Miscibility Level and Properties of Poly(Ether Imide)/ Poly(Ethylene Terephthalate) Blends

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SYNOPSIS

Blends composed of poly(ether imide) and poly(ethylene terephthalate) were obtained both by kneading followed by compression molding and by direct injection molding. Both procedures gave rise, probably at all compositions, to biphasic structures with similar homogeneity that showed wide single T_g peaks by dynamic-mechanical analysis. The modulus of elasticity and the yield stress values appeared, respectively, close to and above those predicted by the additivity rule, probably due to the density increase and slight orientation observed. The ductility values against composition appeared well below the additive values, probably due to the presence of a dispersed phase together with the notch-sensitive nature of the blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The study of polymer blends is at the present time of capital importance for the development of new polymeric materials. This is because polymer blends often provide successful ways for obtaining materials with a combination of properties difficult to bring together in a monocomponent material. One of the most interesting fields in polymer blends is that of the so-called "engineering polymers." These polymers are characterized by useful combinations of mechanical, thermal, electrical, and chemical properties and have allowed a large number of new applications for plastics materials. Thus, blends of engineering polymers are an obvious research subject.

Poly(ether imide) (PEI) is an amorphous and thermally resistant engineering polymer with increasing practical importance that presents high mechanical strength among other useful properties. Poly(ethylene terephthalate) (PET) is a crystallizable polymer with a very wide range of uses, which include fibers, tapes, bottles, molded products, etc. Different types of PET resins that differ in their crystallinity, glass transition, and melting temper-

ature have been commercialized. Blends of PET with other polymers, such as bisphenol A polycarbonate, polyesters, polyamides, polyolefines, etc., have been extensively studied in the literature and provide the possibility of modifying the abovementioned parameters and hence the properties of the final products.

Recently,[1,2] it has been found that PEI and PET form blends with single T_g by differential scanning calorimetry (DSC) over the whole composition range when melt mixed. Although this is an indication of miscibility, some heterogeneity[1] was seen because of the widening of the glass transition region of the blends compared with those of the pure components. This border miscibility is supported by the fact that the presence of one or two amorphous phases in the blends when obtained by solution-precipitation depends on the solvent used.[3]

It is known that monophasic blends, or at least biphasic blends but with an important presence of both of the components in each phase, show rather often favorable and even synergistic properties.[4] Hence, in this work, we have performed additional work on the miscibility level of PEI/PET blends by dynamic-mechanical analysis (DMTA) and scanning electron microscopy (SEM), because these techniques are usually more sensitive[5] than DSC[1-3] to the presence of inhomogeneity on a fine scale.

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Additionally, the most representative mechanical properties of the blends have been determined by means of the tensile and impact tests. As mechanical properties of the blends depend, sometimes clearly,[6] on the molding method followed they have been obtained both by compression and injection molding.

EXPERIMENTAL

The polymers used in this work were commercial products. PEI, Ultem 1000 (General Electric Plastics) was obtained from Novoquimia S.A. (Barcelona, Spain). It has an intrinsic viscosity of 0.5 dL/g as measured at 23°C in chloroform.[7] PET was supplied by Brilen S.A. (Barbastro, Spain) and had a molecular weight M_n = 25,000, determined by viscosimetry in o-chlorophenol at 35°C. Both polymers were dried in vacuo at 80°C for 24 h before melt mixing.

PEI/PET blends in 100/0, 75/25, 60/40, 50/50, 40/60, 25/75, and 0/100 compositions were prepared by two processing methods. In the first method, the polymers were mixed at 300°C in a Brabender Plasticorder at a mixing blade rate of 30 rpm. The mixing operation was maintained for a time of 14 min. The blends obtained in the Brabender were compression molded (CM) in a Schwabenthan 200-T press at 300°C. After molding, the sheets, with an approximate thickness of 1 mm, were cooled by immersing them in a water/ice mixture. The specimens for tensile tests (ASTM D638, type IV) were obtained from the sheets by careful copying by roll milling using a computer aided modeling machine. This was because of the inadequate quality obtained by punching out with a pneumatic die. High-quality specimens were not easily obtained, and hence, break data were widely dispersed; thus, only the values of the modulus of elasticity and yield stress are shown.

In the second processing method, dry PEI/PET mixtures in the mentioned compositions were directly mixed and injection molded (IM) using a Battenfeld BA 230 E reciprocating screw injection molding machine. The barrel temperature was 300°C and the mold temperature 15°C. A screw rate of 150 rpm during plasticization and an injection speed of 4.5 cm/s were used. Tensile (ASTM D638, type IV) and impact (ASTM D256) specimens were obtained.

Samples for DSC, DMTA, and density measurements were obtained both from the compression molded sheets and from the injected tensile specimens.

Calorimetric analysis of the samples was carried out in a DuPont DSC cell equipped with a DuPont 2000 Thermal Analyst System at a heating rate of 20°C/min. Dynamic-mechanical analysis was carried out on a DMTA from Polymer Laboratories that provided the storage (E') and loss (E'') moduli and the loss tangent (tan δ). A heating rate of 4°C/min was used at a frequency of 1 Hz. The specimens were taken from the central zone of both CM and IM tensile specimens. Density measurements were performed at 23°C in a gradient density column using potassium carbonate solutions. Birefringence could not be measured because the blends were not transparent enough. For this reason, orientation was estimated by means of the contraction, when could be measured because of the lack of crystallization, after maintaining the specimens above the T_g.

Tensile tests were performed by means of an INSTRON 4301 tensile tester. A crosshead speed of 10 mm/min was used. The tests were carried out at 23°C and the different mechanical properties (Young's modulus E, nominal yield stress σ_y, and ductility as measured from the nominal deformation at break ϵ_b) were determined from the force-displacement curves. Izod impact tests were carried out on notched specimens using a CEAST pendulum. The notches (depth = 2.54 mm) were machined after injection molding. A minimum of eight specimens was tested for each determination in both tensile and impact tests. The mechanical properties of the blends were measured from repeat blends. The lack of presence of error bars in any plotted value indicates that the error is smaller than the symbol.

The fracture surfaces of some tensile specimens were observed, after gold coating, using a scanning electron microscope Hitachi S-2700 operated at 15 kV. A reduced coating time provided clearer images of the dipersed phases.

RESULTS AND DISCUSSION

Miscibility Level

Figure 1 shows the torque and log(torque)-composition relationships obtained for PEI/PET blends kneaded in the Brabender at 300°C. The reported torque values correspond to a mixing time of 14 min at which a steady-state torque was seen. As is known,[8] the torque required to operate the Brabender during mixing is related to the melt viscosity. Thus, the data reported in Figure 1 indicate that a great viscosity decrease with respect to that of pure PEI takes place even when a low PET amount is added to PEI. This
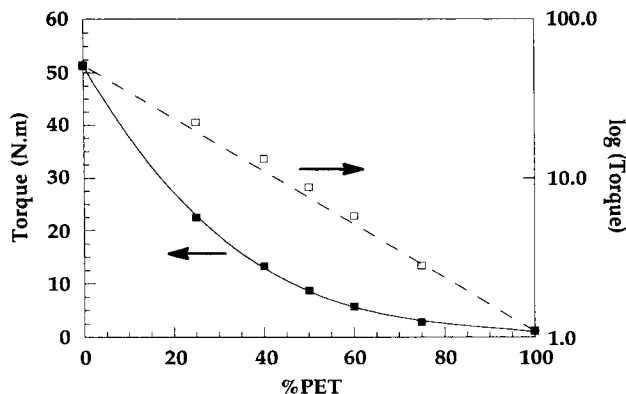
Figure 1   Torque (■) and log(Torque) (□) composition plots of the kneaded blends at 300°C.

is since a 25% content of PET reduces the torque of the blend to a half of that of pure PEI. However, relative to immiscible blends, the decrease is not so important. This is because, in the usual log(torque) - composition plot, a small positive deviation from linearity is seen, and in immiscible blends negative deviations may appear.[9] All blends in the melt state appeared opaque with a maximum transparency at the 75/25 blend, that is, they are not miscible at the melt temperature of 300°C.

Besides blending in the Brabender mixer, direct blending in an injection molding machine was also used. The former is common way to obtain polymer blends, whereas direct blending in injection molding has been proved to be possible in the case of miscible polymer blends such as poly(methyl methacrylate) PMMA/phenoxy[10] and also in the case of partially miscible PET/PAr blends.[11] This was possible despite the high viscosity difference between the blend components in both polymer pairs (torque needed for PMMA 42 Nm and for phenoxy 16 Nm; 2.7 and 53 Nm, respectively, for PET and PAr). In the solid state, whatever the mixing method, and with the exception of the very rich PET compositions, that were translucent, all the PEI/PET blends were almost transparent. Additional proof of the fact that a suitable mixing level is also achieved by direct mixing in PEI/PET blends as well as additional work on the heterogeneity observed by DSC[1] were carried out by means of the dynamic-mechanical properties studied both for kneaded-compression molded and injection molded PEI/PET blends.

In Figure 2, the E'-temperature [Fig. 2(a)] and the tan δ-temperature [Fig. 2(b)] relationships corresponding to the IM blends are shown. These plots are very similar to those of the Brabender mixed-CM blends. This indicates that the mixing level attained by both methods is, in these blends and con-

ditions, at least similar. This fact was later corroborated by SEM observations.

With respect to the miscibility level in the solid state, it is observed that a single glass transition appears in all cases for the blends, in good agreement with the calorimetric results previously obtained.[1] In most blends, a second maximum is observed in Figure 2(a) at high temperatures. It is a consequence of PET crystallization that is not so clearly observed in the plot of the tan δ against temperature of Figure 2(b).

The width of the transitions is greater in the blends than in the pure polymers, and this effect is more important in the medium-composition region. The merging of a single loss peak suggests a considerable amount of intermixing between the two polymers. The presence of PEI mixed with PET was also seen[1] because of the decrease in crystallization and melting heats. However, it is doubtful whether the system should be regarded as completely miscible after mixing in the melt state. Besides the lack of full transparency, this doubt is due to, as in the case of PET/polyarylate blends,[11] the widening of the transitions of the blends, which indicates the existence of compositional heterogeneity at the usually higher detection level associated with DMTA results. Moreover, it is known that T_g is not a measure of miscibility but of the state of dispersion,[12] and although it has been noted that the minimum domain size observable by T_g is sometimes 10–15 nm,[13] domains of even 0.01 μm have given a single E'' peak.[4] Hence, the miscibility level was also investigated by SEM observations.

The morphology of the IM 25/75 blend is shown in Figure 3. It corresponds to the most representative zones of the specimens. In the 75/25 composition, a less clear structure with a smaller amount of dispersed phase appeared as only holes which were smaller than those of Figure 3. No sign of multiphasic structure was evident in the 50/50 composition probably because of the fully cohesive fracture. Intermediate structures were observed in other compositions and in minority zones of some specimens.

The morphologies of the CM and IM blends were very similar, as was also suggested by the similar DMTA results. This good mixing level attained by direct injection molding was remarkable and took place in other blends.[14,15] Adhesion between the phases is good because cohesive fracture of the matrix takes place in many compositions and, as seen in Figure 3, after fracture many of the dispersed particles are still connected to the matrix.

As indicated, despite the single and wide T_gs, many of, and probably all the compositions, are biphasic.
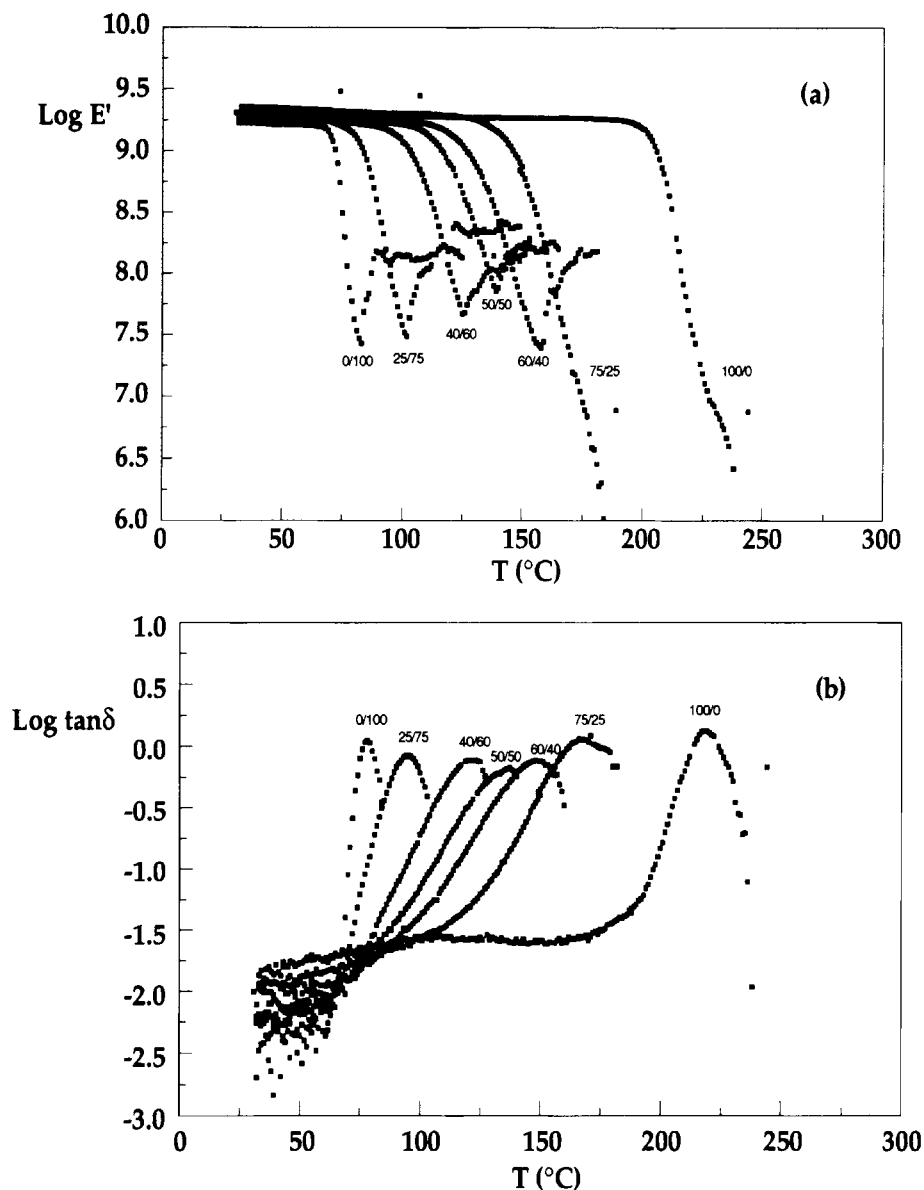
Figure 2 Dynamic mechanical properties plots of the IM blends: (a) storage modulus; (b) loss tangent.

The absence of a second transition both by DSC[1] and DMTA may be due to a fairly similar composition of the two phases as a consequence of a high partial miscibility. It may also be due to the detection of only the transition of a less homogeneous matrix, given the very small size of the dispersed phase that is close to the detection level of the techniques. This has been found in other blends[16]; moreover, it has been reported[4] that when the area of the surface per unit volume of the dispersed phase is larger than 25 μm^{-1}, one peak is detected. In the case of spheres, the value of the specific area of 25 μm^{-1} gives a radius of 0.12 μm that is smaller than the particles of Figure 3 but close to the mean size of other compositions. Partial miscibility in the matrix would also be necessary in this case to explain the drift of the T_g toward that of the other component. Thus, it appears that both the partial miscibility of the blends at all compositions, and probably the small particle size, are responsible for the observed morphologies and phase behavior.

Mechanical Properties

The crystalline content of PET in the blends can change with composition and should influence the mechanical properties and obviously the density.
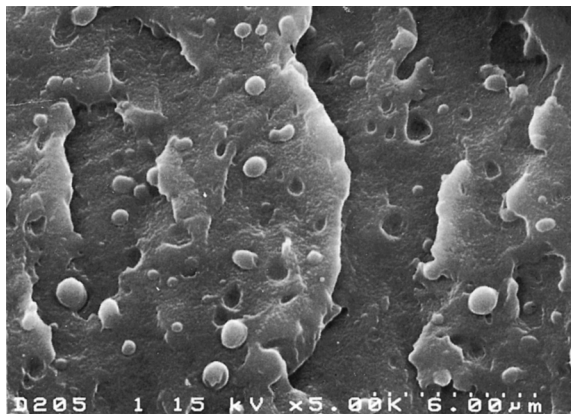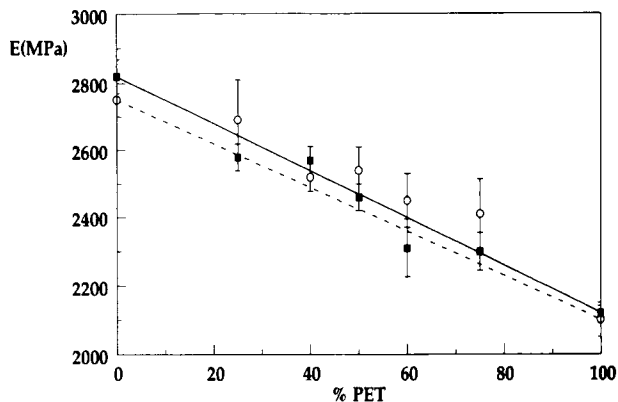
Figure 3 SEM photomicrograph of an IM PEI/PET (25/75) blend.

Figure 4 Young's Moduli against blend composition for the CM (O) and IM (■) blends.

Hence, the crystalline content was measured by DSC in both CM and IM blends. The values are collected in Table I. As can be seen, the crystalline contents are very similar both after compression and injection molding. That of PET is low, that of the 25/75 blend is very low, and it is negligible and close to the sensitivity of the technique in the rest of the blends. These differences in crystalline contents could hardly influence the mechanical properties of the blends but slightly influence density.

In Figure 4, the Young's modulus-composition relationships obtained for PEI/PET blends are shown. As can be observed, blends obtained by both processing methods show an overall behavior close to additivity. This behavior is similar to that observed in other mixtures.[14,17,18] The plot of the yield stress of the blends, a parameter that is related to the modulus of elasticity,[19] appears in Figure 5 against composition. A distinct behavior above linearity is seen both in IM and CM blends. The modulus, mainly, and also the yield stress are usually related to changes in the free volume of blending;

hence, the specific volume-composition relationship is shown for both IM and CM blends in Figure 6.

Although it is known that miscibility level and positive or negative excess volume of mixing are not always related,[6,20,21] an unexpected negative deviation from the additive values of roughly 0.3% is repeatedly obtained from the intermediate compositions. The densification of the amorphous phase of the blends would be slightly higher than that which appears in Figure 5, because the plotted value of pure PET is low, due to its large crystalline content relative to the blends. This densification, and the correspondent negative volume of mixing, is comparable with that observed in a prototype miscible polymer blend like polystyrene/polyphenylene oxide.[22] Its effects on the modulus behavior are not clearly seen in Figure 4. This is because although a slight synergism might appear in CM blends, it does not take place in the complete data of Figure 4. The tendencies of the plot of the yield stress, however,

Table I Crystalline Content of the Blends as a Function of Composition, Referred to the Overall Blends

Composition of the Blends (PEI/PET)	Crystalline Content (%)	
	Compression Molded	Injection Molded
0/100	11.1	10.3
25/75	4.0	4.3
40/60	3.1	1.2
50/50	2.4	1.4
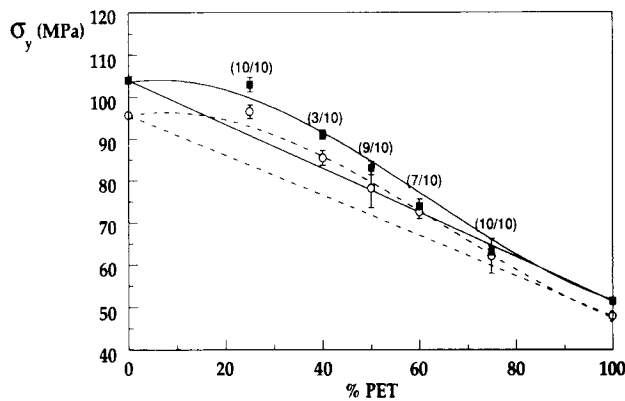
Figure 5 Yield stress against blend composition. Symbols as in Figure 4. All the CM samples yielded. The amount of IM samples that yielded is in parenthesis.
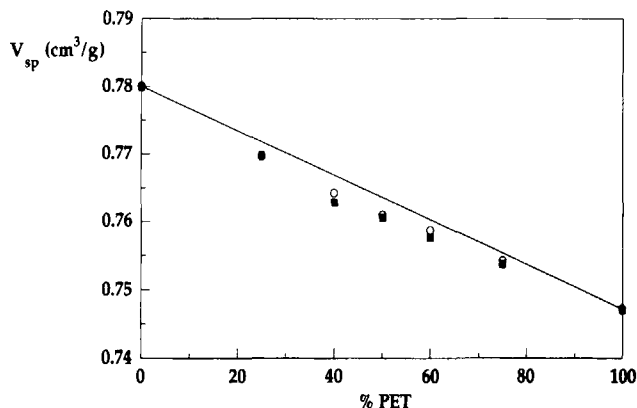
Figure 6 Specific volume values against blend composition. Symbols as in Figure 4.

are much clearer than those of modulus and are clearly related to those of the specific volume. Moreover, the higher overall density observed in IM compositions, compared with that of CM, parallels the yield stress behavior. However, the behavior of the yield stress and the modulus of elasticity do not seem to be a consequence of only the density behavior. This is because when density is fairly constant, as in pure PEI, the yield stress and slightly the moduli of IM specimens are higher than those of CM.

It is known that, besides density, orientation often plays an important role in determining the modulus of elasticity. Usually IM polymers show higher modulus than CM ones due to higher orientation in the test direction. Hence, a measure of the orientation of the blends was carried out by looking at the contraction of the tensile specimens after maintaining them above their T_g. The contraction, and thus orientation, of the IM PEI (18%) was higher than that of the IM blends (11% for the 60/40 and 9% for the 75/25 blends) and that of IM blends was clearly higher than that of CM blends and pure PEI, which were almost negligible. Thus, the average contraction difference between IM and CM PEI and PEI-rich blends is roughly 13%. The contraction of PET and PET-rich blends could not be measured because of crystallization.

This explains the modulus and the yield behavior of the pure PEI, because the modulus and yield stress of the IM PEI are higher than those of CM, probably because of the higher orientation. Both higher orientation of the IM blends, and their smaller specific volume, will give rise to the observed yield stress behavior, although the relation is not so clear in the case of the modulus behavior, which is not fully defined. Different effects on the blends and on the pure

components have also been seen in the case of the effect of annealing on the modulus.[23]

The modulus of elasticity and the yield stress may appear above the additive values in miscible as well as in immiscible blends, so they cannot be used to inform about the miscibility state of the blends. However, break properties such as ductility, when they appear well below the additive values in isotropic blends and when the T_gs of all compositions are above the test temperature,[24] should correspond to immiscible blends. This is in spite of the fact that increased miscibility levels do not always produce greater ductilities.[25] Thus, the ductility-composition plot should be a consequence of the observed phase behavior and morphology.

The ductility of the blends is shown against the composition of the blends in Figure 7. As can be seen, the ductility values are far from those of the additivity rule. Most of them are almost constant and very similar to that of pure PEI. These ductility data are clearly worse, i.e., lower than the additive values, than those observed in other blends with, to a first approximation, similar[10] or even worse[17,26,27] miscibility, as measured by the change of T_gs. This points to the immiscible state of all the blend compositions that could not be fully showed by SEM. Additionally, the impact strength of IM PEI/PET blends, which is represented in Figure 8 against the blend composition, also shows very low values. This is because the impact strength of the blends is very close to the line connecting the impact strength of PEI with zero.

Negative deviations of breaking properties from the additive values[23] appear in partially miscible blends. But, the negative deviations in ductility observed in Figure 7 are very large,[18] taking into account that the presence of both components in each phase is significant as seen because of the change
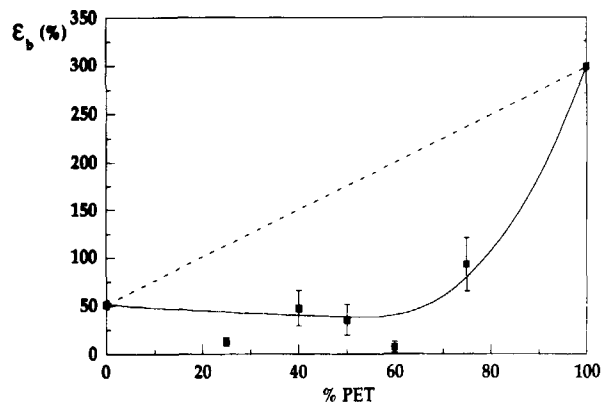
Figure 7 Ductility of IM blends against composition.
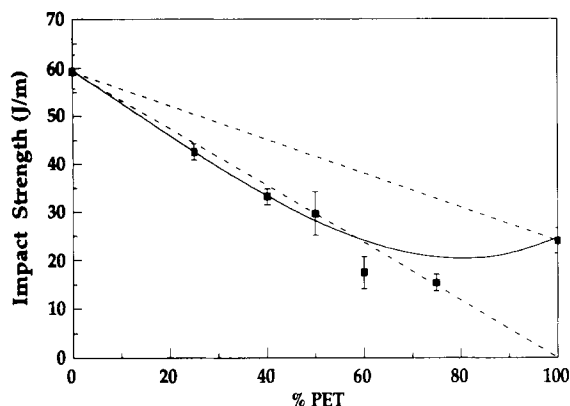
Figure 8 Impact strength of IM blends against composition.

of T_g. This is unexpected, because adhesion must be fairly good. The overall behavior of these blends cannot be due to the crystalline content or to densification, which are both fairly low. The dispersed phases sizes are very small (from 0.3 μm to unobservable), which is not necessarily bad for properties.[28] However, PEI is very notch-sensitive, so that the mere presence of a dispersed PET phase may have a negative effect on ductility. This agrees with the slighter effect of the dispersed phase in the impact resistence, which might be due to the notched nature of the impact specimens.

CONCLUSIONS

PEI/PET blends show wide single T_g peaks by DMTA both after kneading followed by compression molding and also after direct injection molding. However, they have two amorphous phases at some compositions, as seen by SEM and probably at all compositions as seen from the ductility values. The modulus of elasticity and the yield stress are, respectively, close to and above the additivity rule, this being a consequence of the concomitant effects of negative volume of mixing and orientation. Ductility as well as impact strength, however, are below additivity probably due to the presence of small dispersed phases in the, mainly in the case of PEI, notch-sensitive polymeric matrix.

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