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Influence of interchange reactions on the nature and properties of miscible 50/50 poly(butylene terephthalate)/phenoxy blends

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The combined influence of miscibility and interchange reactions on the thermal and mechanical properties of 50/50 blends of poly(butylene terephthalate) (PBT) and phenoxy, and the nature of the reactions, have been studied. It has been proved by means of Fourier transform infrared spectroscopy and solubility tests that the reaction occurs through the hydroxyl of the phenoxy. Evidence is presented for the additivity of the beneficial effects of miscibility and interchange reactions on the mechanical properties of the quenched, not-fully-crystalline material.

1. Introduction

Much work has been carried out on different techniques to improve the compatibility of immiscible polymer blends. As a result, the mechanical properties of the already interesting blends have been improved and a number of new polymer blends have begun to be developed.

Among the different ways of improving compatibility (that is, addition of adhesion promoters, copolymers of the two components of the blend, and others) interchange reactions between the constituents of the blend during the processing in the melt state have received great attention in the past few years. It is known that these interchange reactions give rise to different types of copolymers that may improve the interphase conditions and, as a consequence, the mechanical properties of the blends.

Most of the interchange reactions studied occur in blends composed of two polyesters or of a polyester and bisphenol A polycarbonate (PC) [1-16]. The study of these blends has shown that the reactions give rise to block copolymers in the first stages and to random copolymers at longer reaction times. Less work [17-23] has been dedicated to the reactions of these polymers with poly(hydroxy ether of bisphenol A) (phenoxy), a polymer with lateral hydroxyl groups which can give branched and/or cross-linked products that have a strong effect on the properties of the blends.

Among blends of polyesters with phenoxy, the blend composed of poly(butylene terephthalate) (PBT) and phenoxy has been recognized to be miscible [21, 22] and the existence of interchange reactions in this blend has been observed by Robeson and Furtek [21]. However, the mechanism of this reaction has not been verified experimentally to our knowledge; only the influence of the reactions on the thermal behaviour of the blends has been analysed [23]. The influence of the copolymers formed by the reaction on the mechanical properties of the blends has not been studied either.

This PBT/phenoxy blend is of additional interest because, as far as we know, no work has been published on the mechanical properties of reacted blends that present both miscibility and interchange reactions, except recently [24] by Viswanath *et al.* Both miscibility and occasionally interchange reactions give rise to improvements in mechanical properties, and consequently their combined effect may offer an interesting subject for study.

Thus we have followed the interchange reactions in a PBT/phenoxy (50/50) blend by means of torque–time measurements and solubility tests carried out on materials taken out at different processing times, that is, at different reaction levels. Fourier transform infrared spectroscopy (FTIR) was used to examine the nature of the materials obtained. The effect of the reactions on several properties of the blends was investigated by differential scanning calorimetry (DSC) and dynamic and static mechanical analysis. This last study was carried out by means of the tensile test and will allow a quantitative idea of the interchange reactions as a means of improving the mechanical behaviour of the already miscible PBT/phenoxy blends.

2. Experimental techniques

The polymers used in this work were commercial products. Phenoxy PKHH was kindly supplied by Quimidroga S.A., Barcelona, PBT, Ultradur B4500 was obtained from BASF Española S.A., Barcelona. Both polymers were dried *in vacuo* to ensure moisture removal.

The PBT/phenoxy (50/50) blends were prepared by melt mixing in a Brabender Plasticorder at 250 and 230° C. The blends obtained at 250° C were extracted after residence times of 9, 20, 34, 38 and 50 min which

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correspond to the most significant points in the torque–time curve. Non-reacted blends were prepared at 230° C and extracted after a residence time of 4 min. A constant mixing-blade speed of 30 r.p.m. was used. The torque required to turn the Brabender was registered against mixing time.

Solubility tests were performed on all the products by means of a solvent extraction with boiling chloroform (in which phenoxy is soluble and PBT is not) followed by a second extraction with boiling *o*-dichlorobenzene (in which PBT is soluble). Both extractions were performed over a 24 h period. The different fractions were analysed by means of a Nicolet 5DXC FTIR spectrophotometer. The spectra of the *o*-dichlorobenzene soluble fractions had not been adequately used because of the impossibility of total separation of phenoxy from the complex *o*-dichlorobenzene-soluble mixtures.

After the mixing operation, compression moulded sheets were processed at the same temperatures as those of the mixing operation for a period of 5 min, and afterwards quenched in water. It was not possible for the product obtained after 50 min at 250° C to be compression moulded due to the impossibility of obtaining adequate sheets because of its very high viscosity. Specimens for DSC and for dynamic and static mechanical testing were obtained from these sheets. In order to test materials similar to the PBT used in practice, specimens for static mechanical (tensile) testing were also obtained after annealing the sheets at 150° C for 30 min.

The materials obtained by melt mixing at 250° C were analysed by a Perkin Elmer DSC-2 scanning calorimeter. The quenched products were first heated in the calorimeter from 0 to 250° C at 20° C min^{-1} and then cooled to 0° C at 40° C min^{-1}. Finally, a second scan from 0 to 250° C was performed. The different transitions and crystallization enthalpies were determined in the usual way.

Dynamic mechanical analysis was performed on a DMTA (Polymer Laboratories, Loughborough, UK) which provided the storage (E') and loss (E'') moduli and the loss tangent (tan δ) as a function of temperature. A constant heating rate of 4° C min^{-1} was employed at a frequency of 1 Hz.

Tensile test specimens (ASTM D 638 type IV) were punched out from the compression sheets with a pneumatic die. The specimens were tested in an Instron at 10 mm min^{-1} (0.5 mm min^{-1} for the measurements of the moduli) at 25 $\pm$ 2° C. The nominal tensile strength, elongation at break and initial modulus were computed from the recorded load–time plots.

3. Results and discussion

3.1. Blending torque

Figure 1 shows the torque–time relationship obtained for a PBT/phenoxy (50/50) mixture at 250° C. After the first stage in which the initial torque decreases, an approximately constant value is attained at a mixing time of 9 min. Initially it may be assumed that the material at this torque value corresponds to a homogeneous and non-reacted blend, that is, to a 'physical mixture'. After the torque steadies, an increase is clearly observed when the mixing is maintained. The torque–time curve shows a maximum at 104 min with a shoulder at approximately 34 min. This behaviour, together with the power-like material obtained at the maximum of the torque, is the same as that observed by Robeson and Furtek (21) in the same mixture and has been attributed to the existence of interchange reactions between the blend constituents. However, the time at which the reactions take place increases in our case. As the mixing temperature is the same in both cases, the difference will be a consequence of the different types of PBT used, or more probably, of the different mixing-blade speed of the Brabender. During the mixing operation the melted mixture was transparent, indicating the existence of miscibility in the molten state.

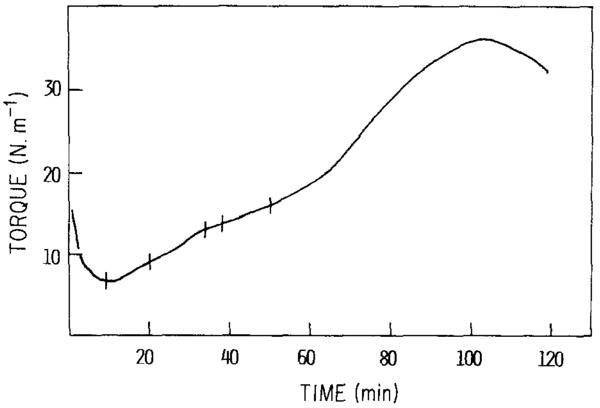

Figure 1 Blending torque against processing time of 50/50 PBT/phenoxy blends at 250° C. The traces correspond to the reaction time of the selected materials.

To look into the influence of processing time on the nature and properties of the different materials, five blends that correspond to different reaction times were obtained. The selected points on the torque–time curve were at the steady-state torque (9 min), on the jump to the shoulder (20 min), at the shoulder (34 min) and at two points in the jump to the maximum (38 and 50 min). These five materials were used in subsequent studies.

All the quenched sheets obtained by compression moulding were transparent, indicating both miscibility and the absence of crystallization in these mixtures. The annealed sheets were opaque and white due to PBT crystallization.

3.2. Solubility tests

The occurrence of the reactions during processing is also shown by the solubility tests in Table I. These results correspond to the different points selected in

TABLE I Solubility in chloroform of 50/50 PBT/phenoxy blends

Mixing time (min)	Mixing temperature (° C)	Solubility (%)
4	230	25.3
9	250	22.1
20	250	14.6
34	250	13.8
38	250	13.3
50	250	9.8

the torque–time curve at 250° C, and also to the blend obtained at 230° C which was used as a reference for a non-reacted product.

The reference mixture shows a solubility of 25.3%, a much lower value than that of 50% which might be expected given the composition of the original mixture and the solubility of phenoxy in chloroform. This can be explained if we take into account the fact that PBT crystallizes in contact with chloroform, thus making the solvent diffussion among the polymer chains difficult, and the total dissolution of phenoxy impossible. The solubility of the mixtures obtained at 250° C decreases continuously as the mixing time increases. This behaviour indicates that the phenoxy chains react and are progressively incorporated into PBT chains. It must be pointed out that the solubility of the 'physical blend' which corresponds to a mixing time of 9 min is very close to that of the non-reacted reference mixture obtained at 230° C. This also allows for the use of this blend as a reference, with the advantage of having the same processing temperature.

As far as the solubility in boiling *o*-dichlorobenzene is concerned, the data obtained showed some error. This was possibly due to the fact that PBT is soluble only in boiling *o*-dichlorobenzene and precipitates as the solvent is cooled. Consequently it was very difficult to separate adequately the *o*-dichlorobenzene-soluble fraction and to obtain correct solubility data.

At reaction times of 34 min or longer, a fraction of the product is insoluble in both chloroform and *o*-dichlorobenzene. This points to the formation of a cross-linked product after these reaction times; all the material was dissolved at processing times of less than 34 min. It should be pointed out that 34 min is the time needed for the shoulder in the torque–time curve (Fig. 1) to appear. Thus, it seems that the shoulder marks the border between grafted products at low mixing times and cross-linked products at high processing times.

3.3. Infrared spectroscopy

The nature of the reactions has been studied by FTIR. Figure 2 shows the 1800 to 1425 cm^{-1} region of the FTIR spectra of pure phenoxy and PBT, and of the chloroform soluble fractions. In pure phenoxy no absorption bands appear in the 1800 to 1600 region. On the contrary, in pure PBT the carbonyl stretching absorption appears at approximately 1720 cm^{-1}, although in this case the absorption band is very wide, possibly due to the high crystallinity of the product. The spectrum of the chloroform-soluble fraction of the reference product shows a very small carbonyl stretching band at 1720 cm^{-1}, indicating, in the absence of interchange reactions, that a small quantity of PBT is dissolved by chloroform. The increase in the intensity of the carbonyl absorption band in the spectra of the chloroform-soluble fractions is clear, as compared to the 1600 cm^{-1} band corresponding to the aromatic rings, as the mixing time increases. Similar comments may be made about the band at 730 cm^{-1} of the $-(CH_2)_4$- group of the PBT, which is shown in Fig. 3. The band at 756 cm^{-1} that appears mainly in Figs 3b and c corresponds to chloroform residues.

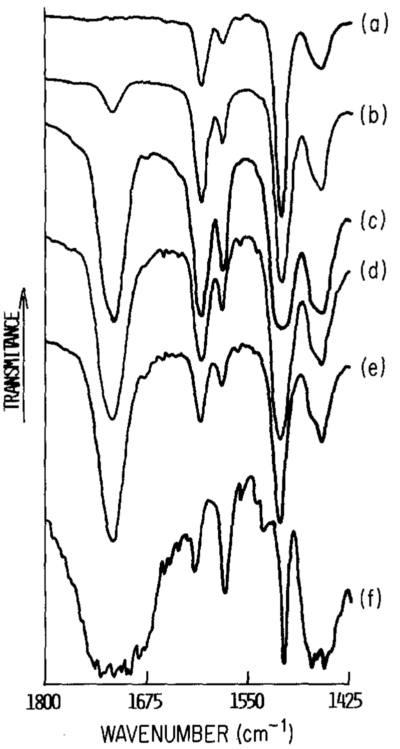

Figure 2 FTIR spectra of (a) pure phenoxy and (f) pure PBT, (b) chloroform-soluble fractions of materials with reaction times of 4 min at 230° C, and (c, d and e) 9, 20 and 50 min at 250° C in the 1800 to 1425 cm^{-1} region.

The amount of reacted product at long processing times must be higher than the relative size of the peaks suggests, because the cross-linked product is not present in the solution. The above results are proof of the progressive incorporation of PBT into the phenoxy chains by means of interchange reactions in the

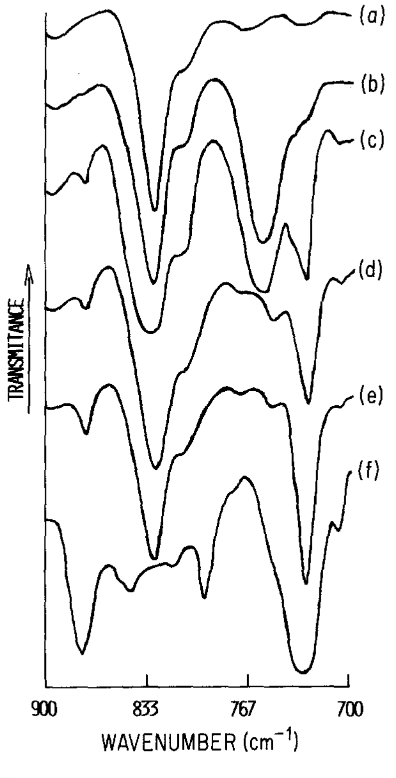

Figure 3 FTIR spectra of (a) pure phenoxy and (f) pure PBT, (b) chloroform-soluble fractions of materials with reaction times of 4 min at 230° C, and (c, d and e) 9, 20 and 50 min at 250° C in the 900 to 700 cm^{-1} region.

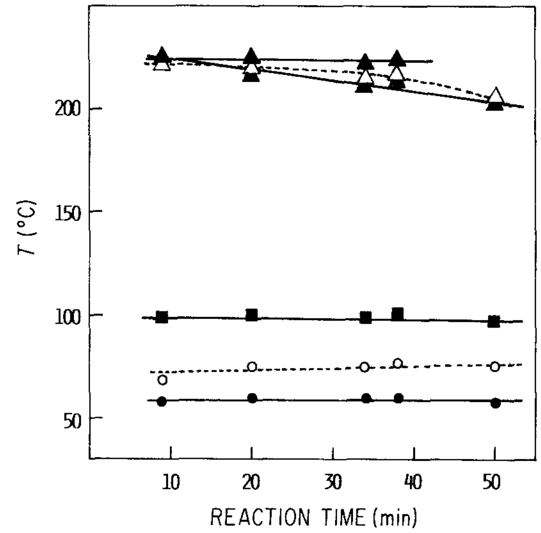

Figure 4 Thermal transitions of 50/50 PBT/phenoxy blends as a function of reaction time. First scan: (●) T_g; (■) T_c; (▲) T_m. Second scan: (○) T_g; (△) T_m.

molten state. According to the solubility results, the copolymers produced must at first be branched copolymers; after a processing time of 34 min under these conditions, the production of cross-linked structures will commence.

3.4. Scanning calorimetry

Figure 4 shows the different thermal transitions of PBT/phenoxy (50/50) blends in the first and second scans as a function of mixing time. Single glass transition temperatures (T_g s) appear in both scans at approximately 60 and 75° C, respectively, as expected in view of the blend miscibility. These T_g s appear to be almost constant with the processing time; in fact only a slight tendency of the T_g to increase can be seen in the second scan.

The crystallization temperature, unaffected by the time of mixing, has increased to 99° C. This makes it possible to use this PBT/phenoxy blend, not as is usual in PBT, in the fully crystallized state, but in a rather amorphous state thanks to its having a higher T_g than PBT. Moreover the reactions, although they do not affect the T_c, as was to be expected, make crystallization difficult, as seen by the lower crystallization enthalpy values after a processing time of 50 min (3.4 cal g^{-1}) with respect to those obtained up to 34 min (4.8 cal g^{-1}).

As may also be seen in Fig 4, the melting behaviour of PBT is clearly affected by processing time because both the shape and the position of the peaks changed with it. After a processing time of 9 min a single endotherm was seen, but after 20 min two overlapped melting peaks were observed and a broad peak with a shoulder was seen after a processing time of 50 min. It is our opinion that the high temperature peak of the 20 min material and the shoulder of the 50 min material should correspond to the melting of the crystals formed by reorganization of the less perfect original crystals during the scan, as has been found for other polymer blends [15]. This is in accordance with the observed lack of dependence of the T_m of these crystals on processing time.

The low-temperature melting peak should correspond to the crystals primarily formed, so that as the reaction time increases the PBT crystallization is progressively hindered, and thus, as shown in Fig. 4, melting takes place at decreasing temperatures. The melting behaviour in the second scan can be explained in a similar manner to that mentioned above. Moreover, it must be pointed out that the relation between the areas of the two melting peaks in the first scan decreases as the mixing time increases. This indicates that the longer the mixing, the smaller the fraction of PBT that undergoes reorganization.

3.5. Dynamic mechanical analysis

Figure 5 shows the dynamic spectra of the PBT/phenoxy (50/50) blends obtained at 250° C after a mixing time of 9 and 38 min. Because of the similarity between the spectra, only those of materials with the shortest (9 min) and longest (38 min) processing times are shown. This similarity also appears between the

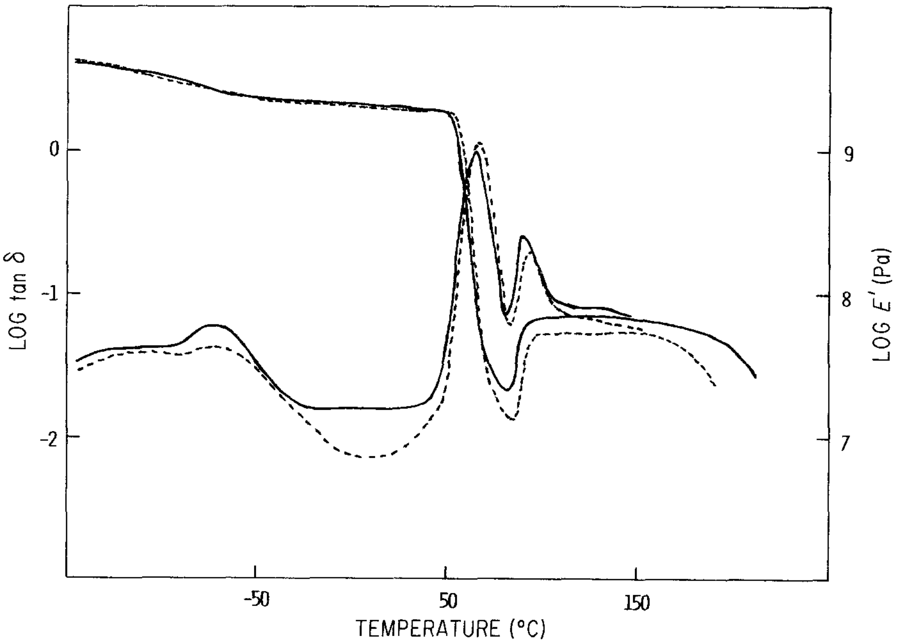

Figure 5 Dynamic spectra of quenched 50/50 PBT/phenoxy blends after (——) 9 min and (— —) 38 min reaction times.

spectra that correspond to the 9 min material and that found beforehand [21] for non-reacted blends.

As expected, the single sharp T_g at 64° C in the tan δ plot demonstrates the homogeneity of the blends. The increase of E' and tan δ observed after T_g at approximately 90° C is due to the crystallization of PBT. As seen in Fig. 5, even the expected progressive difficulty of the material in responding to external loads as a result of cross-linking, which would give the translation of the tan δ peaks at increasing temperatures, is very difficult to observe. In fact, only variations in the T_g of 2° C (from 64 to 66° C) and of 6° C in the temperature of secondary transition (T_β) (from -75 to -69° C) are observed. No change at all in the width of the transitions is observed. This behaviour indicates that though cross-linking exists, as seen in the solubility tests, it takes place at a low level.

3.6. Static mechanical properties

Quenched and annealed tensile specimens obtained after a residence time of 4 min at 230° C and after 9, 20, 34 and 38 min at 250° C were analysed. Figure 6 shows the elastic moduli of the different materials. It can be observed that the annealed samples show a modulus greater than that of the quenched samples, due to the further crystallinity generated during annealing. A tendency of the modulus to increase as the mixing time increases is found in both cases. This is probably due to the development of the reaction. The increase of the modulus is more pronounced at times in excess of 34 min, in accordance with the cross-linked materials of high rigidity that begin to appear at these processing times, as seen from the solubility tests. This effect is somewhat more pronounced in the quenched amorphous products than in the crystalline products.

These increases of the modulus of elasticity and the yield stress which will be seen later (5% in the case of the modulus and close to 10% in the case of the yield stress, both with respect to the 9-min-processed material) are interesting in the case of a blending time of 20 min under the present processing conditions. The interesting thing is that at these low reaction times few cross-links are produced; as a consequence, the usual decrease of properties at break that accompanies this kind of reaction [17, 18, 20] will not, perhaps, be observed and a satisfactory balance of properties may take place.

Figure 7 is a plot of the yield stress against mixing time for both sets of products obtained. In the annealed products no change is observed (taking into account experimental error). In the case of the quenched samples a slight increase is observed, perhaps because of the more evident rigidifying effect of the reactions in these less rigid materials. This increase speeds up after 34 min, as was the case with the elastic moduli plot, and seems to be a consequence of the appearance of cross-linked products from the interchange reactions. That is, as expected because of the more complex molecules obtained, the reaction gives rise to an increase in small deformation properties. It would be interesting to carry out tests to see if the miscibility of the blend counteracts the usual negative effect of these reactions on the mechanical properties of the blend at break, such as ductility or tensile strength at break.

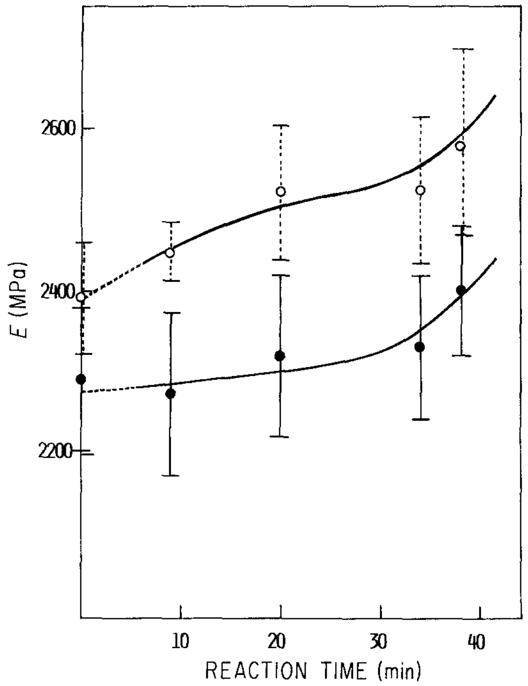

Figure 6 Young's modulus of (●) quenched and (○) annealed 50/50 PBT/phenoxy blends as a function of reaction time. The points at 0 min correspond to the reference material obtained at 230° C and 4 min.

Figure 8 shows the break strength data. For quenched samples this parameter remains almost constant with time during a mixing time of up to 34 min. After this, a slight decrease is observed. In the annealed samples no clear tendency in the break strength is observed. This behaviour seems to be closely related to that previously observed in the case of the yield stress. In fact no change in the property is observed in the case of the annealed material, and the change in the quenched material was also observed after 34 min. Both effects must be a consequence of the change in the nature of the material observed previously at these processing times.

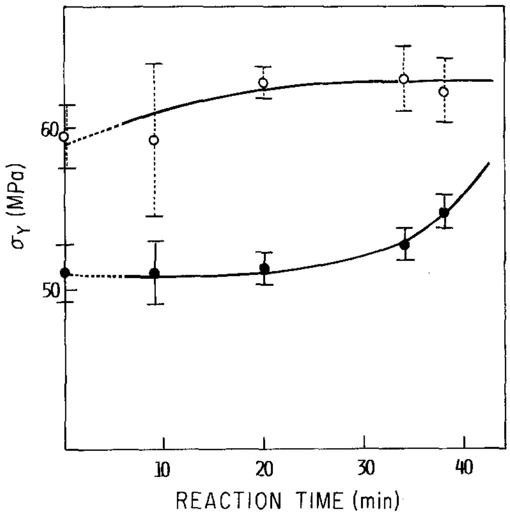

Figure 7 Yield stress of (●) quenched and (○) annealed 50/50 PBT/phenoxy blends as a function of reaction time. The points at 0 min correspond to the reference material obtained at 230° C and 4 min.

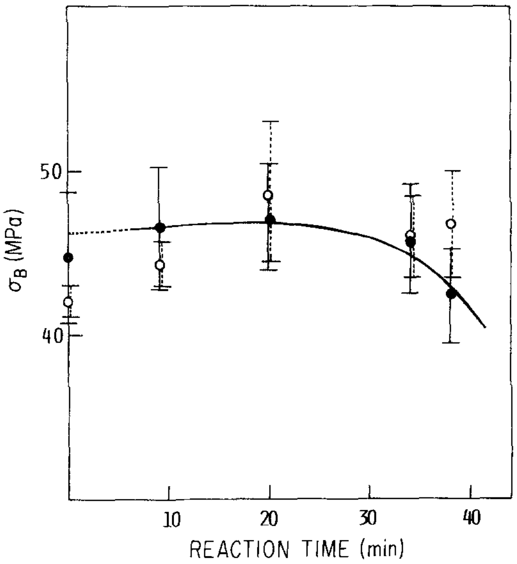

Figure 8 Break strength of (●) quenched and (○) annealed 50/50 PBT/phenoxy blends as a function of reaction time. The points at 0 min correspond to the reference material obtained at 230° C and 4 min.

Finally, the deformation values at break for the quenched samples are shown in Fig. 9. The values of the deformation at break of the annealed samples have not been represented because their low values (approximately 10%) and great dispersions turn out not to be representative values. However, in spite of the usual great dispersion of the data, it can be seen that in the case of the quenched samples this parameter decreases at high mixing times, after which cross-linked products are obtained. The appearance of such products causes a decrease in ductility, as expected.

However, this decrease in ductility is not high even after a processing time of 38 min. This behaviour of the break properties in polymer mixtures which react in the melt state, giving cross-linked products, is not common. This behaviour is very similar to that of mixtures in which block and random copolymers are produced, as in polycarbonate/polyarylate blends [16], and must also be a consequence of a slow reaction speed that allows the presence of branched copolymers to be comparatively stable. This is in good agreement with the dynamic mechanical results, and with the slight change observed in solubility.

4. Conclusions

Interchange reactions are clearly present in PBT/phenoxy blends. The reaction is an alcoholysis between the hydroxyls of the phenoxy and the ester groups of the PBT that gives rise in the first instance to branched products, and afterwards to cross-linked copolymers.

The reaction speed is low, giving rise at not very long processing times to the production of copolymers which, in the quenched material, increase most of the more important mechanical properties of the already interesting PBT/phenoxy miscible blends. That is, in this blend the beneficial effects of miscibility and interchange reactions are additive. The increase in the mechanical properties shows what is perhaps a more interesting balance at a processing time of more or less 20 min, when the reaction is clearly in progress but the production of crosslinked material is still low. These results show the additivity of two of the facts that give rise to commercially interesting blends: miscibility and reactions in the melt state.

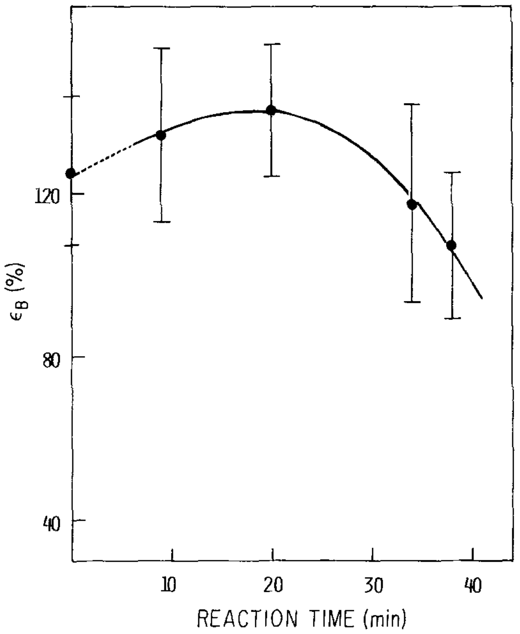

Figure 9 Deformation at break of quenched 50/50 PBT/phenoxy blends as a function of reaction time. The point at 0 min corresponds to the reference material obtained at 230° C and 4 min.

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