

# 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 work<sup>1</sup> 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<sup>2,3</sup>. Kimura *et al.*<sup>2</sup> 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, Robeson<sup>3</sup> 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.*<sup>2</sup> 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 reported<sup>4</sup> 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 mixtures<sup>5</sup>. 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 elsewhere<sup>6</sup>.

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 mixture<sup>7</sup>.

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  $\Delta H_f$  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

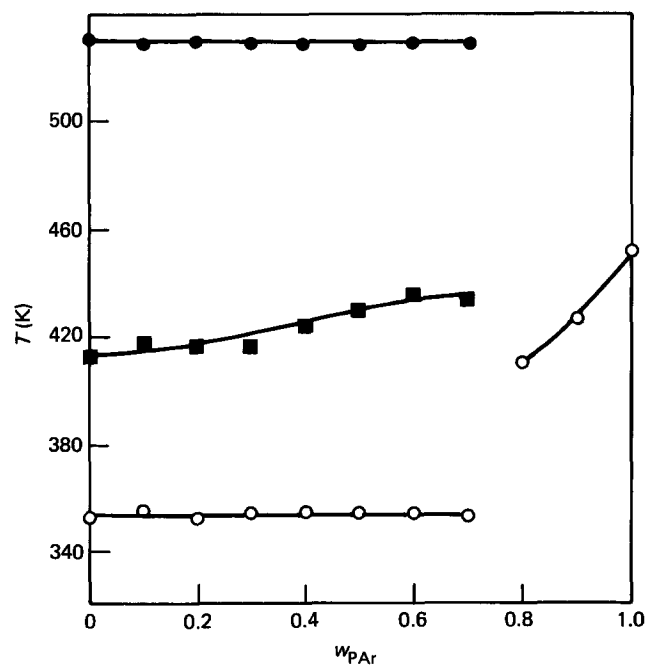


Figure 1 Thermal transitions of PAR/PET blends without treatment at 570 K: (○),  $T_g$ ; (■),  $T_c$ ; (●),  $T_m$

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