

# PBT/PAr Mixtures: Influence of Interchange Reaction on Mechanical and Thermal Properties

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## SYNOPSIS

The effect of the interchange reactions in PBT/PAr blends on thermal and mechanical properties has been studied as well as the influence of the concentration of tetrabutyltitanate on these properties. These studies have been carried out by means of differential scanning calorimetry (DSC) and tensile tests. The results based on DSC studies allow us to conclude that the capacity of the transesterified blends to crystallize decreases when compared with the physical blends, due to the formation of copolymers. Furthermore, an enhanced effect is observed when the amount of the catalyst is increased. In addition, a slight decrease in the low deformation mechanical properties and a significant increase in the deformation at break is observed as a consequence of the interchange reactions. The presence of tetrabutyltitanate, which accelerates the interchange reactions, has a 2-fold effect on these properties. On the one hand, it enhances the aforementioned process, but on the other hand, the associated effect of the degradation reactions decreases the mechanical properties, particularly those of the deformation at break. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer blends constitute one of the most useful ways to produce new materials. It is known that certain type of polymers, such as polyesters or polyamides, can undergo interchange reactions when submitted under processing conditions. This method can be thought as a new way of obtaining new materials.

In our previous work,<sup>1-3</sup> we studied mixtures of PBT/PAr. First, the presence of new absorbances in the <sup>1</sup>H-NMR spectra of those samples, submitted to thermal treatment, was demonstrated. Furthermore, it was possible for us to identify all these new absorbances by making use of model compounds. Thus, the existence of monosubstituted units was proved, and at high reaction levels, absorbances due to chain end groups and disubstituted units were identified. In a third work, and throughout the calculation of triads by <sup>1</sup>H-NMR, we carried out a statistical study of the evolution of the system with the

reaction variables<sup>4,5</sup> (taking into account concepts such as random degree and sequence length). Thus, we estimated the random degree and the sequence length for the mixture PBT/PAr in a composition range between 50 and 90% of PBT at three different temperatures (533, 543, and 553 K). For reaction times between 0 and 40 min we observed for all systems, independently of the composition, a variation of the random degree in the range 0.15–0.22, while the average sequence length varied between 15 and 30, as a function of the thermal treatment. This means that the polymers in these blends have transesterified to the extension of forming block copolymers. This lack of dependency between the random degree and the mixture composition may seem to contradict other literature reports,<sup>5</sup> but we have to stress that in our experiment, the amount of catalyst was minimal, because of the previous purification process performed.

However, when the samples were submitted at a temperature of 553 K during 400 min, the random degree obtained was close to 1. This value indicates that a random copolymer has been formed.

Based on the work developed by Devaux et al.,<sup>5</sup> we reported a kinetic study of the interchange re-

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actions. Finally, in this paper, we present the thermal and mechanical properties of the aforementioned system as well as the influence of the interchange reactions on them.

Thermal properties of polyester blends have been extensively reported.<sup>6-16</sup> Thus, some authors have studied, by DSC, the systems PET/PAr,<sup>6</sup> PBT/BAPC,<sup>7</sup> and PBT/PAr.<sup>13,15-18</sup> Other studies have described the influence of the interchange reactions on the thermal properties of the system. Among them, those of Kimura et al.,<sup>19,20</sup> Eguiazabal et al.,<sup>21,22</sup> Suzuki et al.,<sup>23</sup> Runt and Miley,<sup>24</sup> and Smith et al.<sup>25</sup> are worth mentioning. In the same line, a series of papers described the mechanical properties of these systems.<sup>7,26-32</sup> However, we found that few authors have studied in detail the influence of the interchange reactions on the mechanical properties of the system,<sup>32,33</sup> with the exception of Eguiazabal et al.,<sup>35,36</sup> who described the influence of the processing conditions on these properties.

In the present work, we present the variation of the thermal properties of the PBT/PAr system with the interchange reaction conditions studied by DSC, as well as its influence on the mechanical properties measured by tensile tests. Furthermore, the effect of catalysts on these mentioned properties is also reviewed.

It is well established that the PBT/PAr mixture is miscible in the whole range of compositions.<sup>13,15,16</sup> This aspect is responsible for the small modifications observed in the properties of the glass phase of the system when interchange reactions take place. On the contrary, this does not happen with immiscible and/or partial miscible systems. However, interchange reactions can foster important changes in the crystallinity of the systems. Thus, the possibilities of modifying the systems offer interesting ways of obtaining materials with new properties.

## EXPERIMENTAL

The two polymers used in this study (PAr and PBT) were supplied by Union Carbide and Polysciences, respectively. Their molecular characteristics and blend preparations were described elsewhere.<sup>1,2</sup> The catalyst employed (tetra-*n*-butyl titanate) was purchased from Aldrich.

A Mini Max molder (CSI) was used to run the reaction. Reaction temperature was 533 K, and reaction times ranged between 3 and 40 min. All mixtures contained a Ti concentration of  $5 \times 10^{-3}\%$ . This concentration corresponds to the residual catalyst from PBT polymerization after polymer purification. Additional catalyst was added to some of the samples in order to increase its concentration

up to 0.05, 0.1, and 0.2%. Atomic absorption spectrophotometry was used to measure titanium concentration.

After reaction, the blends were compression molded at 538 K. After molding, the sheets were rapidly cooled by immersion in an ice water bath. From the square sheets obtained, specimens for measurement of properties were extracted.

Tensile specimens (ASTM D638 type V) were punched out by a pneumatic machine. Tensile tests were performed in an Instron 4301 at a speed of 10 mm/min at room temperature. The Young's modulus  $E$  (defined as the initial tangent of the stress-strain curve), nominal yield stress  $\sigma_y$ , nominal break stress  $\sigma_b$ , and ductility  $\epsilon_b$  (measured as strain at break) were obtained from the load-elongation plots. An average of 9 specimens was tested for each reported value.

All the calorimetric scans were carried out in a Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a Perkin-Elmer TADS 3700 system. The heating rate was 20 K/min. A nitrogen flow was maintained through the sample and reference chambers. The temperature and the enthalpy were calibrated with reference to indium standard. The  $T_g$  was defined as the midpoint of the glass transition region of the DSC. The crystallization and melting temperatures were measured at the maxima of the corresponding peaks and the melting endotherm was defined by a baseline constructed from 140°C to a temperature above which no melting was observed. Degrees of crystallinity were obtained by using the ratio of the heat of fusion measured from the endotherm area to that of perfect crystalline PBT, which is 31.8 kJ/mol.<sup>20</sup>

NMR spectra were registered in a Varian VXR 300 spectrometer in a mixture of deuterated trifluoroacetic acid and deuterated chloroform (50 : 50); tetramethylsilane (TMS) was used as internal reference. <sup>1</sup>H-NMR (300 MHz) spectra were registered in 5-mm-i.d. tubes in 10% w/v solutions with a spectral width of 4000 Hz, flip angle 90°, and acquisition time 3.7 s; 16K data points for Fourier transform.

Density measurements were performed with the help of a calibrated pycnometer at 25°C and *n*-butanol was used as solvent.

## RESULTS AND DISCUSSION

### Physical Blend Quenched

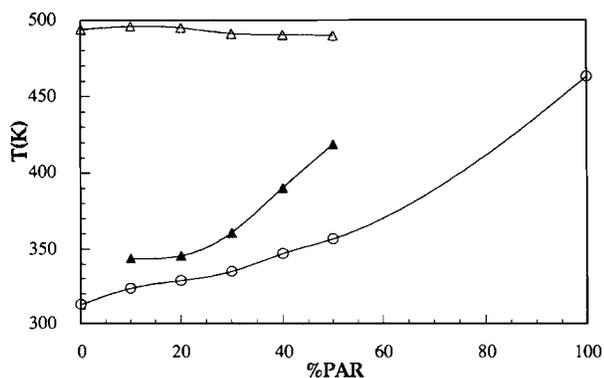
The physical blend was kept in the reaction medium 3 min at 533 K. The <sup>1</sup>H-NMR study revealed that the system did not undergo any interchange reaction.

### Thermal Properties

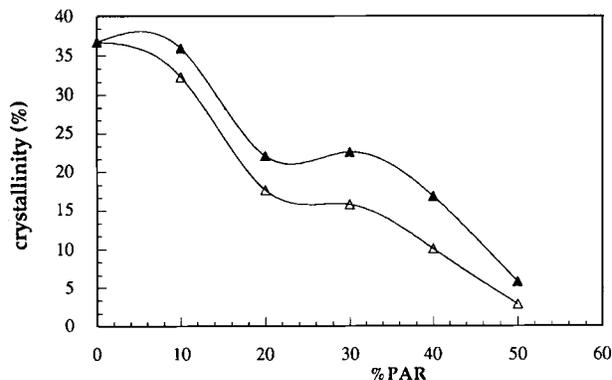
Figure 1 shows the phase diagram of the quenched samples of this physical blend. The results are similar to those reported in the bibliography.<sup>16</sup> All compositions present a unique  $T_g$ , which is in accordance with the miscible character of the amorphous phase of the mixture. Furthermore, the diagram shows a small deviation from linearity, a common behavior for miscible blends.<sup>15</sup> When heated, all blends exhibit an exothermic peak ( $T_c$ ), due to PBT crystallization. The crystallization temperature ( $T_c$ ) increases with the content in PAr due to the increase in  $T_g$ , and, as a consequence, a higher temperature is needed to mobilize the chains to crystallize.

The melting temperature ( $T_m$ ) of the blend increases for those compositions with a low content in PAr, and then decreases for those blends rich in PAr. The  $T_m$  goes from 494 K for PBT up to 496 K for a blend PBT/PAr 90/10 and down to 490 K for a 50/50 blend. This behavior seems to contradict the melting point depression observed for miscible blends. Thus, for these systems, due to the presence of amorphous polymer, the crystallizable component crystallizes much more slowly than purely crystallizable polymer. This difference in kinetics could result in formation of larger and relatively more perfect crystals. Although a melting point depression exists in these blends, the experimental melting points do not necessarily decrease as a consequence of added PAr in the blends.<sup>16</sup>

Figure 2 shows the crystallinity values, obtained from  $\Delta H_m$  and  $\Delta H_c$  data, as a function of composition. The crystallinity decreases with PAr content because PAr hinders the crystallization capacity of PBT. However, as an exception, when PAr composition is between 20 and 30%, an increase in the crystallinity is found. This behavior is similar to that reported by Sanchez<sup>7</sup> for the PC/PBT system.



**Figure 1** Phase diagram for the physical blend PBT/PAr: ( $\Delta$ )  $T_m$ , ( $\blacktriangle$ )  $T_c$ , ( $\circ$ )  $T_g$ .



**Figure 2** Crystallinity (%) vs blend composition: ( $\Delta$ ) referred to the mixture, ( $\blacktriangle$ ) referred to PBT.

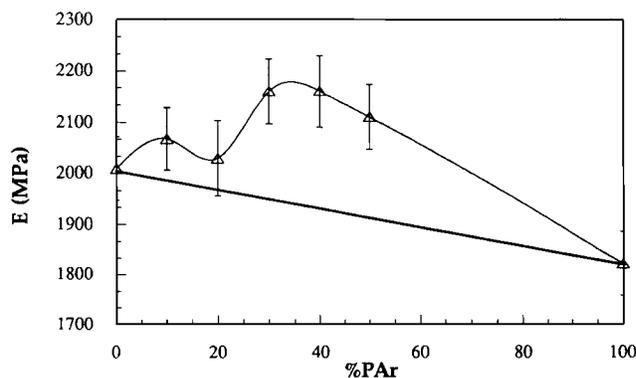
### Mechanical Properties

Beginning with the properties of low strain, Figure 3 shows the variation of Young's modulus with composition. As can be observed, there is a clear positive deviation from linearity, even exceeding the value of pure PBT. This behavior is not very common and it has been reported only on a few occasions.<sup>24</sup>

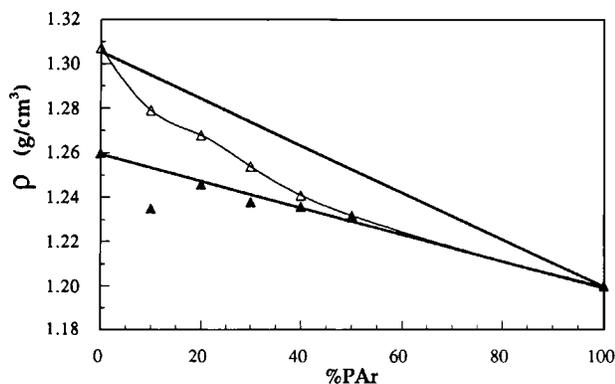
Synergistic behaviors in Young's modulus have been explained frequently as a consequence of a densification of the mixture due to component interactions. Density measurements in semicrystalline blends are not an easy task, because there are some factors, such as crystallinity, which affect the density of the mixture. In order to calculate the density of the amorphous part, the following expression can be used:

$$\frac{1}{\rho_b} = \frac{1 - X_{\text{PBTc}}}{\rho_a} + \frac{X_{\text{PBTc}}}{\rho_{\text{PBTc}}}$$

where  $\rho_b$  is the overall density of the mixture,  $\rho_a$  is the amorphous part density,  $\rho_{\text{PBTc}}$  is the density of



**Figure 3** Young's modulus-composition relationship for PBT/PAr blends.

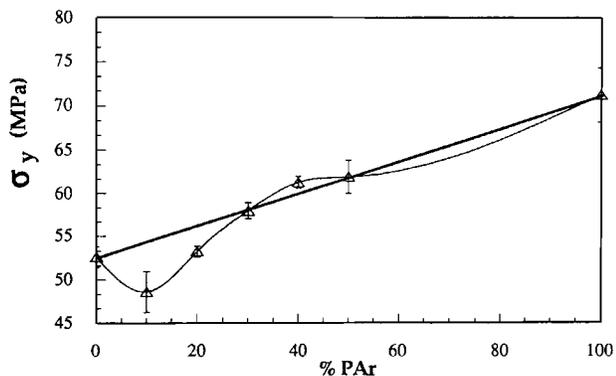


**Figure 4** Density of PBT/PAr blends as a function of composition: ( $\Delta$ ) overall density, ( $\blacktriangle$ ) amorphous fraction.

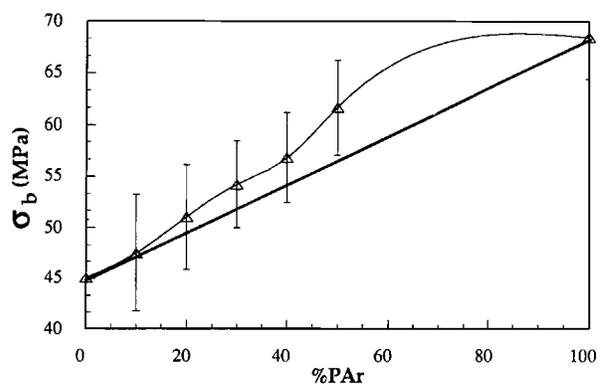
the fully crystalline PBT (a value of 1.396 g/cc has been assumed for  $\rho_{\text{PBTc}}$ )<sup>5</sup> and  $X_{\text{PBTc}}$  is the crystalline content of the mixture, obtained by the aforementioned method. Figure 4 shows the overall density of the mixture ( $\rho_b$ ) and the density referred to the amorphous part ( $\rho_a$ ) as a function of composition. As can be observed, there is a negative deviation from linearity for the overall density; however, the density of the amorphous part is almost within the linearity. Thus, we must conclude that the densification of the mixture cannot be a reason for the observed synergistic effect in the Young modulus.

In Figure 5 we show the yield stress composition relationship. A negative deviation from linearity can be observed for those compositions with a higher content in PBT (90/10, 80/20) whereas the values for the rest of compositions are closed to linearity.

In reference to the break properties in relation to the composition of the mixture, Figures 6 and 7 show the representation of the break stress and the elongation at break, respectively. While the values



**Figure 5** Yield stress-composition relationship for PBT/PAr blends.

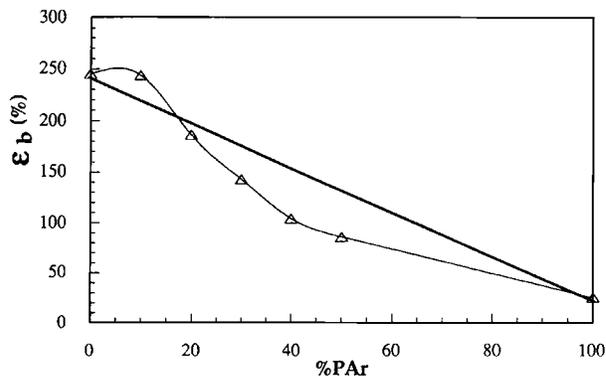


**Figure 6** Break stress-composition relationship for PBT/PAr blends.

of the break stress show a positive deviation from linearity, those of the deformation at break display a different behavior. The compositions with a higher content in PBT show a slight positive deviation or are within the linearity, but the compositions with a lower content in PBT show a negative deviation. This behavior is the reverse to the one observed for the yield stress. There is a relationship between the evolution of crystallinity and mechanical properties with the composition. Given the fact that at a composition of 70% of PBT the crystallinity increases, the system becomes more rigid. Consequently, an increase in the low deformation properties (Young's modulus and yield stress) is observed together with a decrease in the deformation at break.

#### Effect of the Reaction Time

By means of <sup>1</sup>H-NMR spectroscopy and, based on a previous study,<sup>1,2</sup> we have shown the existence of



**Figure 7** Deformation at break-composition relationship for PBT/PAr blends.

**Table I**  $T_m$  (K) as a Function of Composition and Reaction Time

Reaction Time (min)	90 : 10 PBT/PAr	80 : 20 PBT/PAr	70 : 30 PBT/PAr	60 : 40 PBT/PAr	50 : 50 PBT/PAr
0	495.6	494.8	491.0	490.2	489.7
20	495.2	492.3	487.1	487.2	483.8
30	495.1	492.3	486.4	485.1	485.0
40	494.9	492.3	487.0	484.2	483.1

interchange reactions under the experimental conditions employed.

### Thermal Properties

Tables I, II, and III summarize the variation of  $T_m$ ,  $T_c$ , and  $T_g$  with the reaction time. With respect to the  $T_m$  values, the PBT melting point is increasingly depressed as PAr content increases for all the compositions studied. The existence of interchange reactions decreases the perfection of the crystals of PBT.

Figure 8 shows the variation of the melting endotherm with the reaction time. At zero reaction time, the peak is at 490 K and corresponds to the melting of crystals formed by a recrystallization process during the DSC scan (endotherm II). As a consequence of the thermal treatment, a shift toward lower temperatures of the melting peak is generated. Simultaneously a small shoulder appears and becomes more apparent as the shift increases. The maximum of this shoulder coincides with the maximum of the melting peak of the physical blend. This behavior can be explained by the existence of two endotherms in the overall melting peak. The first one can be attributed to the melting of crystals grown by normal primary crystallization (endotherm I) and the second one to the recrystallization of the melted crystals during the scanning procedure. When there is no reaction this last process becomes more prevalent. Nevertheless, the interchange reactions, by the fact that they break the chains reg-

ularity, make the recrystallization process and the formation of more perfect crystals more difficult. This fact gives more weight to the primary crystallization process and, as a consequence, the maximum of the peak shifts toward lower temperature values. The existence of the above mentioned shoulder in the same position found for the melting peak of the physical blend indicates that a small part of the material recrystallizes during the melting process. On the other hand,  $T_g$ s of the transesterified blends have a different behavior.  $T_g$ s for compositions with a high content in PBT (90/10, 80/20, and 70/30) show an erratic behavior, difficult to explain. The rest of the compositions, nevertheless, give  $T_g$ s that remain almost constant with reaction time. This behavior is consistent with the miscible character of the mixture.

Figure 9 shows the variation of the crystallinity with the reaction time. For all compositions, the crystallinity decreases with reaction time. This is due to the fact that interchange reactions decrease the crystallization capacity because of the formation of copolymers that break the regularity of the chains of PBT. At high reaction times an increase in crystallinity is observed for some compositions. This small increase, which can almost be considered within the experimental error, could be perhaps explained on the basis of an associated crystallinity of the chain ends, which appears as a consequence of the existence of degradation reactions, under these conditions.

**Table II**  $T_c$  (K) as a Function of Composition and Reaction Time

Reaction Time (min)	90 : 10 PBT/PAr	80 : 20 PBT/PAr	70 : 30 PBT/PAr	60 : 40 PBT/PAr	50 : 50 PBT/PAr
0	343.7	345.5	360.7	390.3	419.1
20	345.6	348.0	367.3	396.7	434.7
30	343.7	349.4	369.2	403.9	434.3
40	342.4	349.0	367.9	402.5	435.7

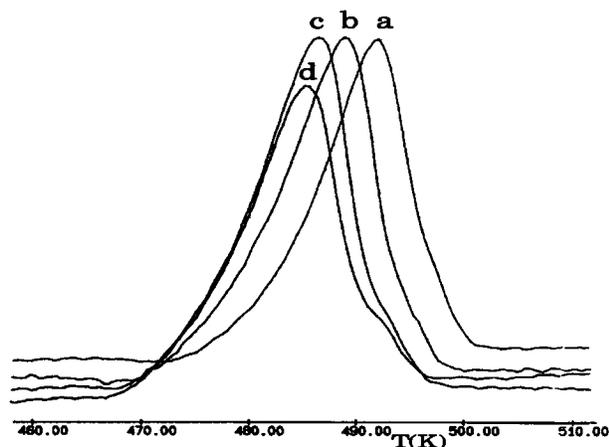
**Table III**  $T_g$  (K) as a Function of Composition and Reaction Time

Reaction Time (min)	90 : 10 PBT/PAr	80 : 20 PBT/PAr	70 : 30 PBT/PAr	60 : 40 PBT/PAr	50 : 50 PBT/PAr
0	323.5	328.4	335.0	346.9	356.6
20	327.4	337.9	326.6	346.5	356.9
30	327.0	336.0	328.4	344.7	356.4
40	325.7	341.2	329.0	345.0	356.3

### Mechanical Properties

Table IV summarizes the variation of Young's modulus with the reaction time. As can be observed, there is a small decrease of the modulus with the reaction time, although, in practice, this can be considered to fall within the experimental error. Compositions with a higher content in PBT show a marked decrease in crystallinity, which provokes a higher decrease in Young's modulus (10% in the highest case). Yield stress for these blends shows a similar behavior to that of the modulus of Young.

The decrease in crystallinity provokes an increase in the strain at break. Figure 10 presents the variation, with the reaction time, of the strain at break. It can be observed that this property increases with the reaction time, and that the higher the crystalline content of the blend, the greater the increase in the strain at break. The increase goes up to 27% for the composition 90/10 and up to 38% for the 80/20. However, at high reaction times (40 min), a decrease in the deformation at break is observed due to the appearance of degradation reactions. The presence of these reactions is based on the chain final groups detected by NMR spectroscopy.



**Figure 8** Variation of melting peak with the reaction time for PBT/PAr blend (60 : 40) transesterificated at 533 K: (a)  $t = 0$  min, (b)  $t = 20$  min, (c)  $t = 30$  min, and (d)  $t = 40$  min.

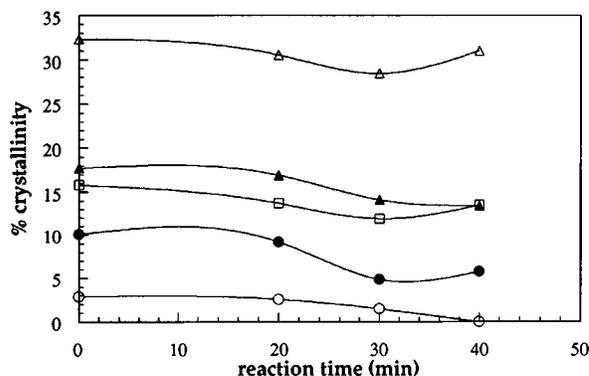
### Effect of the Catalyst Concentration

In accordance with the results obtained in the preceding section, the following reaction conditions were chosen:  $T = 533$  K and  $t = 20$  min. Using  $^1\text{H-NMR}$  and by means of the values of the random degree and sequence lengths,<sup>3</sup> it was possible to prove that the employed catalyst (tetrabutyl titanate) accelerates the extension of the interchange reactions.

### Thermal Properties

Table V summarizes the variation of  $T_m$  with the catalyst concentration. As can be observed, there is a marked decrease of  $T_m$  for all compositions. In the same way described by other authors, the values of  $T_m$  are, due to the catalyst effect, even lower than those given in the preceding section. The existence of copolymers as a consequence of the interchange reactions results in irregularities in the polymeric chains, which make the perfection of the crystals decrease.

Figure 11 shows the crystallinity as a function of the catalyst concentration. As in the previous case, the appearance of copolymers leads to a lower crystallization capacity.



**Figure 9** Variation of crystallinity (%) with the reaction time for PBT/PAr blends at different compositions: ( $\Delta$ ) 90 : 10, ( $\blacktriangle$ ) 80 : 20, ( $\square$ ) 70 : 30, ( $\bullet$ ) 60 : 40, ( $\circ$ ) 50 : 50.

**Table IV**  $E$  (MPa) as a Function of Composition and Reaction Time

Reaction Time (min)	90 : 10 PBT/PAr	80 : 20 PBT/PAr	70 : 30 PBT/PAr	60 : 40 PBT/PAr	50 : 50 PBT/PAr
0	2068	2030	2160	2160	2110
20	2003	2000	2084	2080	2080
30	1860	2065	2120	2150	2130
40	1981	1980	2100	2140	2150

### Mechanical Properties

The properties of low strain, modulus, and yield stress almost do not suffer any modification, except for the compositions 90/10 and 80/20, where a small decrease in modulus is observed. However, the deformation at break, as shown in Table VI increases when compared with those of the physical blend, specially for the more crystalline compositions and for the lowest catalyst concentration. Nevertheless, except for the 90/10 composition, this increase is lower than the one obtained with a residual concentration of catalyst. As the catalyst concentration increases, there is a progressive decrease of properties as a consequence of degradation reactions. It can be concluded, therefore, that under the reaction conditions employed, the catalyst accelerates not only the interchange reactions, but also the degradation reactions, in accordance with the results obtained by NMR.

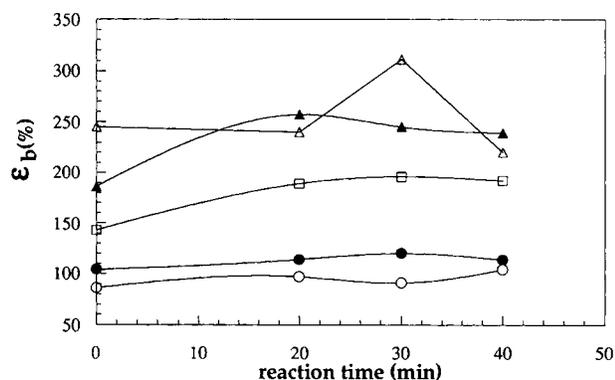
### CONCLUSIONS

Properties of the PBT/PAr mixture have been measured. Young's modulus data for these blends are above linearity and they are even higher than

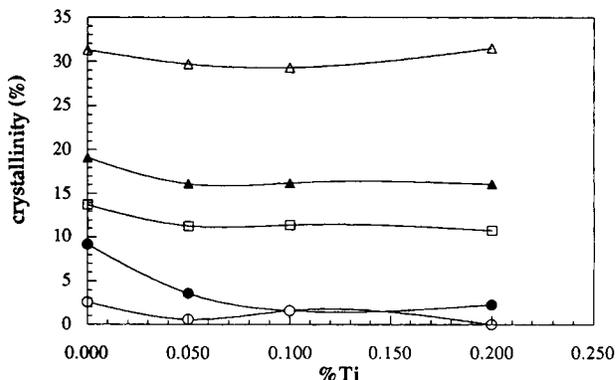
those of pure components, similar to what has been observed for other systems.<sup>27,28</sup> In addition, the mixture does not suffer a drastic decrease in the properties at break. On the contrary, these properties are closed to linearity, probably due to the miscible character of the mixture. The results obtained for thermal properties are in accordance to those reported in the literature.

The formation of copolymers, as a consequence of interchange reactions, diminishes the perfection of the crystals as well as the capacity for crystallization of the system. Due to these two facts, mechanical properties undergo some variations. Thus, both the Young's modulus and the yield stress decrease slightly. The lower capacity for crystallization results in an increase of the deformation at break. Although the overall behavior of the material does not change, owing to the reactive processing of the material we have been able to improve some of the properties of the system.

To improve this process we have studied the effect of the catalyst (tetrabutyl titanate) on the interchange reactions. This effect has been studied on the thermal properties of the blends, and we have observed an amplified effect produced by the interchange reactions. In relation to the mechanical



**Figure 10** Evolution of the deformation at break with the reaction time for PBT/PAr blends at different compositions: (Δ) 90 : 10, (▲) 80 : 20, (□) 70 : 30, (●) 60 : 40, (○) 50 : 50.



**Figure 11** Variation of crystallinity (%) with titanium concentration for PBT/PAr blends at different compositions: (Δ) 90 : 10, (▲) 80 : 20, (□) 70 : 30, (●) 60 : 40, (○) 50 : 50.

**Table V**  $T_m$  (K) as a Function of Composition and Titanium Concentration at a Reaction Temperature of 533 K and Reaction Time of 20 min

Ti Concentration (%)	90 : 10 PBT/PAr	80 : 20 PBT/PAr	70 : 30 PBT/PAr	60 : 40 PBT/PAr	50 : 50 PBT/PAr
	495.2	492.3	487.1	487.2	483.8
0.05	490.2	487.7	483.6	479.7	478.5
0.1	489.8	486.5	483.3	479.5	476.8
0.2	491.6	485.8	482.4	476.7	475.5

**Table VI** Elongation at Break as a Function of Composition and Ti Concentration at a Reaction Temperature of 533 K and Reaction Time of 20 min

Ti Concentration (%)	90 : 10 PBT/PAr	80 : 20 PBT/PAr	70 : 30 PBT/PAr	60 : 40 PBT/PAr	50 : 50 PBT/PAr
Residual	240	257	189	114	97
0.05	286	255	166	104	86
0.1	271	247	158	106	75
0.2	153	235	137	95	18
Physical blend	244	186	143	104	86

properties, it must be stressed that the existence of degradation reactions, when using the catalyst, provokes a decrease on the properties at break, with respect to those compositions with a residual content of catalyst. Only for the most crystalline composition (90/10) and lower catalyst concentration, is an increase of these properties observed. The use of the catalyst can be considered valuable only for those systems processed, to minimize reactions of degradation, under inert atmosphere conditions.

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