

Poly(ethylene terephthalate)/Polyarylate Blends: Mixing and Interchange Reactions in Injection Molding

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SYNOPSIS

Blends composed of poly(ethylene terephthalate) and a polyarylate have been melt-mixed and molded in a reciprocating screw injection-molding machine for different plasticization times. Interchange reactions between the blend components occur during processing and at a greater level as the plasticization time increases. These reactions led to a progressive homogenization of the blends as well as to a hindered crystallization of PET. The effect of the plasticization time on the mechanical properties of the blends seems to be a consequence of interchange reactions as well as of the degradation of the blends at the highest plasticization times. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends based on engineering polyesters have great basic and practical importance. First, the ester groups in the main chain of polyesters have a high potential for specific interactions, which leads to miscibility. Thus, polyesters may interact via hydrogen bonding with hydroxyl groups or via $n-\pi$ interactions with aromatic rings, etc. Second, polyesters may give rise to interchange reactions in blends with other condensation polymers during mixing or processing in the melted state. These interchange reactions may lead to the production of different types of copolymers of both blend components. These copolymers may influence the miscibility level of the blends and thus offer great possibilities to control their structure and properties.

Poly(ethylene terephthalate) (PET) is a very important engineering polyester that has been studied as a component of many polymer blends. Thus, polycarbonate, phenoxy, a polyarylate, and poly(butylene terephthalate),^{1,2} as well as polyamide 6, and polyamide 6,6,³⁻⁸ among other polymers, have been mixed with poly(ethylene terephthalate). These blends have been studied from different points of view.

All the mentioned PET/second-component systems have a common feature: They may give rise to interchange reactions when they are maintained at high temperatures in the melted state. Although the interchange reactions have been extensively studied in some cases, the effect of these reactions on the different properties of the blends has received limited attention in the literature.

Blends of PET and the polyarylate of bisphenol A and 50/50 isophthalic/terephthalic acids (PAr), as well as the possible interchange reactions, have been studied by different authors.⁹⁻¹⁴ The miscibility studies were carried out mainly by calorimetric and dynamical-mechanical analysis and indicated the existence of partial miscibility between the blend components. The interchange reactions that can take place in this polymer blend were also studied.

In the case of blends where one of the components can crystallize, as in the case of the PET/PAr system, one of the effects of interchange reactions is that the reactions give rise to a decrease in the length of the crystallizable segments. This results in a decrease in the ability to crystallize and, eventually, in the crystallinity degree, the perfection of the crystallites, etc. Thus, the interchange reactions may be used to control crystallinity and, therefore, the properties of the blend. This is an interesting aspect of PET/PAr blends, which can also be of practical applicability.

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The mechanical properties of these blends have been studied¹³ only in the case of the low reaction level achieved after a minimum time in the injection machine. Additionally, melt blending of polymers is usually carried out by discontinuous processes, like Brabender mixing. This process provides, by means of the variation of torque with time, the opportunity to control the development of the blending process as well as that of the reactions that eventually may be produced. The possibility of direct blending of polymers in an injection machine, which is much closer to practical needs, has been recently reported¹⁶ and used.¹³ However, this method has not been used to produce blends with different reactions levels.

These are the reasons why, in this work, we have studied the effects of the level of interchange reactions on the thermal and mechanical behaviors of 75/25 PET/PAr blends. The reactions were produced during direct mixing PET and PAr in an injection-molding machine. Knowledge of the effects of these reactions will possibly allow practical utility of this method in PET applications, such as in blow molding for bottle production. In this process, an increase in the glass transition temperature and a reduction of the crystallization ability of PET are required to maintain a high level of the product's mechanical properties.

EXPERIMENTAL

The polymers used in this work were commercial products. Polyarylate (PAr), Arilef U-1060, was kindly supplied by SOLVAY & Cie. It is a copolymer of bisphenol A and 50/50 isophthalic/terephthalic acids, with a molecular weight $M_w = 34,900$. The M_w was determined by viscometry in THF at 25°C using the equation $[\eta] = 4.00 \times 10^{-4} M_w^{0.68}$.¹⁶ The poly(ethylene terephthalate) (PET) was kindly supplied by Brilen S. A., Barbastro, Spain. This polymer had a molecular weight $M_n = 27,000$, measured in a phenol/tetrachloroethane (50/50) mixture, at 20°C, using the equation $[\eta] = 7.55 \times 10^{-4} M_n^{0.685}$.¹⁷

The pellets of both polymers were dried *in vacuo* at 80°C for 24 h before processing to avoid degradation reactions caused by moisture. PET/PAr (75/25) mixtures were prepared directly in the screw plasticizer of a Battenfeld BA230E injection-molding machine. The barrel temperature was 300°C and the mold temperature was 15°C. Different interchange reaction levels were obtained by changing the plasticization time of the injection-molding machine. Pure PET was subjected to the same pro-

cessing conditions. Tensile specimens (ASTM D638, Type IV) were molded for the different levels of interchange reactions.

Differential scanning calorimetry (DSC) was used to characterize the thermal properties of the obtained products. DSC measurements were carried out in a DuPont DSC cell equipped with a DuPont 2000 Thermal Analyst System, at a heating rate of 20°C/min. The thermal transitions were determined in the usual way on samples obtained directly by injection molding.

NMR spectroscopy was used to follow the interchange reactions in PET/PAr blends. A Varian VXR 300 spectrometer was used. The samples were dissolved in a deuterated chloroform/deuterated trifluoroacetic acid mixture. Tetramethyl silane was used as the internal reference standard.

Tensile tests were carried out in an Instron 4301 tensile tester at room temperature and at a crosshead speed of 10 mm/min. The different mechanical properties (Young's modulus, E ; yield stress, σ_y ; nominal stress at break, σ_b ; and ductility, ϵ_b , measured as the break strain) were obtained from the force-displacement curves and are averages of at least eight samples.

The fracture surfaces of some tensile specimens were observed after gold coating. A scanning microscope (SEM) Hitachi S-2700, operated at 15 kV, was used.

RESULTS AND DISCUSSION

Interchange Reactions and Phase Behavior

The occurrence of increasing levels of interchange reactions in the PET/PAr (75/25) blends after plasticization times of 8, 38, 90, and 160 s in each injection-molding cycle has been tested. With this aim, in Figure 1, we show the aromatic region of the NMR spectra of the PET/PAr (75/25) blends after different plasticization times, as well as those of pure PET and PAr. As observed in previous works,^{13,14,18} the two double peaks that appear between the signal centered at $\delta = 8.16$, which corresponds to the terephthalate protons of PET, and that centered at $\delta = 8.41$, which corresponds to the terephthalate protons of PAr, are attributed to the aromatic protons of the terephthalate unit asymmetrically substituted as a consequence of the transesterification reactions. The plastication time of 8 s leads to a minimum, if any, reaction as seen in Figure 1 and is the same as that of the same composition used in Ref. 13. It is also observed that the intensity of these new signals is greater as the plasticization time increases.

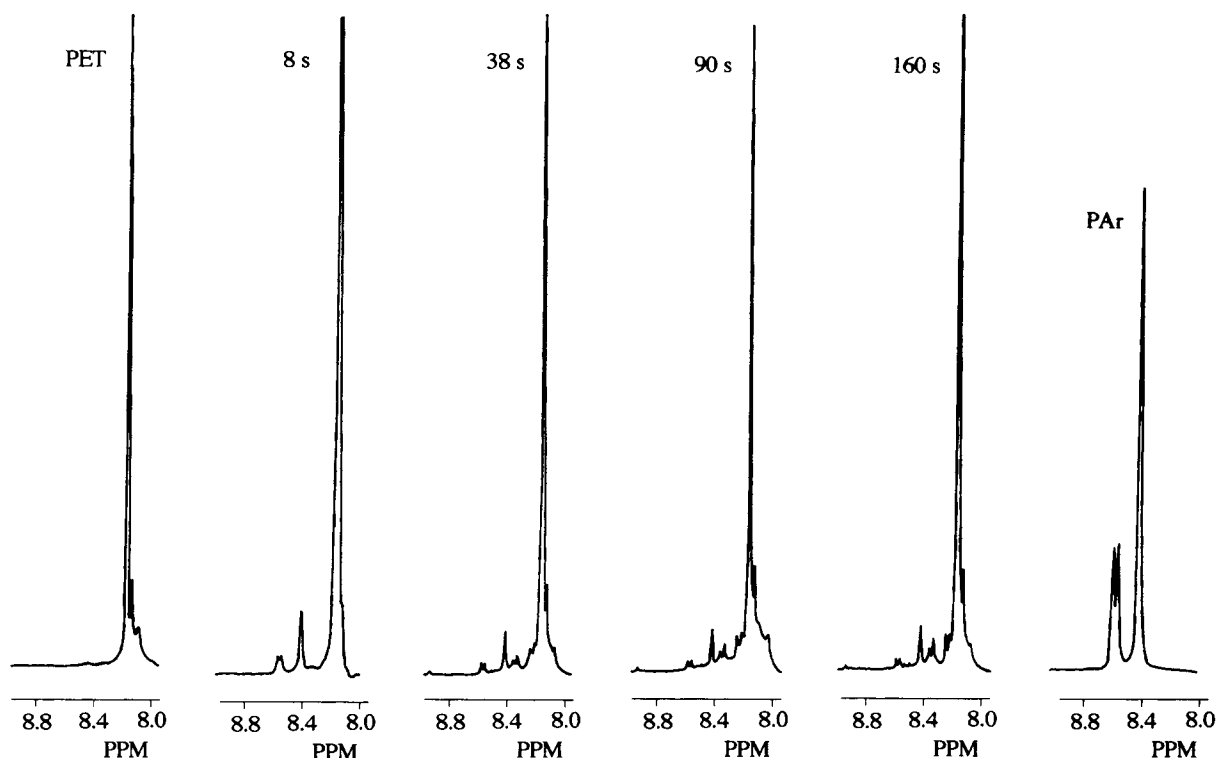


Figure 1 $^1\text{H-NMR}$ spectra of PET and of PET/PAr (75/25) blends after different plasticization times.

This proves that a greater level of reaction is obtained at higher plasticization times.

Figure 2 shows the DSC thermograms obtained for the PET/PAr (75/25) blends after different plasticization times. The thermogram obtained for pure PET at 38 s plasticization time is also shown. A different thermal behavior is observed for the pure crystallizable polymer and for the different blends. PET shows a glass transition with a T_g value of 73.6°C and after that a crystallization exotherm. This exotherm is due to the rapid cooling of the melt in the mold, which makes the full crystallization of PET difficult. Finally, the DSC scan shows the melting peak of PET. This thermal behavior was independent of the plasticization time.

With respect to the DSC scans of the PET/PAr (75/25) blends after different plasticization times, there is practically no effect of increasing plasticization times on the T_g of PET/PAr (75/25) blends. This is because they vary from 76.6°C for a plasticization time of 8 s to 78.8°C for a plasticization time of 160 s. This represents a small increase in the T_g of the blends with respect to that of pure PET (73.6°C). This increase must be due to the existence of a mixed PET-rich PET/PAr phase in the blends. The slight increase in T_g is a consequence

of the small PAr content in the blends. A possible second T_g of a PAr-rich phase should be detected at low plasticization times due to the immiscibility of the blends,⁹ but it is impossible to detect due to its superimposition on the crystallization peak.

A more important and interesting effect of the plasticization time is observed, however, when the crystallization-melting behavior of the blends is considered. As observed in Figure 2, with the exception of the longest 160 s plasticization time, a crystallization exotherm of PET appears in the blends. This exotherm is broader in the blends than in the pure crystallizable polymer, indicating a hindered crystallization of PET. Moreover, this effect is also supported by the fact that the crystallization temperature, measured at the minimum of the crystallization exotherm, increases in the blends with respect to that of pure PET. It also increases as the plasticization time increases, as observed in Figures 2 and 3 where the T_c and T_m values are plotted against plasticization time. For a plasticization time of 160 s, no crystallization exotherms appear, indicating that PET is already unable to crystallize during the calorimetric scan.

With respect to the melting behavior (Figs. 2 and 3), a clear decrease of the melting temperature is

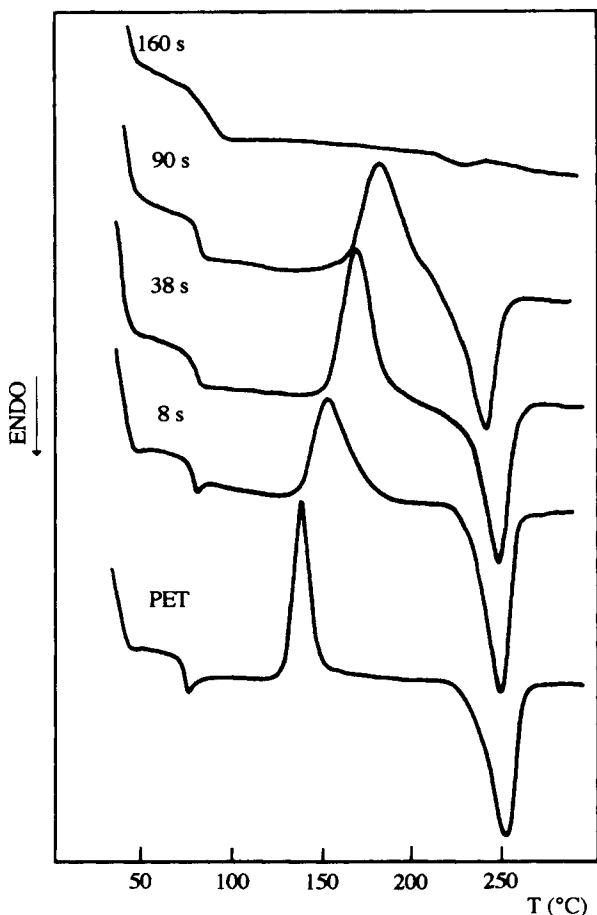


Figure 2 DSC thermograms for PET and for PET/PAr (75/25) blends after different plasticization times.

found in the blends with respect to that of pure PET. Moreover, the higher the plasticization time, the more important is this decrease. This indicates that the PET crystallites are less perfect in the blends and that they continue losing perfection as the plasticization time increases.

In Table I we show the crystallization and melting heats as well as the $\Delta H_m - \Delta H_c$ for pure PET and for the different PET/PAr (75/25) blends. As would be expected, the melting heat in the blends decreases as the plasticization time increases. However, almost identical ΔH_m values are obtained after 8 and 38 s plasticization time, indicating that similar crystallinity levels are obtained in both samples. For higher plasticization times, a decrease in the melting heat is observed. This decrease may be attributed to a hindered crystallization of PET, due to the interchange reactions, and to the concomitant decrease in the crystallized segment length of PET.

The crystallization heat shows a more complicated behavior with plasticization time. Thus, from a value of 23.3 J/g for a plasticization time of 8 s, it increases up to 29.7 J/g for a plasticization time of 38 s. Afterward, ΔH_c decreases and the crystallization exotherm disappears for a plasticization time of 160 s. These variations may also be explained as a consequence of interchange reactions.

The blend with a plasticization time of 8 s showed a very small level, if any, of interchange reactions. PET is capable of crystallizing from this blend during cooling in the injection mold, and the $\Delta H_m - \Delta H_c$

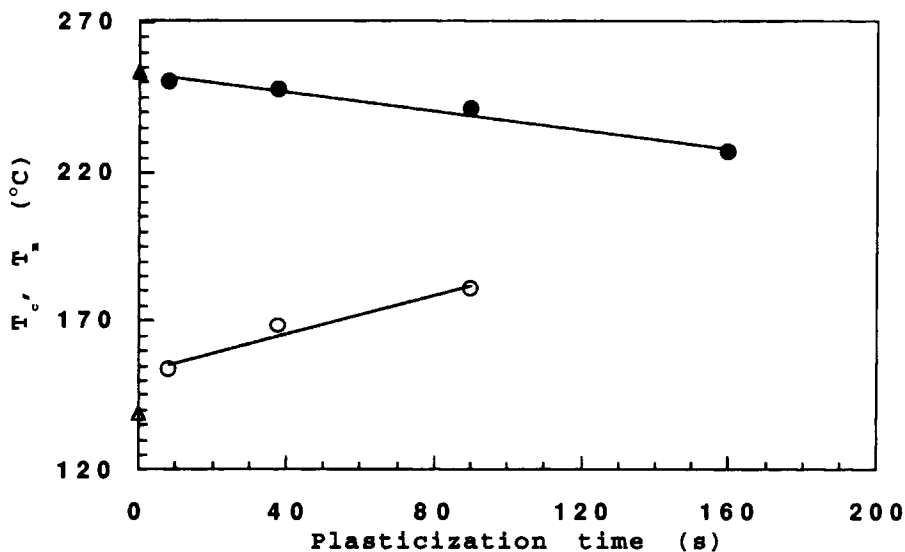


Figure 3 Crystallization and melting temperatures of PET in PET/PAr (75/25) blends after different plasticization times. The points at 0 min plasticization time correspond to pure PET.

Table I Crystallization and Melting Data of PET and of the PET/PAr (75/25) Blends

Sample	ΔH_c (J/g)	ΔH_m (J/g)	$\Delta H_m - \Delta H_c$ (J/g)	% Crystallinity After Molding
PET, 38 s	33.0	44.7	11.7	8
PET/PAr (75/25), 8 s	23.3	30.0	6.7	4.6
PET/PAr (75/25), 38 s	29.7	29.7	0	0
PET/PAr (75/25), 90 s	17.8	18.1	0.3	0.2
PET/PAr (75/25), 160 s	—	1.0	1.0	0.7

value, equal to 6.7 J/g, corresponds to the PET fraction that crystallizes in such conditions. The PET/PAr (75/25) blend prepared with 38 s plasticization time undergoes some interchange reactions during plasticization. Thus, the crystallization of PET during cooling in the injection mold is hindered. As a consequence, PET crystallizes only during the calorimetric scan, with a ΔH_c value of 29.7 J/g and $\Delta H_m - \Delta H_c = 0$. For higher plasticization times, PET is also unable to crystallize during cooling in the mold until the point after a plasticization time of 160 s has been reached. This is where crystallization nearly does not take place during molding or during the calorimetric scan.

Thus, different levels of interchange reactions have been produced directly during injection molding. The change of nature of the material produced by the reactions leads to a progressive hindrance of PET to crystallize. This is due to the decrease in the crystallizable segment length of PET. This gives rise to a decrease in crystallinity of PET that can be controlled by means of the plasticization time. Finally, the presence of PAr in the PET phase increases the T_g of the blends with respect to that of pure PET.

Morphology

The interchange reactions also have an important effect on the morphology of the PET/PAr (75/25) blends. In Figure 4, we show SEM photomicrographs of the fracture surfaces of the blends. As observed, a clear evolution takes place as the plasticization time increases. The sample obtained after 8 s plasticization time [Fig. 4(a) and (b)] shows clearly the biphasic nature of the blend, with a dispersed PAr phase bonded rather well to a PET-rich matrix. In the sample with a plasticization time of 38 s [Fig. 4(c) and (d)], a clear decrease in the particle size is observed. This is possibly due to a compatibilizing effect of the copolymers formed during the interchange reactions. Moreover, the volume fraction of

the dispersed phase in the sample with a 38 s plasticization time is clearly smaller than that indicated in the composition as well as that observed in Figure 4(a). This is in accordance with the progressive incorporation of PAr to PET due to the change of crystalline PET to an amorphous PET-rich phase and to the development of interchange reactions.

The effect of this progressive incorporation and its corresponding compatibilizing effect give rise to Figure 4(e). The fracture surfaces of the PET/PAr (75/25) blends after a 90 s plasticization time (those after 160 s were very similar) do not show a matrix-dispersed phase morphology but a continuous phase. This continuity indicates the almost total homogenization of the blends as a consequence of the interchange reactions that take place during plasticization in the injection-molding machine.

Mechanical Properties

Interchange reactions, due to their compatibilizing effect on the PET/PAr blends, are expected to affect the mechanical properties of the blends. In the case of small strain properties, this effect is practically negligible. Young's modulus and yield stress are slightly higher for the blends (2180 and 55 MPa, respectively) than for pure PET (2090 and 51 MPa, respectively). Both small strain properties are independent of the plasticization time. This indicates that, even for the lowest plasticization times, a good adhesion level exists, at least at low strains. This is consistent with the presence of PAr in the PET-rich phase that was seen because of the T_g change of pure PET to that of PET in the blends.

If we compare this mechanical behavior with that of other reacted Brabender mixed blends, like PC/PAr,¹⁹ PC/phenoxy,²⁰ PAr/phenoxy,²¹ or PBT/phenoxy,²² we realize that the modulus is constant or has a small increase in the case of PC/PAr as well as in these PET/PAr blends. Meanwhile, large modulus increases were produced in the case of phenoxy blends. This experimental fact is related

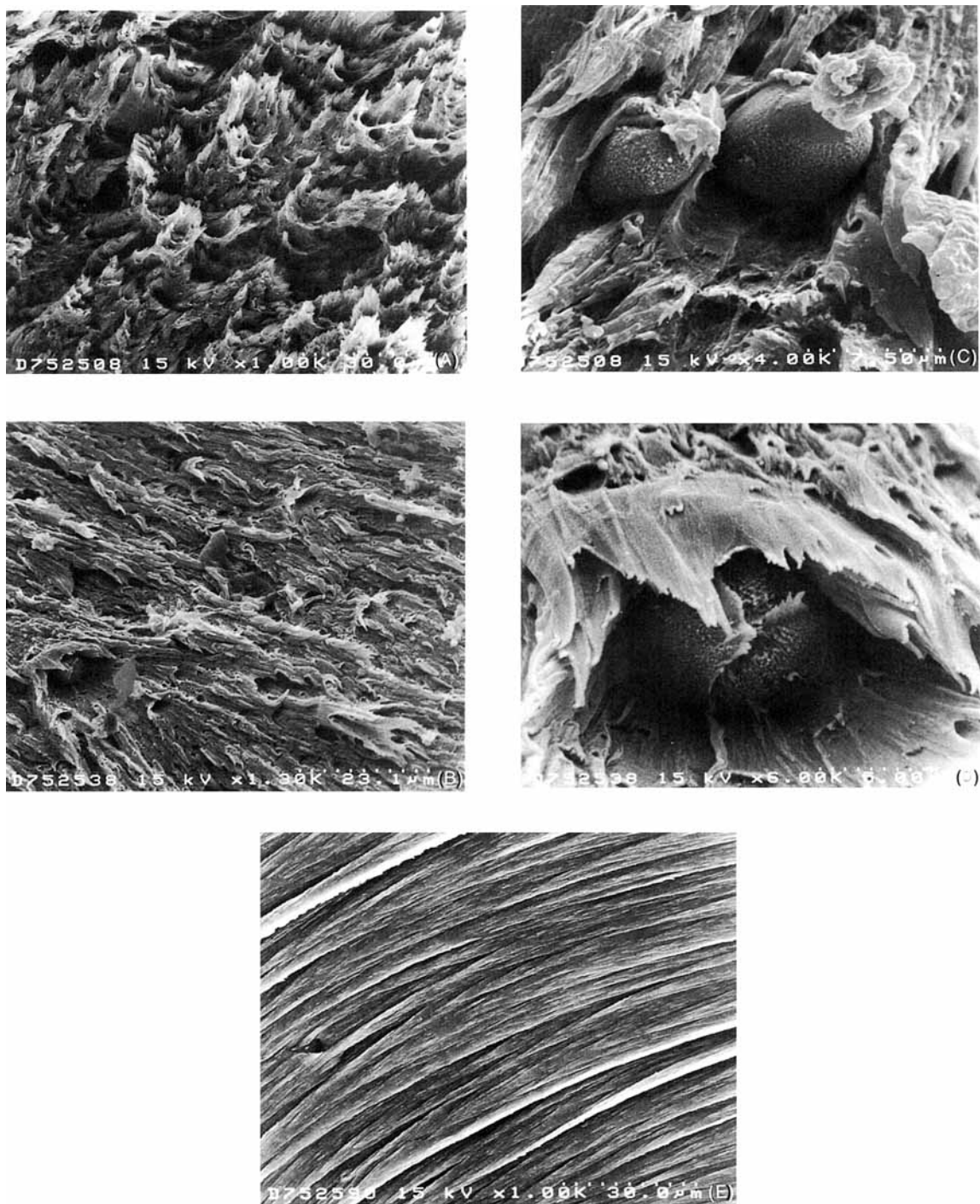


Figure 4 SEM photomicrographs of PET/PAr (75/25) blends after different plasticization times. (A, B) 8 s; (C, D) 38 s; (E) 90 s.

to the nature of the interchange reactions that give rise to linear products, in the case of PC/PAr and PET/PAr blends, and to branched/cross-linked products, in the case of PC/phenoxy, PAr/phenoxy, and PBT/phenoxy blends.

A more important effect of plasticization time is observed if we look at the break properties. As observed in Figures 5 and 6, both the break stress and the ductility show relatively low values in blends prepared with an 8 s plasticization time. This is in

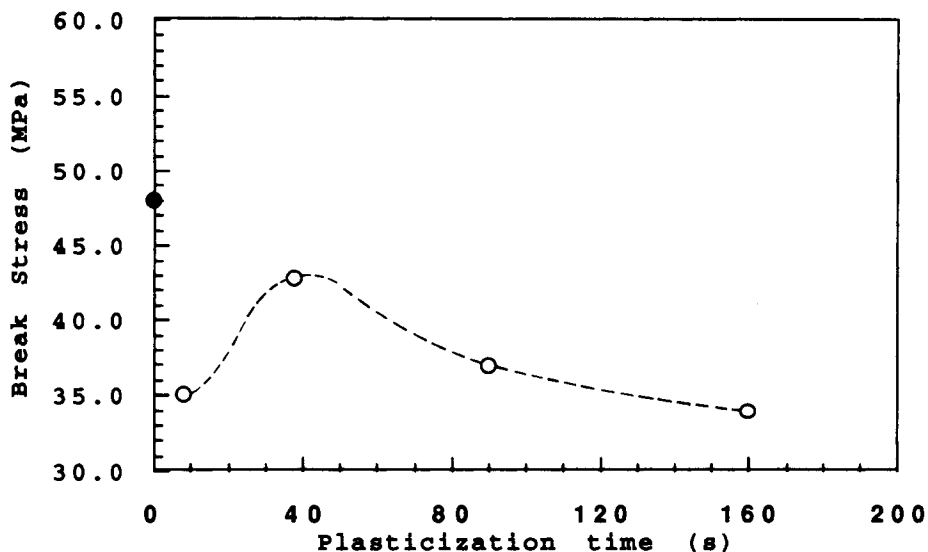


Figure 5 Break stress of PET/PAr (75/25) blends as a function of plasticization time. The point at 0 min corresponds to pure PET.

relation to those of pure PET that are plotted as 0 s plasticization time. An increase followed by a new decrease are obtained for higher plasticization times. This variation may be explained on the basis of interchange reactions and of possible degradation processes taking place in the blends during plasticization. Thus, at 8 s plasticization time, the relatively low break stress and strain values may be attributed to the phase separation that exists in the blends, as shown by SEM. After 38 s, as was also seen by SEM, interchange reactions produce a clear

compatibilizing effect and a decrease in the particle size of the dispersed phase. This explains the increase in the break stress and strain obtained after this plasticization time.

For higher plasticization times, and in spite of the homogeneous nature of the blends, the break stress and strain slowly decrease. The explanation for this decrease is difficult to relate to only the interchange reactions. In fact, these reactions, with the subsequent homogenization of the blends demonstrated by SEM, would give rise to an improve-

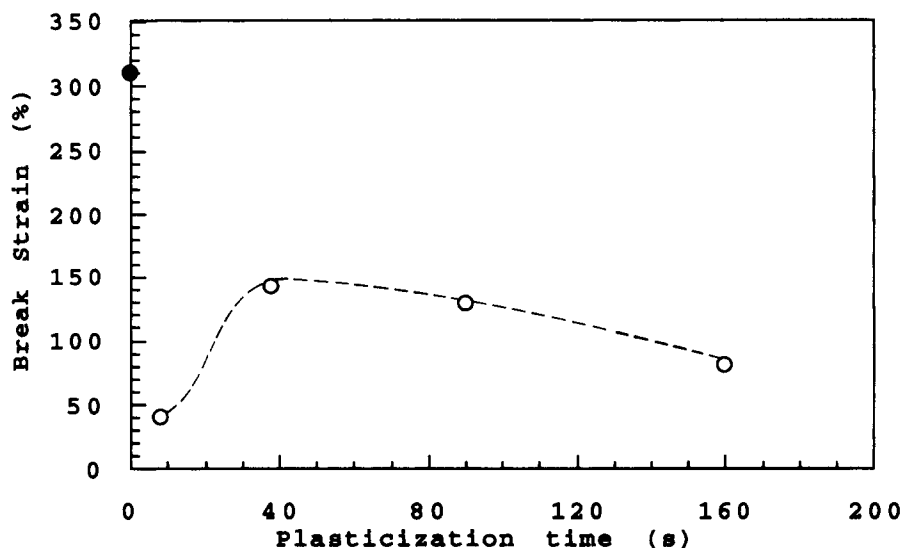


Figure 6 Break strain of PET/PAr (75/25) blends as a function of plasticization time. The point at 0 min corresponds to pure PET.

ment in the break properties. This becomes more important as the plasticization times increase. Thus, the observed deterioration as the plasticization time increases must be attributed to another process, such as thermal and/or mechanical degradation of the blend. It has been recently demonstrated²³ that PET degradation during processing gives rise to a decrease in the break properties of the polymer. As a consequence, the observed ductility and break stress decreases after long plasticization times and are proposed to be due to degradation processes superposed on the interchange reactions. Moreover, it should be pointed out that, in spite of this degradation, within the conditions tested here, the blends with long plasticization times maintain a ductility level higher than that obtained in the case of blends with a very low reaction level.

The results obtained in this work indicate the possibility of modification of the homogeneity and thermal behavior of PET-rich PET/PAR blends by means of interchange reactions. These reactions can be carried out and controlled in a processing machine such as an injection-molding machine. The main effect of interchange reactions is the decrease in the crystallization ability of PET. That may be of interest for applications such as blow molding for obtaining bottle-like products. With respect to mechanical properties, the reactions give rise to an improvement in the break properties as compared to those of blends with small reaction levels. This improvement achieves a maximum after a plasticization time of 38 s under the conditions of this work. The maximum in properties is followed by a slow decrease probably due to degradation.

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