vicinity of the melting temperature provokes the appearance of interchange reaction products when standard methods for determining macroscopic miscibility (d.s.c., d.t.a., t.m.a., transparency, etc.) are applied. It has been established that these interchange products, mainly constituted by block and random copolymers of the original components, could play a decisive role in miscibilizing two immiscible polymers. Consequently, when these products appear in the reaction medium, they complicate the conclusions about the location of possible phase diagrams of the blends.

In a recent work¹ we discussed in a preliminary manner the influence of composition on the glass transition temperature and the melting point of polyarylate(PAr)/poly(ethylene terephthalate) (PET) blends. After heating at 550 K for 20 min in order to eliminate the last traces of PET crystallinity, only one

glass transition was observed for each composition. At the same time, a large melting point depression was also observed. In this paper, we already pointed out the difficulties in establishing whether we had a true miscible pair or not, given our previous and limited evidence of the ester exchange reactions that occur to some extent in this blend. Our reasonable doubt arose from the fact that, given that blends containing less than 30% PET were completely amorphous, it was not necessary to heat them up to 550 K prior to d.s.c. scans. Consequently, the influence of possible interchange reactions could be disregarded. The interesting experimental observation was that these amorphous and so conditioned blends showed only one glass transition temperature.

Two other more complete papers have recently been published studying these PAr/PET mixtures^{2,3}. Kimura *et al.*² concluded that physical blends of PAr and PET had two amorphous phases, given the dual glass transition temperatures observed in the 25/75, 50/50 and 75/25 compositions studied. They followed the ester exchange reactions by means of the changes in the melting and crystallization temperatures, glass transition temperatures and melting heat. In their work, polymers were mixed by means of solution/precipitation after which films were prepared by pressing the samples at 280°C for 4 min.

In a more recent work, Robeson³ has studied melt mixtures of polyarylate with poly(ethylene terephthalate), phenoxy and three different cyclohexanedimethanol-based polyesters by means of a torsion pendulum. As far as the PAr/PET blends are concerned, his conclusions agree in general terms both with the Porter *et al.*² work and with our previous results mentioned above. Some differences may be attributed to the different methods employed in preparing the samples.

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This paper will primarily discuss some additional evidence for the existence of ester exchange reactions in PAR/PET blends. To obtain further insight into the changes which occur during the high-temperature conditioning, selected samples were subjected to solvent extraction, followed by Fourier transform infra-red spectroscopy (FTi.r.) and d.s.c. examination of the soluble and insoluble fractions. Additional data will be presented on the influence of annealing treatments in the evolution of the phase behaviour of PAR/PET blends. Nowadays it is well known that the introduction of covalent bonds between the moieties of immiscible homopolymers may enhance miscibility. Some examples in A/(BC) mixtures have recently been reported⁴ where homopolymer A is immiscible with homopolymer B and homopolymer C, but miscible with some compositions of the BC copolymer. Miscibility has been attributed to unfavourable intramolecular interactions that occur between the copolymer functional groups; these interactions are 'diluted' by the presence of homopolymer A. This type of argument would explain the miscibilizing role of block and graft copolymers in mixtures of their original homopolymers.

Finally, we have simulated spinodal curves in order to explain the influence of concentration in the miscibility of our pair. It is well known that asymmetrical shapes of the phase separation curves are a normal feature of polymer/polymer mixtures⁵. This asymmetrical shape depends on the values of the characteristic parameters of the pure components, p^* , v^* and T^* , on the nature of the interactions between functional groups, on the molecular weight distribution, etc.

EXPERIMENTAL

The polyarylate (PAR) used in this investigation was a copolyester, Arilef U-100, obtained from Solvay. It is a copolyester of bisphenol A and 50% terephthalic/50% isophthalic acids. Its average molecular weights were $M_w = 43\,000$ and $M_n = 19\,000$, determined by g.p.c. in THF at 30°C; the Mark-Houwink constants were previously determined, as reported elsewhere⁶.

The poly(ethylene terephthalate) (PET) used was supplied by Polysciences (catalogue number 4301). Its viscosity average molecular weight $M_v = 18\,000$ was established in a 50:50 phenol/tetrachloroethane mixture⁷.

Solution/precipitation blends of the different compositions employed were prepared by dissolving an amount of PAR/PET in the desired weight ratio in phenol at 60°C. The total concentration was in the vicinity of 10% in weight. These solutions were stirred for 2 h and then added dropwise to a large excess of cold methanol at 0°C, causing rapid coprecipitation. The precipitate was filtered off and washed with methanol in order to remove the phenol completely. The final precipitate was dried *in vacuo* at 90°C for 48 h.

In order to study the ester exchange reactions, the polyester blends were transesterified by heating the precipitate described above at 297°C (570 K) and for different reaction times. Blends were placed in a sealed metallic receptacle, immersed in a silicone bath. Reactions were previously indirectly identified, by solubility tests. In chloroform, PAR is soluble and PET is not. As reaction conditions are held, the appearance of transesterified products in the mixture modifies to a great

extent the solubility of the sample in the selective solvent, as described below. Soluble and insoluble fractions in chloroform were separated, dried and weighed.

Physical mixtures without transesterification and the soluble and insoluble fractions of the different transesterified compositions were investigated by FTi.r. and d.s.c. The FTi.r. spectrophotometer was a Nicolet MX-1. The glass transition temperature T_g , the cold crystallization temperature T_c , the melting point T_m and the melting heat ΔH_f were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter. The T_g was determined as the intersection of the lower-temperature specific heat and the transition region data. T_c was considered to be the maximum of the exothermic peak of the cold crystallization and T_m that of the endothermic melting peak. Melting heats were determined from the areas under the respective curves, calibration being previously carried out with the aid of metal standards.

RESULTS AND DISCUSSION

All the precipitated PAR/PET mixtures subjected to a first d.s.c. scan between 320 and 570 K only showed clearly a melting peak corresponding to PET fusion, at a temperature of 530 K, independently of the blend composition. This result indicates that the presence of PAR does not affect the PET crystallization obtained during the precipitation. After this first scan, mixtures were quickly cooled down to 320 K and a second scan in identical conditions was performed up to 570 K. During this second scan it was observed that all the mixtures except 80:20 and 90:10 PAR/PET exhibited a glass transition identical to that of the pure PET polymer, as shown in *Figure 1*. This glass transition indicated that the blend amorphous matrix is composed of two well differentiated phases. It would be logical to observe a second glass transition temperature corresponding to the PAR phase. However, the existence of a PET crystallization peak in the thermograms in a temperature range close to this second T_g makes the observation

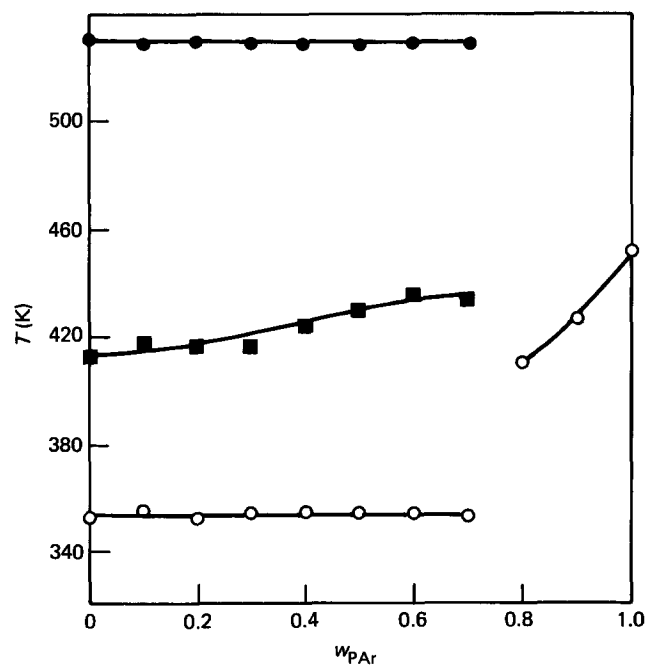


Figure 1 Thermal transitions of PAR/PET blends without treatment at 570 K: (○), T_g ; (■), T_c ; (●), T_m

impossible. These results would appear to indicate the immiscibility of the system and are in good agreement with those obtained by Porter *et al.*² and Robeson³.

The PAr/PET (80:20 and 90:10) blends presented only one glass transition temperature in the second scan, intermediate between those of pure PAr and PET polymers, indicating the presence of a unique amorphous phase. A similar result has also been observed by Robeson³ in a recent paper.

As described above, all the blend samples, except those of 80:20 and 90:10 compositions, showed a PET crystallization peak in this second scan. The peak temperature was practically independent of the composition at low PAr contents and increased when the PAr percentage was higher than 40%. This variation with composition seems to indicate the existence of some interactions between the pure polymers. A similar tendency has been observed by Robeson³ whereas Porter *et al.*² observed just the opposite behaviour.

The last characteristic of the second scans carried out in the PET-rich blends is a melting peak at a constant temperature of 528 K, independent of composition and slightly lower than that encountered in the pure PET (530 K). This result seems to confirm the immiscibility of the system, given that these differences are extremely small and cannot be attributed to interactions between the components of the mixture. A similar result was reported by Porter *et al.*² whereas Robeson³ found a more pronounced decrease in the melting temperature with the blend composition in PAr.

If mixtures are kept at high temperature for longer periods of time, a different behaviour may be observed. As an example, Figure 2 shows the glass transition temperatures of the different compositions after 15 min at 570 K. As can be seen, all the compositions showed a single glass transition, intermediate between those of the pure components and dependent on the composition. The transitions were narrow enough to conclude the presence of a unique amorphous phase in the mixture. In a parallel manner, samples containing more than 70% PET showed

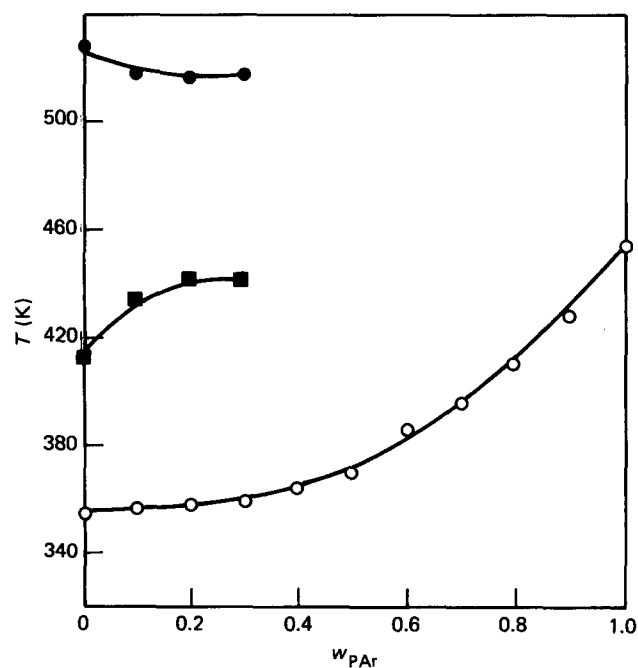


Figure 2 Thermal transitions of PAr/PET blends after 15 min at 570 K: (○), T_g ; (■), T_c ; (●), T_m

a crystallization peak, whose temperature increased when the PAr content increased. At the same time, these mixtures exhibited a melting peak in the vicinity of 518 K, 10 K lower than that observed in the second scan described above. As we will see in the following lines, all these results may be explained on the basis of the ester exchange reactions that take place in the mixture as a consequence of the prolonged time at 570 K.

It has been reported⁸ that blends of two different polycondensation polymers, such as polyesters or polyamides, can react if their chain links are broken as a consequence of high-temperature treatments, as occurs in technological processing. The mechanisms of interchange reactions that occur in polycondensation blends involve well known alcoholysis, aminolysis, acidolysis, amidolysis and transesterification reactions. Recent papers about different aspects of the interchange reactions in different polyester blends have studied mixtures like bisphenol A polycarbonate (PC)/poly(butylene terephthalate) (PBT)⁹⁻¹¹, PC/PET¹², PAr/PET^{2,3}, PAr/PBT¹³, PAr/phenoxy³, PAr/PC¹⁴, etc. In these papers, the existence of transesterification reactions has been shown and the mechanism of the reaction has been well established as well as the kinetics of the process. On the other hand, the microstructure of the products that appear during transesterification has been investigated by different experimental techniques. In the following lines we explain our monitoring of the PAr/PET transesterification reaction that takes place when different compositions are subjected to a heating treatment.

The first evidence of the evolution of the ester exchange process is the change in blend solubility with reaction time. In chloroform, the selective solvent we have used in this work, polyarylate is fully soluble whereas PET is completely insoluble with pure homopolymers as can be easily demonstrated. Consequently, in a 50:50 mixture, approximately 50% solubility must be expected, as must similar behaviour in other blend compositions. Figure 3 shows the solubility evolution of the 50:50 blend after different heating treatments at 570 K. At short times, a decrease in the solubility has been observed. After that, a sharp increase and subsequent stabilization of the

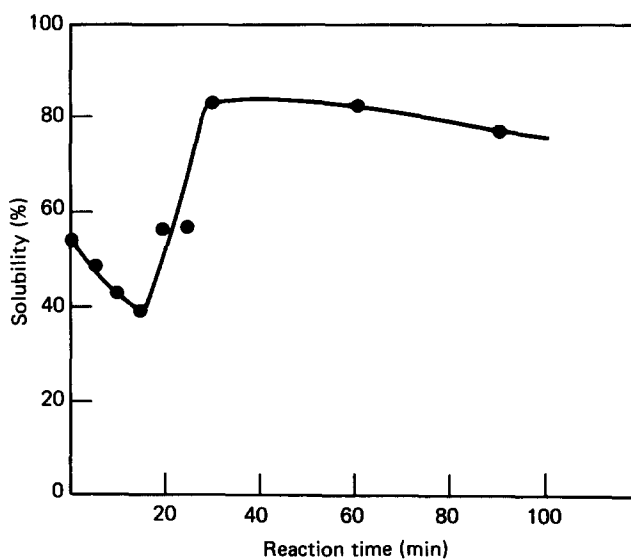


Figure 3 Solubility in chloroform of a PAr/PET (50:50) blend, after treatment at 570 K

solubility becomes clear in the diagram. As pointed out by other authors¹³ and experimentally demonstrated by Devaux *et al.*⁹, the transesterification reaction leads, at short times, to the production of block copolyesters with reduced solubility. For increased reaction times, the composition of the copolyesters becomes statistical and a nearly completely soluble product is obtained. The resultant initial block and eventual random copolymers are expected to exhibit better mutual miscibility than the unreacted components, based on theoretical and experimental results concerning copolymers¹⁵.

When soluble and insoluble fractions are separated and dried, important changes may be observed in their FTi.r. spectra and d.s.c. thermograms. Figure 4 illustrates the evolution of the FTi.r. spectra of the soluble and insoluble fractions when a 50:50 PAR/PET blend is heated at 570 K for different periods of time. Similar behaviour may be observed in the other compositions. At 0 min, the C=O stretching bands of pure PAR and PET can be clearly distinguished (the PAR band appears at 1739 cm^{-1} and the PET band at 1719 cm^{-1}). After only a few minutes, blocks of PAR appeared in the insoluble fraction and PET sequences in the soluble fraction, and time caused the two bands to come closer together. After 25 min the two bands are very similar and have a very similar maximum and shape.

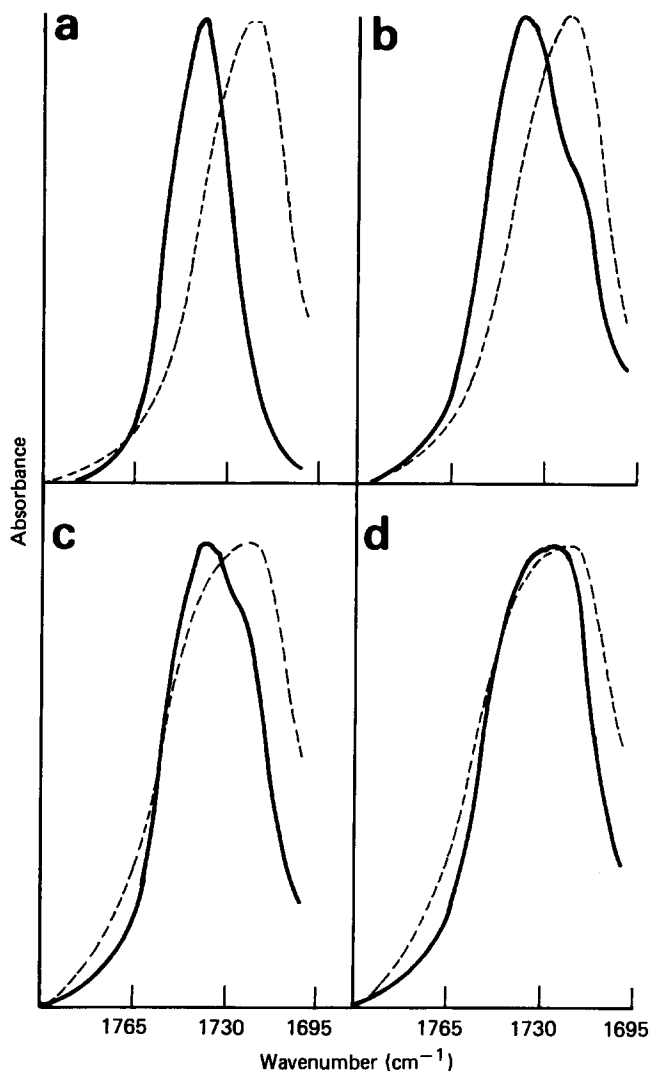


Figure 4 Evolution of the C=O stretching bands after different treatment times: (a) 0 min, (b) 5 min, (c) 15 min, (d) 25 min; (—), soluble fraction; (---), insoluble fraction

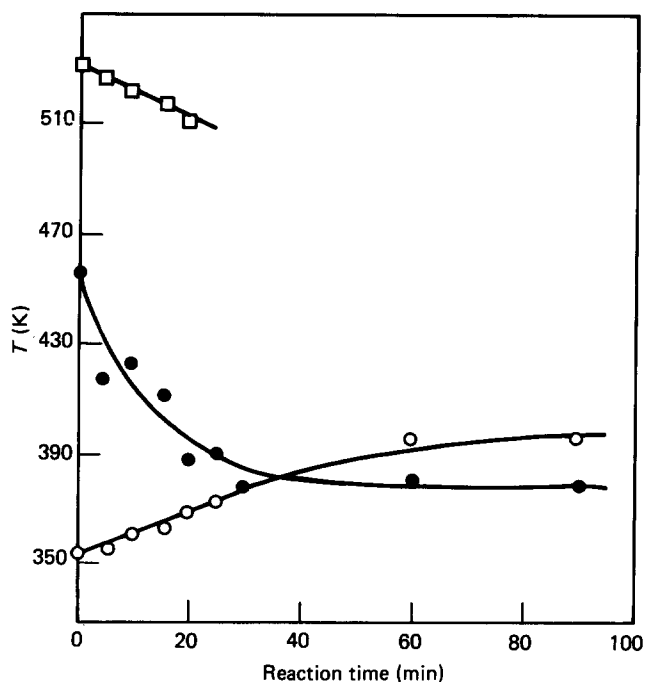


Figure 5 Thermal transitions of the soluble (●, T_g) and insoluble (○, T_g ; □, T_m) fractions

Figure 5 shows the thermal transitions of the soluble and insoluble fractions. The soluble fraction exhibited only one glass transition temperature whereas in the insoluble fraction and at short times both T_g and T_m were observed. After 30 min, the melting peak disappeared and only one glass transition was also observed. There is a decrease in the glass transition temperature of the soluble fraction during the heat treatment, starting in the pure PAR T_g . This behaviour may be explained on the basis of the incorporation of PET segments into the PAR chains. An opposite effect should be the cause of the T_g increase of the insoluble fraction. Other blend properties affected by the evolution of the interchange process are the PET melting point (Figure 5) and the PET heat of fusion in the insoluble fraction (Table 1). Both exhibited a progressive decrease with time. These results are expected to be due to the incorporation of PAR units in the PET chains which cause a decrease in their crystallizable segment length.

All the aforementioned experimental results are clearly indicative of the influence of the interchange reactions in the physical behaviour of the heated samples. These results are consistent with those obtained with other similar mixtures and confirm the existence of these reactions, giving new routes for the production of PAR/PET copolyesters of different properties.

However, some additional comments have to be taken into consideration as far as the samples of high PAR content are concerned. As pointed out in the first part of this section, already in the second scan, after a very short period of time at 570 K, samples with 10% and 20% PET content exhibited a single glass transition temperature and there were no signs of PET crystallinity, as indicated by the absence of a PET melting peak. Then, it is not necessary to attain such high temperatures to destroy the thermal history imposed by the presence of the PET crystals. Consequently, another scan regime has been used with these two blends, starting at 320 K and finishing at 440 K. After a first scan in which no transitions were observed, successive cycles gave only one

Table 1 PET melting heat in the insoluble fraction

Reaction time at 570 K (min)	Melting heat (cal/g PET)
0	11.7
5	11.1
10	8.9
15	6.1
20	0.3

glass transition temperature, confirming our previous results and those of Robeson³. Solubility tests confirmed that no indication of ester exchange reaction can be found up to 30 min at 440 K. Then, it seems clear that both polymers are miscible at these compositions. Moreover, optical experiments carried out with these compositions up to the temperatures at which evident signs of rapid reactions were observed did not allow us to conclude that these blends phase separate with increasing temperature.

With the aforementioned experimental results in mind, it is necessary to think of a phase diagram of asymmetrical shape in order to reconcile all the experimental evidence about the influence of the blend composition in having a one-phase system or a two-phase system.

Binodals and spinodals that shift their minima towards the region of compositions that are poor in one of the components have been experimentally observed in some polymer blends^{16,17} and theoretically predicted by the modern free-volume theories applied to polymer blends, such as the equation-of-state theory¹⁸ and others. Factors such as disparity in numbers of nearest-neighbour contacts, changes in flexibility of polymer chains, molar mass and distribution, concentration, etc., have been proposed¹⁹ as responsible for the complex structure of some phase diagrams in polymer blends. Complete formulations of the expressions needed for the simulation of spinodals and interaction parameter-concentration relationships are given in refs. 17 and 18. Data for the characteristic magnitudes of the pure components have been taken from papers of Zoller *et al.*^{20,21}

As is known, theoretical expressions in the equation-of-state theory include some adjustable parameters, such as the contact surface ratio (s_2/s_1), the contact energy parameter X_{12} and a third one, c_{12} , which reflects the deviations from additivity of the degrees of freedom of the macromolecules as a result of the restrictions imposed by the other component of the blend. In our case, we have calculated s_2/s_1 following Bondi's²² radii and a method proposed by Sanchez and Lacombe²³ in which

$$s_2/s_1 = (v_{sp,2}^*/v_{sp,1}^*)$$

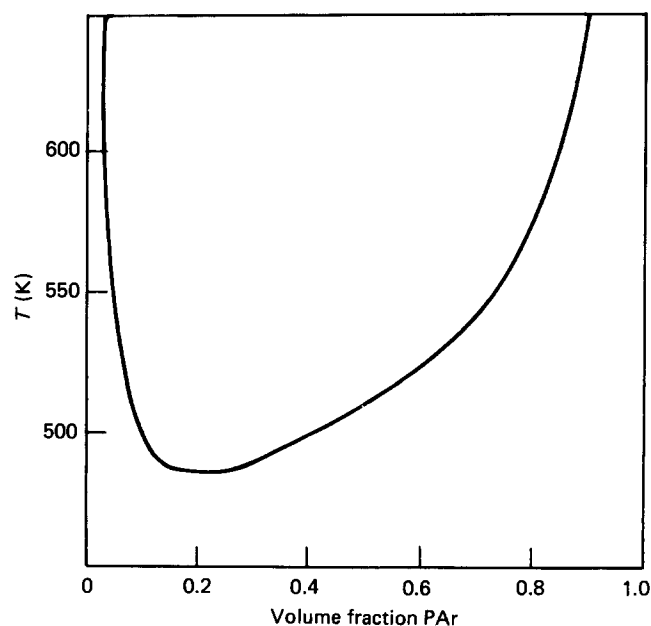
where $v_{sp,i}^*$ are the characteristic specific volumes in the pure components, directly deducible from their respective thermal coefficients. In both methods s_2/s_1 was close to unity, and c_{12} was taken as 0.02, a usual value in other theoretical simulations. Finally X_{12} was adjusted in order to match the spinodal equation to the point $T=570$ K, $\phi_1=0.8$, where ϕ_1 is the volume fraction of the amorphous polymer (PAr).

Figure 6 shows the simulated spinodal for our PAr/PET blend. As can be seen, an asymmetrical shape is the main feature of this diagram. It is interesting to point out that the diagram may be moved up and down only by changing the magnitude of the X_{12} parameter. In the figure, $X_{12} = -2.44 \text{ cal cm}^{-3}$, a reasonable value of the

X_{12} parameter. However, the shape of the curve is retained. Consequently, and despite the polar character of the components, the theory explains the phase behaviour experimentally observed, given the sharp variation of the temperature at compositions higher than 70% PAr. Additional calculations show that the interaction parameter at 570 K goes from 0.030 (at $\phi_1=0.1$) to 0.013 (at $\phi_1=0.9$), a reasonable evolution, given the critical value in the vicinity of zero, which the theory predicts.

In spite of this plausible agreement between experiments and theory and given the uncertainties that the adjustable parameters introduce in the location and shape of the phase diagrams, it seemed reasonable to us to doubt the immiscibility of polymer mixtures having more than 20% PET. It is suitable to bear in mind that PET crystallizes very quickly during the solution/precipitation procedure, and the smaller the PAr content, the higher the crystallization rate. After a first scan, PET melts, but perhaps it requires a certain amount of time to mix together with PAr, especially if we take into account the high PAr viscosity, which may render mutual diffusion difficult. Then, it would not be illogical to consider the possibility of some degree of miscibility between PAr and PET.

In order to study the possible tendency towards miscibilization between PAr and PET, not caused by chemical reactions, some additional studies have been carried out on the PAr/PET (50:50) mixture. In these studies, experimental conditions were chosen in order to disregard or minimize the influence of the transesterification reactions, according to the results previously obtained by other authors¹². So, samples were heated rapidly at 556 K (PET equilibrium melting point) and annealed at this temperature for 2 min, allowing for the total melting of the polymer. After that, they were cooled to 543 K and kept at that temperature for increasing periods of time, in order to allow mixing. According to the experimental evidence of Porter *et al.*², transesterification reactions do not take place at 553 K if the heating time is less than 20 min. Therefore, it seems reasonable to expect an induction time of more than 20 min at 543 K. After the thermal treatment, samples were again cooled to 470 K

**Figure 6** Simulated PAr/PET spinodal curve

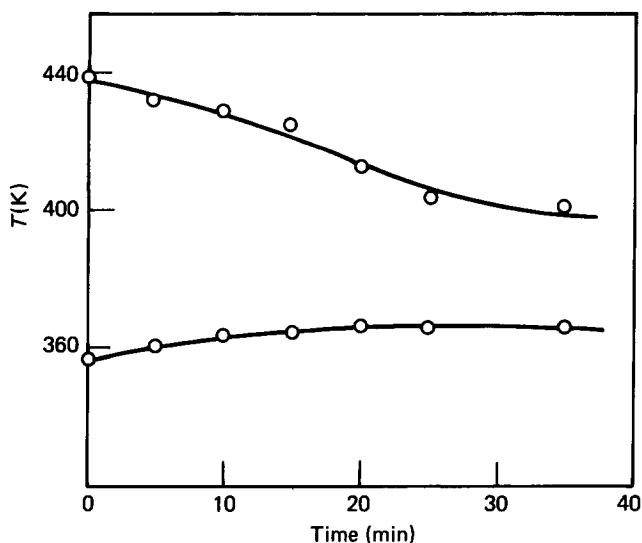


Figure 7 Evolution of the T_g values in a PAr/PET (50:50) blend with time at 543 K

and kept at that temperature for 30 min in order to allow for PET crystallization. Then, they were rapidly cooled to 320 K and a new d.s.c. scan was carried out from 320 to 570 K. Figure 7 shows the evolution of the T_g values of the 50:50 mixture with time at 543 K. As can be seen, both transitions approach each other progressively when the annealing time increases. The time treatment has been limited to 35 min in order to conform to the expected induction time according to the data of Porter *et al.*² Figure 8 shows the influence of the annealing time at 543 K on the PET melting behaviour in 50:50 PAr/PET blends. As can be seen, three endotherms appear in all the conditions investigated. The low-temperature endotherm may be assigned to the fusion of crystallites formed in a process of secondary crystallization between the spherulite lamellae; the intermediate endotherm can be attributed to the melting of crystals formed at 470 K; and the highest endotherm can be attributed to the fusion of the crystals generated during the scan and on the basis of the original ones. If we maintain the rest of the experimental conditions, reorganization may be made difficult by the presence of an amorphous polymer mixed with PET. In Figure 8, it is possible to appreciate that the area of the highest endotherm diminishes when the treatment time increases, whereas the area of the intermediate endotherm increases. This implies that reorganization is made difficult by the annealing time, which, in the absence of transesterification reaction, may be attributed to an increase in the extent of miscibility in the blend. This result is then consistent with the progressive approaching of the T_g values of the components.

Finally and in conclusion, it has been well documented that transesterification reactions take place in PAr/PET blends. However, in our opinion more work is needed in order to elucidate whether transesterification is the only reason for the macroscopic compatibility at high temperatures or whether there is true miscibility between components enhanced by the transesterification reactions when polymers are mixed together at high temperatures. The use of some exchange reaction inhibitors, such as phosphorus compounds used by Devaux *et al.*⁹ in PBT/PC blends may be an attractive route for properly separating both possible factors implicated in the final process.

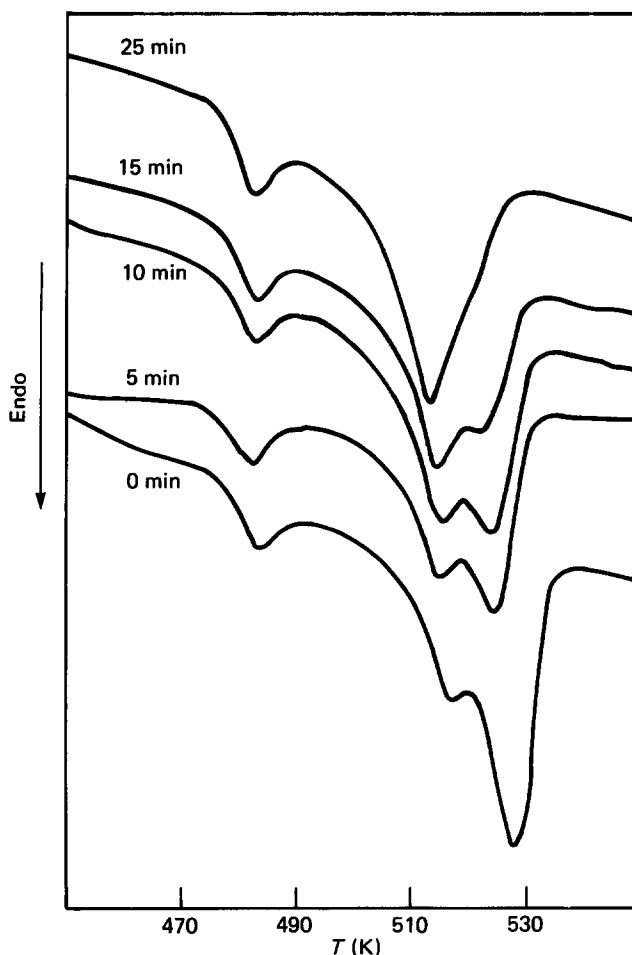


Figure 8 Evolution of the PET melting endotherms with time at 543 K

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