

Phenoxy/Hytrel Blends. I. Miscibility and Melt-State Reactions

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ABSTRACT: Polyhydroxy ether of bisphenol A (phenoxy)/Hytrel (Hy) blends were obtained by melt mixing throughout the composition range and at several processing times. Interchange reactions took place and were followed by the torque behavior, solubility tests, and FTIR spectra. After a mixing time of 15 min, they gave rise to basically unreacted products, but at longer mixing times, they produced both branched and crosslinked products. The blends were miscible at all compositions due to the presence of specific interactions, as was seen because of the presence of a single T_g by DSC that was confirmed by DMTA. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 185–193, 1998

Key words: blends; phenoxy; Hytrel; miscibility; interchange reactions

INTRODUCTION

In the wide field of polymer blends, some subjects as blends of polyesters or polyester-like polymers as polycarbonate (PC) have been rather extensively studied.^{1–7} Among the blends, both miscible^{1–4} and partially miscible^{1,2,5–7} as well as immiscible^{1,2} blends have been studied. The possibility of chemical reactions between the components is clear, either in the presence of catalysts^{8–10} or during the short time at high temperatures found in industrial processing^{8,11,12} and after long residence times in the melt state.^{8,12,13} These reactions, when fully developed, may give rise to a widespread copolymer presence. When these copolymers are branched or crosslinked, they are usually undesirable from the point of view of mechanical properties such as ductility and toughness. However, when they are only slightly developed in immiscible polymer

blends, they may compatibilize the blend. This reactive processing occurs without any previous modification of the original polymer nature and gives rise to, besides miscibility, morphological changes that should modify the performance of the blends.

Elastomers have been traditionally used for toughening brittle¹⁴ or not tough enough^{15–19} polymers. Toughening is produced by the processing-helped presence of grafted copolymers in the interphase and the special morphology developed.¹⁴ Thermoplastic elastomers are materials which combine the processing characteristics of thermoplastics with the physical properties of vulcanized rubbers. The study of blends with a thermoplastic elastomer component has begun only recently,^{20,21} although the study of blends of other rubberlike materials, such as polyolefins, has been a clear subject of interest.^{22,23} Among the blends with a thermoplastic elastomer component, blends of polyester/elastomer block copolymers with PC^{24,25} with other second components^{20,21,26–31} as well as PVC, PBT, chlorinated PE, PA6, PBT, S-EB-S, PAr, and LCP and blends

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based on the other thermoplastic elastomers^{20,21,32–38} have been studied.

Hytrel (Hy) is a segmented elastomer thermoplastic that has as contents a hard and crystallizable tetramethylene terephthalate (PBT) and a flexible polytetramethylene–ether–glycol–terephthalate (PTMEGT). So, besides being an elastomer, it is also a polyester so that it belongs to both of the groups mentioned above. The blends of PBT, one of the Hy components, have been widely studied.^{4–6,16,17,39–45} It is miscible with, among others, poly(hydroxy ether) of bisphenol A (phenoxy, Ph),^{39–41} so that the possible miscibility of Ph/Hy blends and the effect of the modification of the PBT molecule on the miscibility and possibility of interchange reactions are an attractive research subject.

In this article, a study of Ph/Hy melt blends as a function of blend composition and mixing times is presented. The chemical nature of the blends was studied using the time evolution of the torque of blending, solubility tests, and FTIR spectra of the blends. Additionally, the miscibility level was assessed by transparency, DSC, and dynamic mechanical thermal analysis.

EXPERIMENTAL

The Ph used was a Union (Quimidroga S. A., Barcelona, Spain) Carbide commercial product designated as PKHH, with a number-average molecular weight (M_n) of 18,000 and a weight-average molecular weight (M_w) of 50,700.⁴⁶ Hytrel 5556 (Hy) is a segmented copolyetherester as mentioned above. It was kindly supplied by DuPont Ibérica and its PBT weight content is 58%.

The pellets of Hy were dried under the conditions recommended by the manufacturer (DuPont, bulletin informative) in an oven at 120°C for 12 h and those of Ph at 80°C also for 12 h. The temperature was the highest compatible with a lack of clustering of the pellets. The pellets were mixed at the desired compositions, transferred to a Brabender mixer working at 240°C and 30 rpm, and mixed for various times. The torque required to turn the Brabender mixer blades was registered against mixing time. The melt-mixed blends were extracted after residence times of 15, 35, and 55 min, which correspond to the most significant zones in the torque–time plots. These blends were compression-molded at 240°C in a Schwabenthan Polystat 200T press and then quenched in cold water. Specimens for solubility tests, DSC, and

dynamic mechanical testing were obtained from the compression-molded sheets. Solubility tests were performed on all the products using solvent extraction with THF. The different soluble fractions were analyzed using a Nicolet 5 DXC FTIR spectrophotometer.

The calorimetric scans were performed in a Perkin–Elmer DSC-2 calorimeter at a scan rate of 20°/min. The maximum allowed cooling rate was used to cool the specimens between the first and the second scans. The different transitions were determined in the usual way. The dynamic mechanical analysis was performed in a DMTA (Polymer Laboratories) in single-cantilever mode at 1 Hz. The scans were carried out at a constant heating rate of 4°C/min from –150°C until the sample became too soft to be tested. Scanning electron microscopy (SEM) observations of the gold-coated fracture surfaces were performed on a Hitachi S-2700 electron microscope which was operated at 15 kV.

RESULTS AND DISCUSSION

Chemical Nature of the Blends

As is known,^{24,39,40,47–51} when the chemical nature of melt blends changes through chemical reactions, the viscosity and, consequently, the torque of blending may change. This is mainly true when, as a consequence of the reaction between the components of the blend, either branched or crosslinked products appear, as often happens in polyesters blends like those presented here. Thus, with the aim of both determining if reaction had taken place and determining the nature of the products, the melt behavior of the blends and that of the pure polymers as a reference were studied qualitatively using the torque–time plots, shown in Figure 1.

As can be seen, after a plasticization-induced initial and general decrease, the torque levels off in most of the blends and is more or less constant up to a mixing time of approximately 15 min. In the case of the pure polymers, the torque decreased continuously with time. This is a clear indication of degradation,^{24,52} because the presence of a lower molecular weight degradation product decreases the torque. These torque decreases are small and will not be able to significantly modify the increases of Figure 1 that would be, in any case, only a bit higher. In the case of the blends, two different behaviors were found: those

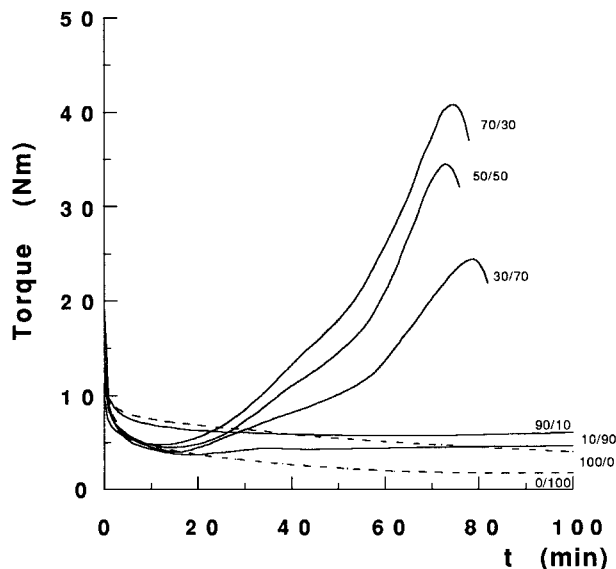


Figure 1 Torque of blending against time of the pure polymers and their blends at 240°C. The torque of the pure polymers appears as broken lines to improve clarity.

of the minority 10/90 and 90/10 compositions and those of the intermediate compositions. In the case of the former compositions, the torque behavior is not very different from that of the pure components. This is although the torque in the 10/90 blend held reasonably constant with a slight maximum at 35 min, which did not appear in the 90/10 blend, even after a mixing time of 5 h. In the case of the three intermediate compositions, clear torque maxima were found with two different slope regions. In the first, which at 240°C extends up to roughly 55 min, the torque increases are important with a shoulder that appears after a mixing time of 35 min. In the second region, at mixing times longer than 55 min, the torque increases accelerate and then reach a maximum where a highly crosslinked and powderlike material^{39,40,47,50,51} appears.

All these torque increases are probably due to the onset of interchange reactions. A similar torque behavior was also seen in the case of blends of Ph with other polyesters^{39,40} or with related polymers⁴⁷⁻⁵¹ and was attributed to an alcoholysis reaction. Such a reaction between the ester and hydroxy groups of the blend components is likely to take place in these blends, as will be seen later. As a consequence of this alcoholysis reaction, a mixture of a crosslinked copolymer, a branched copolymer, and the original polymers are generated.^{39,41,53} The relative

amount of the components of this mixture changes with the reaction time. The slight maximum of the 10/90 composition and the first region of the others should correspond to the branched copolymer. This is because the material is able to flow^{47,49} and because in the intermediate compositions the torque increases may then speed up. When the torque speeded up at the end of the first step of the reaction in the intermediate compositions, it is probable that the crosslinked product began to take on importance, because up to this point the blend was fully liquid. Moreover, in the Ph/PBT blends,⁴⁰ which have the same reactive groups, crosslinking also started at a shoulder of the rising torque.

These different torque behaviors and reaction products may be explained as a function of the composition of the blends and of the degradation of the components. As is known, degradation of Hy takes place by chain scission with THF as a by-product⁵² and that of Ph should give rise to some crosslinking.⁵⁴ With respect to the alcoholysis reaction, in the intermediate compositions, the reaction may be widely developed because of the important presence of both of the components. The alcoholysis is assisted at all compositions by the degradation. This is because the shorter degraded polymer chains⁴⁷ make the contact between the reactive groups easier. However, when one component is clearly present in a minor amount, as in the 90/10 and 10/90 compositions, the alcoholysis cannot be extended to the whole blend.^{47,49} This leads to a clearly smaller torque maximum or even to the lack of one.

It must be remarked that the induction time, that is, the time for the torque increase and reactions' appearance, is rather independent of the composition of the blend, with the exception of the 90/10 blend. This behavior has been attributed⁴⁷ to the low viscosity of the components of the blend at the mixing temperature and to the correspondent lack of effect of the viscous flow heating on the rate of the reactions. With respect to the time for the maximum torque to appear and to the maximum torque value, they are functions of the composition of the blends. The maximum torque value increases as the Ph content of the blend increases up to a Ph content double than that of the other component. The fact that the maximum torque values take place at a Ph/second component ratio of 2 : 1 has been also seen in Ph/PBT,³⁹ Ph/PC,^{47,50} and Ph/PMMA blends,⁵⁵ where it is assumed that the same reaction takes place. No

distinct reason can be stated for this common ratio.

With the aim of investigating the above-stated hypothesis about the effect of mixing time on the chemical nature of the blends, blending was carried out at various compositions and three different times and the products were analyzed both by FTIR and solubility tests. The solubility tests were performed using THF and for mixing times that corresponded to (a) the torque minimum (15 min), (b) the shoulder of the first region (35 min), and (c) the onset of the second region (55 min). FTIR analysis was carried out in the three intermediate blend compositions and at the same mixing times.

With respect to the solubility tests, THF is a good solvent for Ph, but it is not able to dissolve Hy. As a result, the solubility of the blends will decrease when the mixing time and, consequently, the reaction time increases. This will be especially true when crosslinked materials are produced. These solubility results are collected in Table I. As can be seen, the Ph of the 15-min mixed 90/10 blend is almost fully dissolved in THF, and at increasing Hy contents, the solubility is increasingly less than the correspondent Ph content. Thus, all the Ph is not dissolved. This may be because Hy can crystallize in contact with THF^{24,40} and may lead to some Ph being occluded in Hy, avoiding Ph dissolution. However, the possibility of some reaction even after this short mixing time cannot be excluded; the produced copolymer would be partially responsible⁵⁰ for the observed solubility decrease.

When the mixing time increases, in the case of the Hy-rich blends, the data are not relevant enough due to the important amount of occluded Ph, but no remarkable change is seen perhaps

Table I Solubility of the Blends in THF

Composition	15 Min	35 Min	55 Min
100/0	100	100	97
90/10	88.4	85.0	78.6
70/30	47.5	46.9	35.4
50/50	24.1	27.3	21.1
30/70	11.1	10.3	10.7
10/90	4.9	4.7	4.5
0/100	3.4	2.9	4.6

The values correspond to the dissolved weight percent of the blends. The typical deviation was roughly $\pm 0.2\%$ in Hy and Hy-rich blends and $\pm 1\%$ in Ph-rich blends and at intermediate compositions.

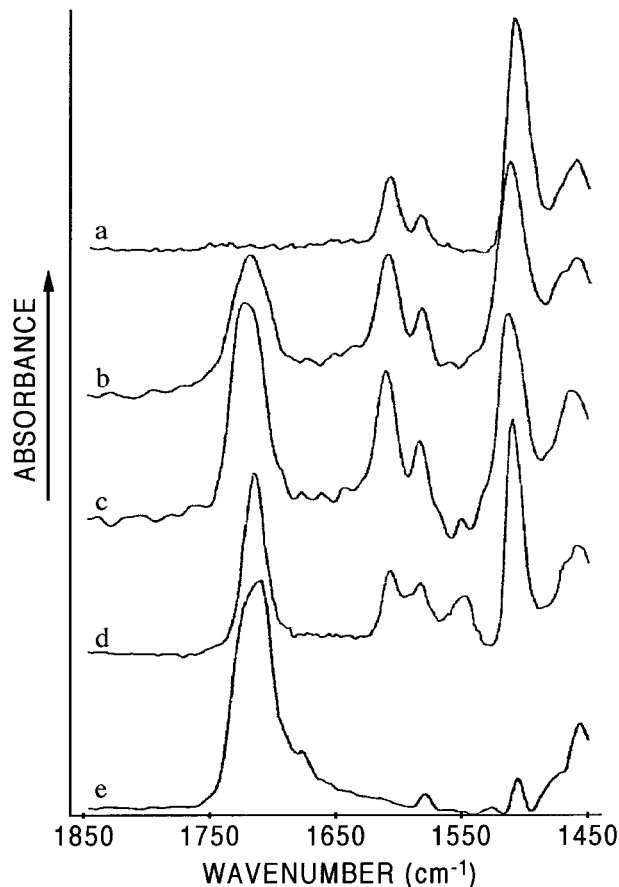


Figure 2 FTIR spectra of the pure polymers and of the dissolved fraction of the 50/50 blends in THF after several mixing times: (a) Ph; (b) 15 min; (c) 35 min; (d) 55 min; (e) Hy.

because the crystalline phase makes the reaction effects even more difficult to be observed. In the case of Ph-rich blends, the data are more significant due to the smaller amount of occluded Ph, and as was expected, solubility decreases with time. The decrease, however, is not very important so that the relative amount of the crosslinked products, if they are present, must be slight. This indicates that branched copolymers are the most important reaction products at these reaction times. After 55 min, the amount of the crosslinked product must be large because of the powderlike product obtained when the torque maxima were attained.

The interchange reactions were also followed using FTIR analysis of the dissolved fraction of the blends in THF. In Figure 2, the FTIR spectra in the 1850–1450 cm^{-1} range of both the pure polymers and those of the solved fraction of the 50/50 blend after several mixing times are col-

lected. The rest of the blends showed a similar behavior. As can be seen, in the spectrum of Ph, there is no absorption band in the 1850–1750 cm^{-1} range. In the case of Hy, however, the carbonyl band appears at 1710 cm^{-1} , but at a frequency slightly lower than that seen in the literature.⁵⁶ In the case of the blends, when mixing time increases, the intensity of the absorption band of the carbonyl becomes higher compared to that of the aromatic ring that appeared at 1600 cm^{-1} . Thus, Hy is present in the dissolved fraction where only Ph ought to be present. This is a clear indication⁴⁰ of the alcoholysis reactions in the melt state that give rise to the presence of the ester groups of Hy in the Ph chains. It must be taken into account that the amount reacted should be greater than that indicated by the relative size of the peaks, since some branched and all the crosslinked products are not present in the dissolved fraction. The presence of degradation products of Hy in the dissolved fraction should be negligible. This is because Hy degradation takes place by chain scission,⁵² and as was mentioned before, shorter degraded polymer chains make the contact between the reactive groups easier.⁴⁷ Moreover, shortening of the polymer chains does not improve solubility.

DSC

A first indication of the *miscibility level* of polymer blends is their transparency level.⁵⁵ In the melt state, all the blend compositions appeared as transparent up to a mixing time of 55 min, indicating miscibility. Thereafter, the transparency was a function of composition. Both the pure polymers and the 90/10 and 10/90 blends became progressively yellow but transparent, probably as a consequence of degradation.⁵² The rest of the blends became progressively opaque probably due, among other factors, to a change of the chemical nature of the components or, less probably, to immiscibility. Finally, they formed a fully opaque powder when the maximum torque was attained. In the solid state, the Hy-rich blends were opaque; the 50/50 blend, translucent, and the Ph-rich blends, transparent. Thus, the Ph-rich compositions appear to be miscible, but nothing can be said about the miscibility of the rest of the blends. Moreover, it must be taken into account that the transparency of the blends is an indication, but not a definitive parameter, to assess miscibility. No significant morphological feature that could inform about the structure was observed by SEM.

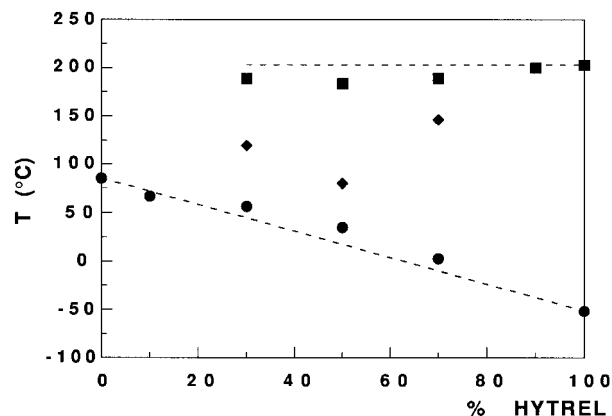


Figure 3 (●) T_g , (◆) T_c , and (■) T_m of the 15-min mixed blends after the first scan against composition.

The phase behavior of the blends was also studied by DSC and is represented in Figure 3 where the glass transition (T_g), the melting (T_m), and the crystallization (T_c) temperatures of the 15-min mixed blends from the first scan are shown. The transitions of the second scan were very similar, with the only difference being that the 30/70 blend did not crystallize. No T_g could be seen in the DSC scan of pure Hy or in the 10/90 blend. This must be due to both the low temperature at which they should appear and the hindrance of the crystalline phase that occluded the appearance of the T_g .²⁴ For this reason, the T_g of Hy, -52°C , was taken from the literature⁵⁷ and is plotted as a reference.

As can be seen, the blends show a single T_g which is between those of the two pure components. This points again to the miscibility of the Ph-rich blends. However, the observance of a single T_g is not evidence of miscibility in the Hy-rich blends. This is because, as stated above, a possible additional low-temperature second T_g could be present, but not detected. However, it is not probable, because the observed continuous T_g change does not indicate the presence of another T_g .

As can also be seen and by taking the required care when comparisons are made with results from other works, the T_g values appeared above the linear addition rule in Ph/Hy blends, whereas they were below the linear rule in PC/Hy blends. This indicates that the interaction level in these Ph/Hy blends is higher than that of PC/Hy blends with the same thermal treatment.²⁴ The positive deviation from the linear rule was also seen in other miscible blends with a semicrystalline component.^{24,39,41,58,59} It may be attributed not only to the nonproportional-to-composition crystalliza-

tion of Hy,^{24,39,41,59} but also to the interaction between functional groups of both polymers which gave rise to miscibility.^{40,55} The use of equations such as the Fox or Gordon–Taylor to calculate the T_g of the blends from those of the pure components is not suitable in semicrystalline blends due to the concomitant effect of the crystalline phase on the T_g value that is not taken into account in those equations. Finally, as can also be seen, with the exception of the 90/10 blend, all the blends showed a T_m which is slightly below that of pure Hy. This T_m decrease has been seen in other miscible blends of similar components^{24,41,60} and indicates miscibility, even in the Hy-rich blends.

With respect to the *crystallization behavior* of the blends, this was studied using both the T_c and T_g values which are collected in Figure 3. As can be seen in Figure 3, the T_c was seen only in the intermediate compositions. The lack of crystallization in the 90/10 blends was expected because of the low Hy content and the miscible nature of the blend. The lack of T_c in the pure Hy and the 10/90 blend indicates full molding crystallization. However, the intermediate composition blends also crystallized during the calorimetric scan. This indicates the hindering effect on Hy crystallization of the increasing presence of the miscible Ph.

Finally, after molding, the blends were cooled and then maintained at room temperature. Under this condition, in low T_g blends, crystallization may continue before the first calorimetric scan. As a consequence, Hy crystallizes, giving rise to a T_g increase. This took place in PC/Hy blends²⁴ and was due, first, to the smaller amount of amorphous Hy phase^{24,41,59} and, second, to the tying of the amorphous phase^{58,59} by the crystalline one.

Dynamic Mechanical Properties

The *miscibility level* of the Ph/Hy blends, the presence of mainly low-temperature Hy-rich phases, was also investigated by dynamic mechanical thermal measurements. In Figure 4, the $\tan \delta$ spectra of the pure polymers and those of the blends after a processing time of 15 min are shown. As can be seen, the spectrum of Ph shows three transitions: the α transition, T_g , close to 100°C, a β relaxation at -68°C that corresponds to the hydroxy ether group,^{48,58,61} and a γ transition at -110°C that appears as a shoulder of the β transition and that corresponds to the diphenylpropane group.^{48,58,61} In the case of Hy, two tran-

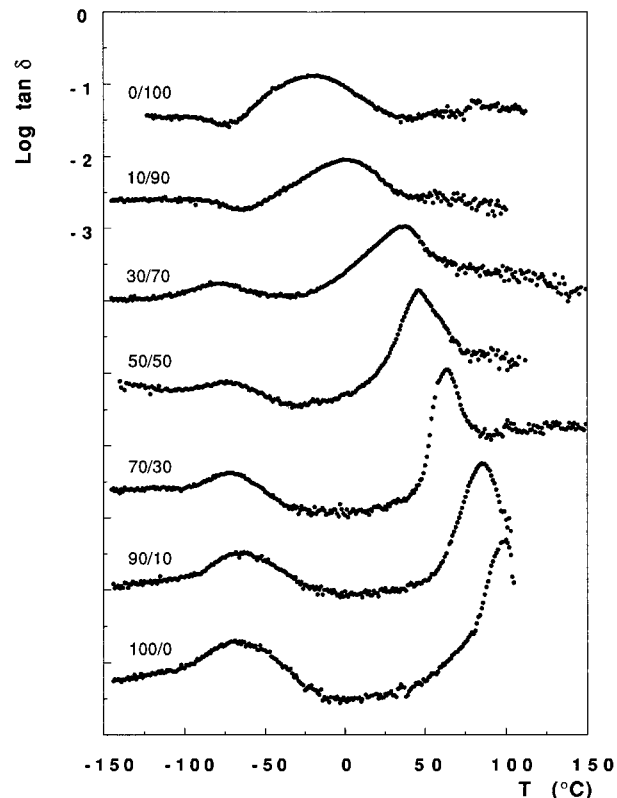


Figure 4 DMTA log $\tan \delta$ versus temperature of the 15-min mixed blends. To aid clarity, the curves are shifted in the vertical axis.

sitions were seen: the T_g at -20°C and a very slight β transition at -100°C that can be attributed to the motion of consecutive $-\text{CH}_2-$ sequences or to the motion of the ether group of an amorphous region and contributions from the local mode motions of carbonyl groups of the PBT component.⁶²

As can also be deduced from Figure 4, the plot of the T_g 's of the blends against composition was very similar to that seen by DSC, because it showed a single T_g which was between the T_g 's of the two pure components. The slight differences observed were probably due to the experimental technique. Moreover, no transition is seen in the surroundings of -20°C where a possible T_g of a Hy-rich phase should appear provided it existed. This is proof of miscibility also in the Hy-rich and intermediate composition blends, which, as a consequence, are composed of a single amorphous phase and a Hy crystalline phase, whereas the Ph-rich blends have a single amorphous phase.

This miscibility of the blends may be due to interactions between the components or to the

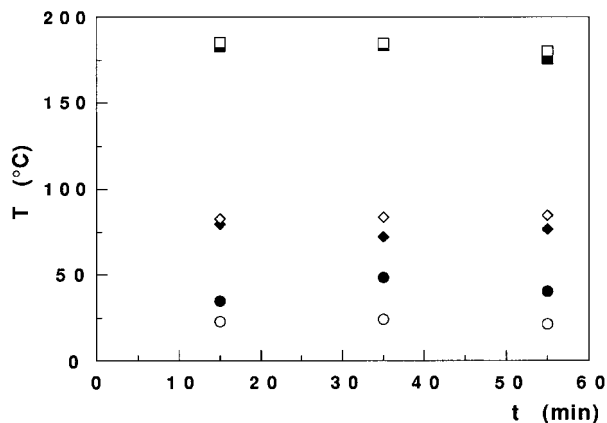


Figure 5 (●) T_g , (◆) T_c , and (■) T_m of the 50/50 blends after the (solid symbols) first scan and (open symbols) second scan against mixing time.

miscibilization effect of the copolymers produced by an alcoholysis reaction. The interaction has to take place because it is known that both the ether groups of PTMEGT^{59,63,64} and also the carbonyl groups of PBT, which are proton acceptors,^{39,40,53,63} interact by means of hydrogen bonds with the hydroxyl groups of Ph, which are proton donors. With respect to copolymer-induced miscibilization, the lack of a significant reaction level at the beginning of the mixing was proved in Table I. Moreover, it has been stated⁶⁵ that after short residence times in the melt state, and 15 min is the shortest time for a homogeneous blend to be produced, the contact between the components, provided that they were immiscible, would take place only in the interphase. Thus, the copolymer amount produced and the miscibilization effect should be small. As a consequence, the miscibility observed in these blends appears to be due to specific interactions.

With respect to the *mixing-time effect* on the transitions, studied by both DSC and DMTA, no remarkable change of the transitions of the blends mixed for 35 and 55 min was seen in the 10/90, 30/70, and 90/10 compositions and only a slight effect on the rest of the compositions. The behavior of the 10/90 and 90/10 blends may be explained by the lack of a widespread alcoholysis reaction. The hindered reaction in the 30/70 composition was also seen in Figure 1 as the lower torque value of this composition as compared to that of the 50/50 and 70/30 blends. It may be due to a difficult accessibility of the reactive group of Hy,⁴⁷ which would be concomitant with the small Ph presence. Both facts would give rise to the

need for a longer reaction time for the reaction to be widely extended.

With respect to the rest of the compositions, in Figure 5, the thermal transitions of the 50/50 blend after the two calorimetric scans are shown against mixing time. The behavior of the 70/30 blend was similar. As can be seen, the T_g shows a slight maximum at intermediate times and T_m decreases as the mixing time increases. The T_m decrease may be explained by means of the decrease in size of the crystalline segments as a consequence of the reaction-produced copolymers.⁴¹ The small decreases testify to a slight reaction level. This slight reaction level was corroborated by the crystallinity values measured from DSC scans which are shown in Table II. As can be seen, the crystallinity did not significantly change with the mixing time. The T_g behavior may be explained as a consequence of two concomitant and opposite processes.⁴¹ First, the reaction-produced increasingly branched copolymers give rise to a T_g increase. Second, the reaction leads to a crystallinity decrease,^{40,41} and as a consequence, the amorphous phase would be richer in Hy and its T_g would decrease. Thus, a maximum appears when the initially more active first process starts to be counteracted by the second.

CONCLUSIONS

Ph/Hy blends reacted during processing in the melt state, giving rise first, to branched copolymers and then to crosslinked products as seen by the solubility tests and FTIR spectroscopy. Both a fairly balanced composition and a slight majority presence of Ph helped the reaction to be fast and widespread. The induction time for the onset of the reaction was, in most cases, independent of

Table II Crystallinity of the Blends with Different Mixing Times Measured by DSC

Composition	15 Min	35 Min	55 Min
100/0	—	—	—
90/10	—	—	—
70/30	—	1	2
50/50	22	18	19
30/70	19	19	22
10/90	23	24	25
0/100	27	26	27

composition and was always longer than 15 min at 240°C.

The addition of PTMEGT to the PBT molecule to produce Hy did not modify the miscibility with Ph. Thus, only a single T_g , which changed with composition, was seen by DSC. This miscibility of the blends after short processing times, however, had to be confirmed by DMTA, which denied the possible presence of a second low-temperature T_g . It was due to specific interactions to the detriment of the small amount of copolymer-induced miscibilization. The ulterior development of interchange reactions had no relevant influence on the thermal behavior of the blends that were a consequence of the probable crystalline decrease.

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