

Solid State Features and Mechanical Properties of PEI/PBT Blends

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ABSTRACT: Extrusion-blended and injection-molded PEI/PBT blends were found to be miscible whatever the composition. The processability of the blends clearly improved with the presence of PBT. The melt pressure at the exit was seen to be a parameter as representative of the processability of the blends as the torque of blending. In the blends with 80 and 90% PBT, a positive volume of mixing and the maintenance of the crystallinity of PBT were seen. However, in the rest of the blends, negative volumes of mixing and important decreases in the crystallinity of PBT were found. These solid state features gave rise to a ductility similar to that of the pure PEI and to a synergism of the modulus of elasticity and of the yield stress in the 90/10 and 80/20 blends such that the values were higher than those of either of the pure components. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 885–892, 2001

Key words: poly(butylene terephthalate); poly(ether imide); miscible blends; processability; mechanical properties

INTRODUCTION

It is known that miscible blends are the exception among polymer blends.¹ For this reason, most of the research in new polymer blends is now carried out on immiscible blends compatibilized in different ways. However, miscible blends remain an important subject from both an academic and an industrial point of view. This is because compatibility is assured, and because no attempt to achieve a suitable morphology is needed. Additionally, synergistic properties are often obtained.

Polyether imide (PEI) is a high-performance thermoplastic of high thermal stability ($T_g = 220^\circ\text{C}$) and remarkable modulus of elasticity and

tensile strength. However, its processability is bad (molding temperatures from 310 to 350°C), and its amorphous nature leads to poor solvent resistance. For these reasons, blends of PEI with both amorphous and semicrystalline polymers that might ameliorate these deficiencies have been studied. Thus, PEI was seen to be fully miscible with poly(ether etherketone),^{2–8} poly(ethylene naphthalate),^{5,9} poly(butylene terephthalate),^{10,11} and with a new thermoplastic polyimide;¹² partially miscible with poly(ethylene terephthalate)^{13,14} and polyarylate;^{15,16} and immiscible with, among others, poly(ether sulfone)¹⁷ and polyamide 66.¹⁸

Poly(butylene terephthalate) (PBT) is a partially crystalline thermoplastic that shows high solvent resistance and low viscosity in the melt state. These properties make it very suitable to be mixed with PEI, because both of these properties are poor in the case of PEI. Blends of PBT are very numerous. Among them, miscible blends

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with phenoxy,¹⁹ poly(ethylene terephthalate),²⁰ polyarylate,²¹ poly(ester carbonate),²² and polycarbonate²³ have been studied. Partially miscible blends have been obtained by compression molding with prior kneading²⁴ and extrusion blending²⁵ with polycarbonate, and by direct injection molding with poly(ester carbonate).²² Polyamide 66,²⁶ linear low density polyethylene,²⁷ a polyetherester,²⁸ polyamide 6,²⁹ and poly(butylene succinate)³⁰ form immiscible blends.

PEI/PBT blends have been found to be miscible after mixing the powder components in the melt state,^{10,31} and also after mixing by dissolution and precipitation.^{11,32} Miscibility was proposed to be due to the presence of a single T_g by DSC,^{10,11} DMA,¹⁰ and DMTA.³² However, to our knowledge, the mechanical properties of the blends, as well as the phase structure of the blends after an industrial-type mixing method, have not been studied.

In this work, pellets of PEI and PBT were blended by extrusion and subsequent injection molding. The processability of the blends, with respect to that of PEI, was studied by a new method based on the measurement of the pressure at the end of the extruder. The solid state behavior of the blends after the mixing procedure used was tested by DSC, DMTA, and specific volume measurements. The mechanical properties obtained from the tensile and impact tests were related to the structural characteristics.

EXPERIMENTAL

The polymers used in this work were PEI (Ultem 1000, General Electric) and PBT (Crastin PBT, DuPont). PEI and PBT were dried (8 h at 110°C) and mixed over the entire composition range in a corotating double screw extruder-mixer (Collin ZK-25).

Due to the different processing temperatures of PEI and PBT, the PEI-rich blends were mixed at a melt temperature of 290°C. The 60/40 blend was used at a melt temperature of 270°C to obtain the rest of the blends by adding the appropriate amount of PBT. The screw speed was 30 rpm and the extrudate was pelletized.

The dried blends (8 h at 110°C) were injection molded in a Battenfeld BA230E reciprocating screw injection molding machine at 260°C in the case of the PBT-rich blends. The barrel temperatures used in the PEI-rich blends are shown in Table I. A mold temperature of 23°C, an injection

Table I Barrel Temperature (T_b) for Injection Molding of the PEI-Rich Blends

%PEI	60	70	80	90	100
T_b (°C)	275	295	315	330	340

In the rest of the blends, the barrel temperature was 260°C.

speed of 6 cm³/s, and an injection pressure of 1,000 bar were used in the injection molding process. The torque of the pure PEI and the PEI-rich blends was measured in a Brabender plasticorder PLE 650 at 290°C and 30 rpm for 12 min.

The calorimetric analysis of the blends was carried out in a Perkin-Elmer DSC-7 calorimeter at a heating rate of 20°C/min. The glass transition, crystallization, and melting temperatures were measured, and the crystallinity was calculated from the crystallization and melting enthalpies of the blends and the melting enthalpy of the 100% crystalline PBT ($\Delta H_m^c = 145.5$ J/g).³³

The dynamic mechanical analysis was carried out in a Polymer Laboratories DMTA using a heating rate of 4°C/min and a frequency of 1 Hz. Specific volumes were measured in an electronic Mirage SD-120-L densitometer with a resolution of 0.0003 cm³/g using butylic alcohol as the immersion liquid.

The tensile tests were carried out using an Instron 4301 at a cross-head speed of 10 mm/min on 1.9 mm thick ASTM D-638 type IV specimens. The mechanical properties [Young's modulus (E), yield stress (σ_y), and ductility, measured as the break strain (ϵ_b)] were determined from the load-elongation curves.

Impact tests (ASTM-D256) were carried out using a Ceast pendulum on injection molded specimens with a cross section of 12.7 × 3.2 mm. The notches (depth: 2.5 mm, radius: 0.25 mm) were machined after molding. A minimum of eight specimens were tested for each reported value in both the tensile and impact tests.

RESULTS AND DISCUSSION

Processability

Due to the fact that the torque is related to the melt viscosity,³⁴ the processability level of a polymeric melt may be estimated in discontinuous mixers or kneaders by means of the torque needed for mixing.^{14,15,18,35,36} In continuous mixing by

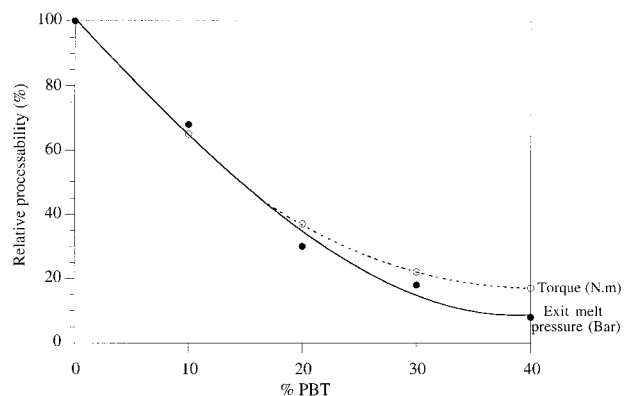


Figure 1 Relative torque (○) and relative exit melt pressure (●) versus composition.

means of extruders, however, the torque cannot be related to the viscosity of the melt. This is because the polymer experiences temperatures from ambient, in the feeding section, to the melt temperature. However, the processability level is an important polymer property that would be interesting to be able to estimate also in the case of the extruders.

It is known that, for Newtonian fluids in laminar flow, the melt viscosity (η) may be related to the pressure at the output end of the extruder (P) by means of the flow rate (Q):³⁷

$$Q = KP/\eta$$

were K is a constant that characterizes the resistance of the die to flow. Taking into account that the screw speed is constant during mixing, Q is constant. Thus, the measurement of the pressure at the exit of the extruder will provide a parameter directly related to viscosity and thus give some indication of the processability of the blends related to that of the pure components. Therefore, the pressure at the exit of the extruder of the pure components and that of the blends was measured and is shown in Figure 1, referred to that of pure PEI (188 bar) versus the composition of the blends. The melt pressures of blends with low PEI contents are not shown because they had to be mixed at a different melt temperature. As can be seen in Figure 1, and as was expected because of the lower viscosity of the PBT, the pressure at the exit sharply decreased with increasing PBT content. This is because the pressure at the exit of the 90/10 blend was only 70% of that for pure PEI, and for the 60/40 blend, only 8%. This clearly indicates that PBT greatly improves the process-

ability of PEI. The reliability of this plot was tested by comparing it with that usually used of the torque against composition, the relative values of which are also shown with respect to that of pure PEI (23 N.m) in Figure 1. As can be seen, both plots are very similar. This is clear experimental support for the reliability of the melt pressure at the exit as a parameter that is equally representative of the melt viscosity and the blending torque.

Solid State Features

The crystallinity level of the blends after injection molding, measured by DSC, are shown in Figure 2. Crystallization did not occur during the DSC scan in the blends with 20, 80, and 90% PBT. The blends with PBT contents from 30 to 70% crystallized both during the injection molding and during the DSC scan. The blend with 10% PBT was amorphous. As can be seen in Figure 2, the crystallinity of the blends with 80 and 90% of PBT was on the tie line between those of the two pure components. This indicated that the crystallinity level of PBT in these two blends was that of pure PBT (34%). However, in blends with a PBT content below 80%, the crystallinity level (and as a consequence, the solvent resistance) abruptly decreased to 7%, and slightly decreased to zero in the blend with a PBT content of 10%. These PEI-rich blends will therefore be less solvent resistant in application.

A comparable crystallinity plot was also seen in PEI/PBT blends obtained by solution-precipitation and annealed at different temperatures,¹¹ but the abrupt change of the PBT crystallinity

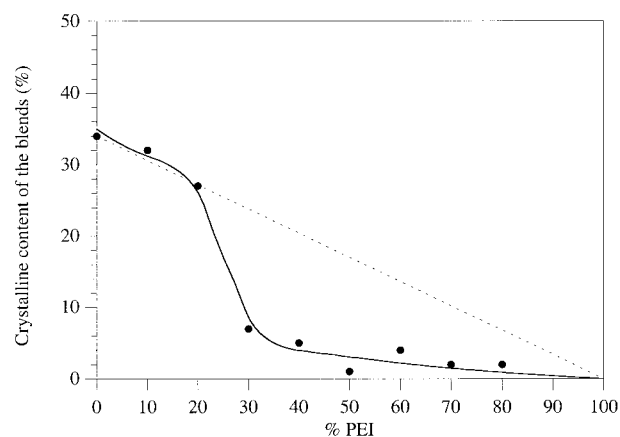


Figure 2 Crystallinity content of the blends after injection molding versus composition.

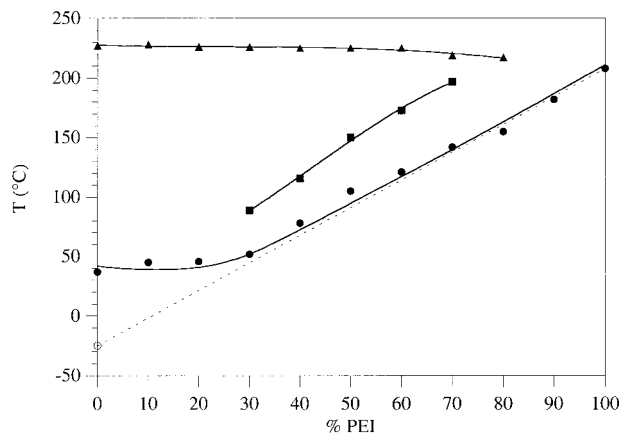


Figure 3 Glass transition temperature obtained by DSC (●), crystallization temperature (■), and melting temperature of the blends (▲) versus composition.

took place at PBT contents smaller than 50%. This was probably due to the fact that the blends were more crystalline than those of this work, probably because the annealing and the solution-precipitation method favors crystallization. This is in contrast to the nonisothermal crystallization from the melt during cooling in the injection mold of this work. Similar behaviors have been seen in other blends. For example, in PEI/PEEK blends,⁴ the crystallinity was maintained up to a PEEK content of 40%. However, in PEI/poly(ethylene-2-6-naphthalenedicarboxylate) blends,⁹ the crystallinity clearly began to decrease below 90% of the crystallizable component. The ability of the semicrystalline component to crystallize, and the crystallization conditions were probably the reasons for the different behaviors.

In Figure 3, the glass transition (T_g , circles), crystallization (T_c , squares), and melting (T_m , triangles) temperatures of the blends measured by DSC are shown against their composition. The T_g values obtained by DMTA followed the same trend as those obtained by DSC.

As can be seen in Figure 3, the T_c increased and the T_m slightly decreased with the PEI content. These results are often seen in miscible blends with a semicrystalline component,^{2,13} and agree with previous results seen in PEI/PBT blends.^{10,11} They indicate that the presence of PEI hindered the crystallization of PBT.

As can be seen and was shown before using other mixing methods which give homogeneous blends,^{10,11,31,32} after the extrusion-injection mixing procedure, a single T_g was observed whatever the composition. As can also be seen in Figure 3,

the T_g -composition curve was apparently asymmetric and exhibited a discontinuity at a PEI weight fraction between 0.2 and 0.3. The T_g change with composition was clearly different in these two composition ranges. At low PEI contents, the T_g hardly increased with increasing PEI content. However, at PEI contents of 30% and above, the T_g of the blends increased sharply with increasing PEI content.

Discontinuities in the T_g plots in blends with one amorphous constituent and the other semicrystalline, such as PEI/PBT, have been attributed, using a free volume approach,¹⁰ to an uneven contribution from the two components to the free volume of the blends. However, the discontinuity can also be due to an abrupt decrease in the crystallinity of the PBT in the blends at decreasing PBT contents. This seems to be the reason for the T_g behavior shown in Figure 3, because the abrupt change of the crystallinity of the blends took place at the same PBT content (between 80 and 70% PBT) as that which gave rise to a change in the slope of the T_g plot in Figure 3. Moreover, the comparatively high T_g values of the blends rich in PBT agree with the fact that the T_g of the amorphous phase of semicrystalline polymers is higher than the T_g they would show in the fully amorphous state. This is due to the severe links and restriction to the deformation^{20,38} that the crystalline phase supposes in the T_g region. In order to support this possibility, in Figure 3, instead of using the T_g of the partially crystalline PBT as the reference for the T_g 's of the blends, that of the nearly amorphous PBT (-25°C)³³ has been used and plotted in Figure 3 as an empty circle. As can be seen, the T_g values of the blends with a low PBT crystallinity are on the linear relationship between the value of fully amorphous PBT and that of PEI. These facts indicate that the crystalline content of the blends is the main parameter that influences the T_g behavior of the blends.

Mechanical Properties

The moduli of elasticity of the blends are plotted in Figure 4 against composition. As can be seen, the modulus is roughly constant up to a PEI content of 30%. Then, it sharply increases to produce a synergism at high PEI contents with values even higher (8% in the 90/10 blend) than that of the pure PEI. This modulus behavior has to be a consequence of one or more of the following parameters: a different free volume in the blends

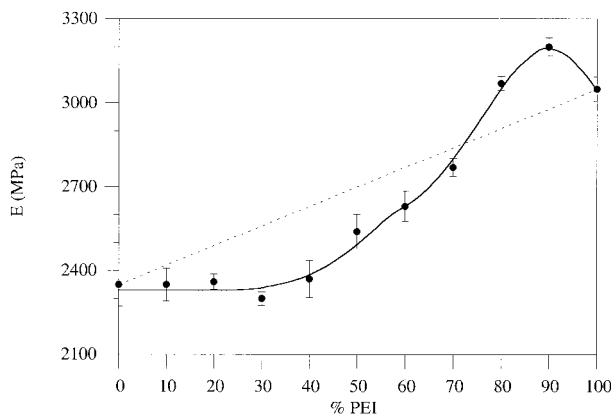


Figure 4 Young's modulus of the blends versus composition.

compared with that of the pure components, the different crystallinity of the PBT in the blends and in the pure state, or possible effects of the change in the injection temperature.

A possible effect of the different processing temperatures of the PEI-rich blends, which may take place, for instance, through different orientation levels, was studied measuring the modulus of elasticity of the 70/30 blend obtained in the temperature range from 295 to 345°C. No significant change in the modulus of elasticity was observed, because the increase in the modulus with temperature, from 2480 to 2630 MPa, was similar to the observed mean standard deviation (150 MPa). Therefore, the different processing temperature did not influence significantly the modulus behavior.

The change of the crystalline content of the PBT in Figure 2 (from 34 to 7%, roughly), despite the low sensitivity of this small deformation property to the crystalline content,^{22,39} appears to be large enough to influence the modulus of elasticity. Thus, high crystalline contents should lead to comparatively high moduli. However, as shown in Figure 3, at middle and high PEI contents, the crystallinity level of PBT was almost constant, but a synergism in the modulus was seen in blends (Fig. 4) with very high PEI contents. Therefore, crystallinity could not give rise to this modulus behavior. Moreover, in the PBT-rich region where the PBT crystallinity was high, the modulus moved to values below the linear tie line. Therefore, besides crystallinity, another parameter had to influence the observed modulus behavior.

A possible change in the free volume of the components of the blends as a result of blending

was studied by means of measurements of the specific volume of the blends. These are plotted against composition in Figure 5. The observed changes in specific volume are significant,^{14,40–43} because their mean value was 0.003 cm³/g (0.5%). As can be seen, the specific volume plot agreed with the modulus behavior. This is because the zone of the blends with middle and high PEI contents, which shows a high slope in the plot of the modulus, corresponds to the zone where the decrease in specific volume takes place. Moreover, in the 80 and 90% PEI compositions, there is a synergism in the modulus just where the deviation of the specific volume from the additivity was greatest. In the blends with 90 and 80% PBT contents, the PBT crystallinity is constant; therefore, the observed decrease from the linearity of the modulus must be due to the specific volume increase induced by blending. A specific volume increase/decrease is often the reason for decreased/increased modulus values from the sum of the contributions of each component.^{14,40–43} Finally, in the case of the 30/70 blend, the effect of the large crystallinity decrease in the modulus (from 34% to 7%) appears to overcome the positive influence that the decrease in the specific volume of 0.3% from the additive values will give rise to. Therefore, with the exception of the 70/30 blend, the modulus behavior is mainly a consequence of the specific volume of the amorphous phase of the blend.

The behavior of the yield stress is shown in Figure 6 against composition. As can be seen, it was very similar to that of the modulus of elasticity. The yield stress of the 90/10 blend was 10% above that of pure PEI. This is usual behavior,⁴⁴ and is due to the small deformation nature of both

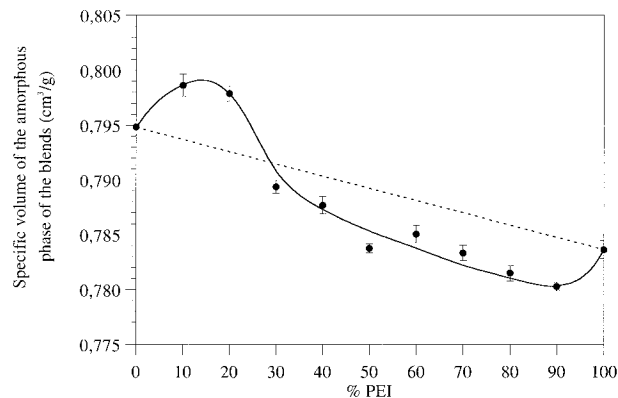


Figure 5 Specific volume of the amorphous phase of the blends versus composition.

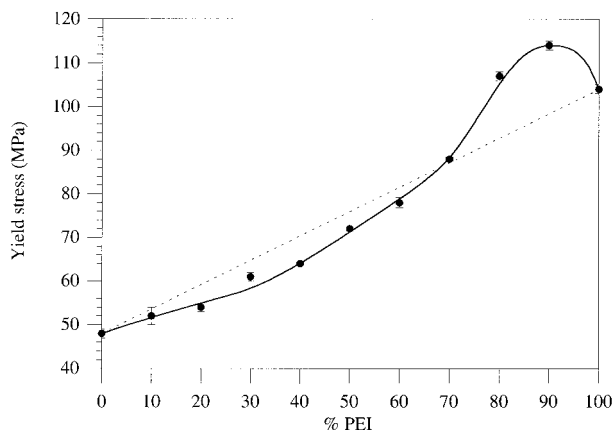


Figure 6 Yield stress of the blends versus composition.

properties, and to the lack of change of the yielding mechanism of the blends with respect to that of the pure components.

The ductility of the blends is shown against composition in Figure 7. As can be seen, most of the blends showed a behavior intermediate between those of the two pure components. Moreover, all the blends showed a clear ductile behavior, with values below the linear tie line. The ductility of the blends was similar to that of the pure PEI in PEI-rich blends, but it clearly increased at lower PEI contents. This ductility behavior may be influenced by: a possible change of the low temperature secondary transition of either of the two components of the blend, the change of the crystallinity content, the difference between the test temperature and the T_g in the blends and in the pure components, or the change of the specific volume of the amorphous phase of

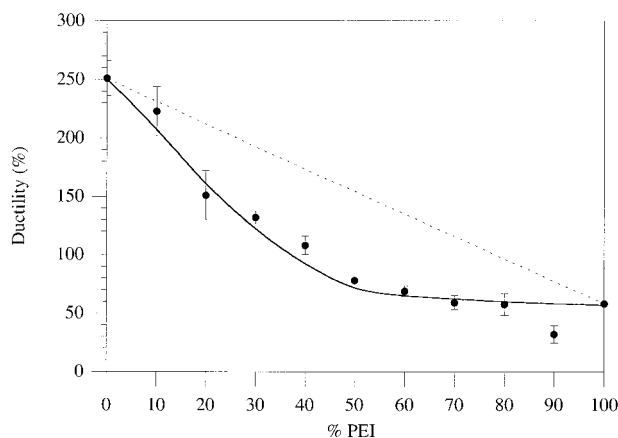


Figure 7 Ductility of the blends versus composition.

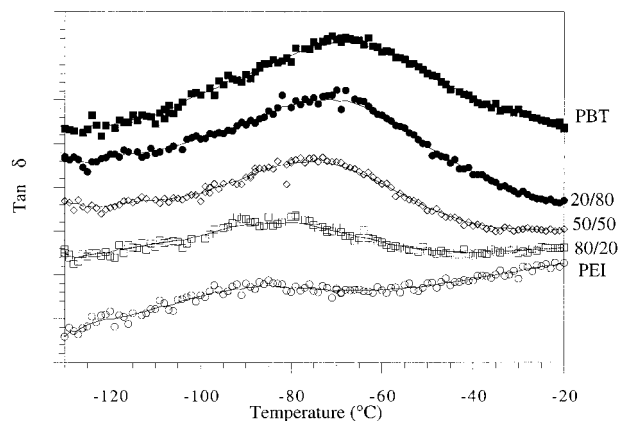


Figure 8 $\tan\delta$ versus temperature for PEI (\circ), 80/20 (\square), 50/50 (\diamond), and 20/80 (\bullet) blends, and PBT (\blacksquare).

the blends compared with that of the pure components.

With respect to the low temperature secondary transitions, the $\tan\delta$ plots of the pure PBT and PEI, and of representative blends in the temperature range where the γ transitions appeared are shown in Figure 8. As can be seen, both the change in the peak temperature and in the intensity of the transitions are a direct consequence of the composition. Therefore, there is no γ suppression as a consequence of blending that could influence the ductility plot. With respect to the abrupt crystallinity change of the blends that took place from the 20% PEI to the 30% PEI compositions (Fig. 2), this had no significant influence on the ductility of the blends, because the curvature of the ductility plot did not change at these compositions. Additionally, the change in the T_g of the blends, as shown in Figure 3, was fairly in accord with the linear value. This was with the exception of the 10 and 20% PEI compositions, but the ductility increase took place in all the PBT-rich blends. Therefore, the temperature difference to the T_g does not seem to be the main parameter that influences the ductility values. Finally, the lack of increase in the ductility values with respect to that of the pure PEI in the PEI-rich blends agrees with the negative specific volume of mixing, as shown in Figure 5, of these compositions. Moreover, the increasing ductility when the PEI content decreases as shown in Figure 7, takes place together with the disappearance of the negative specific volume of mixing and its posterior positive values. Therefore, the specific volume of mixing appears to be the main reason for the ductility values shown in Figure 8.

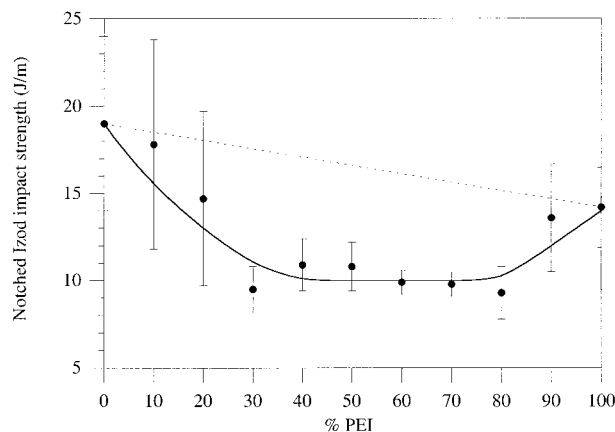


Figure 9 Notched Izod impact strength of the blends versus composition.

This is supported by the fact that the ductility of miscible polymer blends is usually close to additive,^{22,36} although positive^{16,19} and negative deviations^{40,41,45} have been found. The negative deviations are usually attributed to a decrease in the free and specific volumes as a result of mixing.

The notched Izod impact strength is plotted in Figure 9. The low value^{2,3,14} of PEI (14 J/m) in the figure must be due to experimental conditions. As can be seen, the plot is very similar to that of the ductility, with values closer to the tie line in PBT-rich blends. As in the case of ductility, the excess or deficit of volume of mixing appears as the parameter that mainly controls the impact resistance values.

CONCLUSIONS

PEI/PBT blends appear miscible after an industrial-like processing, such as mixing by extrusion and injection molding. The processability of PEI clearly improved when even low amounts of PBT were added. The melt pressure at the exit of the extruder is a suitable parameter to measure the processability of the polymer blends. The presence of PEI hindered PBT crystallization, which gave rise to a large decrease in the PBT crystallinity, from 27 to 7%, when the PEI content increased from 20 to 30%.

A loss of the free volume induced by mixing was observed in all of the blends, with the exception of the blends with 10 and 20% PEI content, where excess volume of mixing was observed. This change in the specific volume is believed to be the main parameter that determines the me-

chanical properties, rather than the injection temperature that did not show any effect, and the crystalline content, which had an effect that was only observed at the 70/30 composition, in which the crystallinity level largely changed. Consequently, in the blends with 10 and 20% PEI content, a lack of increase in the modulus and in the yield stress, and more linear ductility and impact strength values were observed. The rest of the blends showed impact resistance values slightly below, but ductility values similar or even higher, than those of PEI. Moreover, the modulus of elasticity and the yield stress increased to give a strong synergism in the 90/10 and 80/20 blends, with values in the 90/10 blend roughly 5–10% larger than those of the higher of the two pure components.

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