Phase Behavior and Physical Properties of Injection-Molded Polyamide 6/Phenoxy Blends

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ABSTRACT: Polyamide 6 (PA 6)/poly(hydroxyether of bisphenol A) (phenoxy) blends were obtained by direct injection molding over the whole composition range. Differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and scanning electron microscopy (SEM) showed the almost full immiscibility of the blends and the lack of effect of phenoxy on the crystalline phase of PA 6. The rodlike and fine-dispersed phase of the tensile specimens was strongly deformed during tensile testing, giving characteristic fibrilar structures. The Young's modulus and yield stress showed small deviations from additivity that appeared related mainly to the blendinginduced free-volume change. Despite immiscibility, the ductility behavior was also additive, probably due to the fibrilar morphology. However, the thicker impact specimens gave rise to less oriented larger dispersed phases and to full plane strain conditions that, in opposition to ductility, yielded impact strength values well below linearity. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1113–1124, 1999

Key words: polyamide 6; poly(hydroxyether of bisphenol A); blends; miscibility; morphology; mechanical properties

INTRODUCTION

Much attention has been paid in recent years to polymer blending. This is because it is a very useful and low-cost technique to obtain new polymeric materials with specific properties that would be not easily satisfied by a single polymer. In miscible blends, compatibility is assured, but the general rule in immiscible nonreacted blends without rubbery components is a clearly less than additive behavior in mechanical properties, particularly in large-strain properties. This is due to the full or almost full phase separation and to the usual low phase adhesion. However, different behaviors may be obtained depending on the phase morphology, the interaction level, as well as on the composition.¹ The phase morphology is a result of the melt-processing type and conditions which are critical in the processing of an immiscible blend and which have been studied broadly in the literature.^{2-4,5} As regards the interaction level between phases, this is also critical for mechanical properties because a minimum adhesion is usually needed to obtain a synergistic or even additive mechanical behavior.⁶⁻⁸

Poly(hydroxyether of bisphenol A) (phenoxy) is a relatively tough and ductile amorphous thermoplastic with an excellent oxygen barrier property. It has a polar pendant hydroxyl group that, besides being able to react with different polymers,⁹ is capable of establishing strong hydrogen-bonding interactions, giving rise to miscible blends with proton-acceptor polymers such as poly(butylene terephthalate),^{10,11} polycaprolactone,¹² and poly(ethylene oxide).¹³ However, the interac-

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tions are not important enough for miscibility with, for example, poly(ethylene terephthalate),¹⁴ bisphenol A polycarbonate,⁴⁶ and poly(methylene oxide) (POM).¹⁵ Ternary phenoxy blends with different miscibility levels have also been studied in the literature.^{16–18}

 $Poly(\varepsilon$ -caprolactam) (PA 6) is a semicrystalline polyamide of common use. As is usual in most polyamides, it shows good mechanical properties and solvent resistance. Although, recently,¹⁹ PA 6 has been reported to be miscible with an ethylene–vinyl alcohol copolymer, most of the PA 6 blends reported during the last years with the aim of improving physical properties are immiscible, for instance, PA 6 blends containing rubbers,^{20,21} polyolefins or copolymers,^{22,23} other thermoplastics,^{8,24–27} and liquid crystal polymers.^{28,29}

Blends of PA 6 with phenoxy appear to be an attractive research area. This is because of the possible specific interactions between both blend components due to their proton acceptor/proton donor characteristics and also due to the complementary properties that crystalline and amorphous polymers usually show. However, neither the processing nor the mechanical properties of PA 6/phenoxy blends have been studied, to our knowledge, in the current literature. Moreover, it has been shown that in some cases^{6,30} direct blending in an injection machine, that is, without a previous mixing step in an extruder, is possible. This may provide blends comparable in homogeneity with those obtained through other more traditional ways and allows polymer blend parts to be molded in a single step. This is why, in this work, the phase and mechanical behavior and the structure of PA 6/phenoxy blends obtained by direct injection molding were studied. The phase behavior and solid-state characteristics of the blends were analyzed using differential scanning calorimetry (DSC), dynamic thermal analysis (DMTA), Vicat, density, and scanning electron microscopy (SEM) and the mechanical properties were determined using tensile and impact tests.

EXPERIMENTAL

The polymers used in this work were commercial products. PA 6 was Durethan B30S from Bayer Hispania S.A. (Barcelona, SPAIN). It has a molecular weight $M_v = 29,000$, determined by viscometry at 25°C in aqueous formic acid (85%). The poly(hydroxy ether of bisphenol A) was phe-

noxy PKHH from Union Carbide (supplied by Quimidroga S.A., Barcelona, Spain). Their average molecular weights were $M_w = 50,700$ and $M_n = 18,000$, as determined by GPC in THF at 30°C. Both polymers were dried *in vacuo* at 80°C for 14 h before processing in order to avoid moisture-induced degradation reactions.

Pellets of PA 6 and phenoxy were mixed at the desired weight ratios and tumbled together before injection molding. The polymers were directly melt-mixed and injection-molded in a Battenfeld BA230E reciprocating screw injection-molding machine. The barrel temperature was 240°C, and the mold temperature, 30°C. The mold temperature was low to help phenoxy solidification. In contrast to another phenoxy blend,³⁰ the available barrel temperature range was small. It was chosen taking into account the degradation possibility at higher temperatures and the risk of PA 6 crystallization in the nozzle at lower temperatures. The screw of the plasticization unit was a standard screw with a diameter of 18 mm, L/D of 17.8, compression ratio of 4, and helix angle of 17.8°. No mixing devices were present. The injection speed and pressure were 6.1 cm³/s and 1500 bar, respectively. Tensile (ASTM D-638 type IV) and impact (ASTM D-256) specimens were obtained.

The phase behavior of the blends was studied by DSC and DMTA. A Perkin–Elmer DSC-7 calorimeter was used at a heating rate of 20°C/min in a nitrogen atmosphere. Two heating scans were carried out between 15 and 260°C. Cooling between both scans was carried out at the maximum rate provided by the calorimeter. The thermal transitions were determined in the second scan in the usual way. The melting heats and correspondent crystalline contents were measured in the first scan, because the first scan corresponds to the state in which the properties were measured. Dynamic mechanical tests were carried out in a Polymer Laboratories apparatus, at a frequency of 1 Hz in the flexural mode and at a heating rate of 4° C/min from -50 to 150° C. Samples were cut from the injected tensile specimens. Vicat softening points were measured at 50°C/h and with a 1000 g load (ASTM D-1525). The orientation of the mainly amorphous specimens was estimated in an indirect way by measuring their contraction after maintaining them at 150°C for 20 min. Higher times did not yield significant additional contraction. Density measurements were carried out on samples taken from the tensile specimens, which were stored in



Figure 1 Thermal transitions obtained by DSC: (\diamondsuit) T_m and (\circlearrowright) T_g 's of the blends in the second scan against composition of the blends.

a desiccator, by the displacement method in nbutyl alcohol. A Mirage SD-120L electronic densitometer was used. Three determinations were made per value. The temperature of the immersion liquid was determined with 0.1°C precision.

Tensile testing was carried out on an Instron 4301 tester at $23\pm2^{\circ}$ C in 2-mm-thick ASTM D-638 type IV specimens. A crosshead speed of 20 mm/min was used. The mechanical properties [Young's modulus (*E*), yield stress (σ_y), break stress and strain (σ_b and ε_b , respectively)] were determined from the force-displacement curves. Izod impact tests were carried out on 3-mm-thick notched specimens using a CEAST 6548/000 pendulum. The notches (depth 2.54 mm, radius either 0.25 mm or 1 mm) were machined after injection molding. A minimum of eight specimens were tested for each determination in both tensile and impact tests.

SEM (Hitachi S-2700) was carried out after gold coating on both cryogenically and tensile and impact-fractured surfaces at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Phase Behavior

Figure 1 shows the glass transition (T_g) and melting (T_m) temperatures obtained by DSC for PA 6/phenoxy blends in the second calorimetric scan. No crystallization exotherms were observed during the scans in spite of the rapid cooling both in the injection mold and in the calorimeter previously to the second scan. This shows the quick

crystallization of PA 6 and that the phenoxy presence does not noticeably hinder it. The T_m of PA 6 remained practically constant with the blend composition in both scans. This constancy and the practically linear melting heat-composition relationship shown in Figure 2 indicate that the phenoxy presence does not practically affect the PA 6 crystallization.

With respect to the glass transitions, a lowtemperature T_g at approximately 42°C, which corresponds to PA 6, was seen only at high PA 6 contents. This T_g indicates the presence of a practically pure PA 6 phase. It was less clearly observed in the first scan because the contact of the specimen with the sample pan is not usually complete in injected specimens, the opposite to that which takes place after melting. The very short time in the melt state will probably lead to the morphology being essentially maintained. The absence of the low T_{σ} in PA 6-poor blend contents is probably due to its small intensity, a consequence of the high crystallinity of PA 6. Additionally, a second high-temperature T_g , which corresponds to a phenoxy-rich phase, is observed at all blend compositions except at 10% phenoxy content. It shows a slight shift to lower temperatures as the PA 6 content in the blends increases. This T_{σ} decrease indicates a slight presence of PA 6 in the phenoxy phase at high PA 6 contents.

To clarify this slight miscibilization, the blends were also tested by DMTA, which usually provides a higher detection level than does DSC. Figure 3 shows the T_g 's of the phenoxy-rich phase of the blends obtained from the maxima of tan δ in the DMTA measurements. The T_g of the PA 6 phase is not shown because, as from DSC, it held approximately constant with the composition. A



Figure 2 Melting heat of the blends obtained by DSC from the first scan against composition of the blends.



Figure 3 Glass transition temperatures of the phenoxy-rich phase in the blends obtained by DMTA against composition of the blends.

drop of approximately 10°C with respect to that of pure phenoxy is again observed in the T_g of the phenoxy-rich phase of the very rich PA 6 blends. This indicates, again, a slight presence of PA 6 in the phenoxy-rich phase of the PA 6-rich blends.

Given that PA 6 does not need processing aids and that plasticizers were not present according to the manufacturer's information and, thus, supposing that the T_g decrease of 10°C is due to the presence of PA 6, the amount of PA 6 in the phenoxy-rich phase may be estimated using the Fox's equation³¹:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{1}$$

where T_g is the glass transition temperature of the blend; T_{g1} and T_{g2} , the T_g 's of the two pure components, and w_1 and w_2 , the weight fractions of both components. Equation (1) yields a PA 6 content in the phenoxy-rich phase of approximately 12%.

This slight PA 6 presence could be due to some interaction between PA 6 and phenoxy, which is not surprising taking into account the complementary proton-acceptor/proton-donor characteristics of the components. These interactions could give rise to miscible blends, but it is known^{15,32} that the relation between interacting and non-interacting units in the polymer chain also plays a role. This is clearly seen in phenoxy blends because, as already mentioned, poly(butylene terephthalate) is miscible¹⁴ with phenoxy, whereas poly(ethylene terephthalate) is not. A similar effect was found in blends of bisphenol A polycarbonate with polyesters.³³ Thus, it appears that the relation between amide and methylene groups

in PA 6 is not favorable enough to give rise to miscibility in these PA 6/phenoxy blends.

The decrease in the T_g of the phenoxy-rich phase has been attributed to the presence of PA 6. Another possible reason could be the existence of interchange reactions during melt processing. However, the residence time of the blends in the melt state is small (approximately 4 min) and, moreover, a reaction level that would produce the observed T_g variation should also give rise to melting heat and melting temperature decreases that are not seen. Thus, reactions between the amide groups of PA 6 and hydroxyl groups of phenoxy have to be discarded as being responsible for the observed T_g behavior.

Thus, despite the, in principle, possible interactions between functional groups in PA 6 and phenoxy, the DSC and DMTA data show (a) the lack of effect of phenoxy on the crystallizationmelting behavior of PA 6 as a consequence of phase separation, (b) an almost complete immiscibility of the system, and, as a consequence, (c) the presence of, besides a crystalline phase, two amorphous phases: a pure PA 6 phase and an almost pure phenoxy phase with a slight PA 6 presence in the PA 6-rich blends.

Morphology

The surfaces of cryogenically fractured tensile as well as those of the tensile and impact fractured specimens of PA 6/phenoxy blends were observed by SEM. The surfaces of the *cryogenically fractured* tensile 80/20, 50/50, 30/70, and 20/80 specimens at 90° and of the 50/50 specimen at 40° are shown, respectively, in Figure 4(a–e). As can be seen, and as appearing in the rest of the compositions, mixing is homogeneous. This fact, the small dispersed-phase size dispersion, and the overall small dispersed-phase size indicate adequate mixing despite the lack of a first mixing step.

As can also be seen, a dispersed phase-matrix morphology is clearly observed in Figure 4(a,b) for the 80/20 and 50/50 compositions. The 70/30 composition showed a very similar morphology. These morphologies could not be seen directly in most of the blend surfaces. However, when the crack front direction clearly changed, the morphology was evident as seen in Figure 4(b), where the transition zone between two crack propagation surfaces is shown. To assure that this was the morphology of the whole surface, the phenoxy phase was selectively etched by immersing the





Figure 4 Surfaces of cryogenically fractured specimens: (a) 80/20, (b) 50/50, (c) 30/70, and (d) 20/80 compositions; (e) 50/50 composition at 40° .

specimens in a chloroform bath for 90 min. Etching confirmed that the morphologies shown are those of the whole surface. The contrast between the dispersed phases was not enough for an automatic measuring method to be used, but an estimation of the dispersed-phase size from representative micrographs of the tensile specimens yields mean values that, with the exception of the 30/70 blend, range from roughly 0.3 μ m in the 80/20 blend to 0.7 μ m in the 50/50 composition.

The morphology clearly changed in the case of the 30/70 composition of Figure 4(c), where a fairly cocontinuous structure, close to the phase inversion, is seen. PA 6 is the matrix which is also present as inclusions inside the dispersed phenoxy-rich phase. The PA 6 nature of the matrix was tested by selective etching of the phenoxy phase with chloroform as mentioned before. Finally, the usual and fine dispersed-phase morphology which is characteristic of minority compositions is seen again in the 20/80 composition of Figure 4(d).

Although not evident in Figure 4(a–d), because the photographs were taken at 90° from the surface and although some undeformed spheres were also present, the most often seen morphology was broken, roughly cylindrical, rods similar to those of Figure 4(e) in all compositions. This has been found in other PA 6 blends⁸ and is probably due to the flow during injection that is known to produce not only molecular orientation^{6,8} as a consequence of shearing, but also dispersed-phase orientation in multiphase systems. This orientation will affect the large-strain mechanical properties of the blends, as will be seen below.

The *phase inversion* appeared to take place around a 30/70 composition. It is generally accepted that the composition at which phase inversion takes place is related to the viscosity of the components. Thus, the equation

$$\eta_1 \phi_2 \cong \eta_2 \phi_1 \tag{2}$$

has been proposed³⁴ to approximately determine the blend composition where cocontinuous phases should appear. Although no viscosity data of PA 6 and phenoxy at the high shear rates usual in injection molding are available, the torque of the two components at the molding temperature $(240^{\circ}C)$ in a mixing bowl, which is related to viscosity,³⁵ may be used instead of the viscosity. The link is somewhat indirect, but it has been seen to be valuable in other polymer blends.^{35–37} The



Figure 5 Vicat softening temperature of the blends against composition.

torque values may be obtained from the literature.^{10,38} However, taking into account possible batch-to-batch variations, they were measured again. The blending torques were 3.5 and 7.5 Nm for PA 6 and phenoxy, respectively. Substituted in eq. (2), it predicts the phase inversion to occur at a 32% PA 6 content, in agreement with the SEM results.

The existence of the phase inversion in the region of 30/70 composition could also be deduced from the Vicat temperature measurements which are collected in Figure 5 against the blend composition. Vicat softening temperature measurements have been reported^{39,40} to provide information about the phase behavior of blends. But, since they are related to the matrix nature, they also provide preliminary information about phase inversion. Thus, the presence of a PA 6 matrix up to 50/50 and of a phenoxy matrix at and beyond the 20/80 blend composition are seen because of the rather constant Vicat temperature, similar to those of the pure polymers. The inflexion point, where cocontinuous structures should be present, appears at 60% phenoxy composition. It is fairly close to the phase-inversion composition estimated by SEM and by the torque ratio of the components of the blend.

In Figure 6(a,b), selected areas of the fracture surface of the 50/50 and 20/80 *tensile fractured specimens* are shown. They correspond to minority (25%) zones where the morphology could be observed, because no dispersed phase was observed in the rest of the specimens due to cohesive and more brittle fracture. The PA 6-rich compositions showed morphologies similar to that of Figure 6(a). The clear fibrilar fracture of the 30/70 composition avoided the need to take photo(a)







Figure 6 Surfaces of tensile-fractured specimens: (a) 50/50 and (b) 20/80 compositions.

graphs. As can be seen, the PA 6 phase of the blends mainly appears elongated, with particles oriented perpendicular to the fracture surface. This postmolding fibrilation of the PA 6 phases after tensile testing is high, although it was larger in another PA 6 blend.⁸ Moreover, it was not so important after impact testing and was not observed in pure PA 6.

Finally, the surfaces of the core of the *impact* specimens of compositions 70/30 and 20/80 are shown, respectively, in Figure 7(a,b). The 80/20 and 50/50 blends showed a dispersed-phase morphology similar to that of Figure 7(a). The 30/70 composition showed a PA 6 matrix with slightly elongated phases, slightly more oriented, as in the rest of the compositions, in the skin than in

the core. The dispersed-phase size is larger than that of the tensile specimens (roughly between 50 and 100% larger) throughout the composition range. This is probably influenced by the longer time for the dispersed phase to coalesce in the thicker impact specimens. As can also be seen, the morphology is rather similar to that of the cryogenically fractured tensile specimens of Figure 4. Taking into account that this is an impact-tested surface, the initial orientation should be smaller than in the tensile specimens. Moreover, the lower ability of the blends to deform under impact conditions is correlated to the negative behavior of the impact strength of the blends with respect to that of the pure components.

(a)



(b)



Figure 7 Surfaces of impact-fractured specimens: (a) 70/30 and (b) 20/80 compositions.



Figure 8 Young's modulus of the blends against composition. The limits correspond to \pm standard deviation.

Mechanical Behavior

Figure 8 shows the Young's moduli of PA 6/phenoxy blends as a function of composition. Although the experimental values are not far from linearity, a slight positive deviation can be observed in the PA 6-rich compositions, and a slight negative one, in the phenoxy-rich side. Positive modulus deviations are common results of miscible or compatibilized blends, while moduli below additivity may be expected in immiscible blends,⁴¹⁻⁴³ although linear behaviors^{6,44,45} or even positive deviations $^{46-48}$ have also been found. This is attributed to the fact that the adhesion between the blend components is usually good enough to allow efficient stress transfer to the dispersed phase at the low stress and strain levels at which the moduli of elasticity are measured.

Thus, supposing a good enough adhesion for small strains, three possible parameters are considered to explain the modulus behavior. These are blending-induced variations in (a) the free volume,^{49,50} (b) the orientation of the blend, and (c) the crystallinity level of the crystallizable polymer. This is because of the higher modulus brought about by the lower free-volume content, greater orientation, or higher crystallinity.

The crystallinity in these PA 6/phenoxy blends followed a practically linear relationship with the composition, as is seen in Figure 2 from the melting heat data. This indicated a practically similar crystalline content of 30%, both in PA 6 and in the blends. Moreover, the deviations from linearity are too small to influence the modulus and opposite to those which would give rise to the modulus behavior displayed in Figure 8. So, it is not the reason for the observed modulus behavior. With respect to variations in orientation, it is known that the Young's modulus can be higher when very high orientations like those attained during drawing are present. It was estimated in the mostly amorphous phenoxy and phenoxy-rich blends by the contraction after maintaining them above the T_g . Although there was clear (15%) contraction in the case of pure phenoxy, no significant contraction was seen in the blends. This relative slight orientation, and, as a consequence, the higher modulus of phenoxy, should partially account for the observed negative deviation of the modulus of the phenoxy-rich blends.

The free volume, taking into account that PA 6 crystallinity is almost unaffected by blending, may be analyzed from the density measurements. Table I shows the composition dependence of the density of the blends both experimentally and calculated from the law of mixtures, together with the typical deviation of each value. Although the values correspond rather closely to the rule of mixtures, there are significant positive deviations from linearity in the PA 6-rich blends and negative departures in the phenoxy-rich blends. Thus, densification, that is, free-volume decrease, takes place where positive deviations of the modulus are seen and vice versa. As a consequence, free volume seems to be the main parameter that determines the modulus behavior. This densification of the PA 6-rich compositions gives additional support to the slight miscibilization of PA 6 in phenoxy previously stated in this composition region from DSC and DMTA data. Thus, although there are a number of exceptions^{6,15,22,51,52} due to additional concomitant effects, the slight specific interactions that should give rise to this partial

Table IExperimental and Calculated Densities(g/cm³) of the Blends

Composition	Experimental	Calculated	Typical Deviation
100/0	1.1203	_	0.0003
90/10	1.1257	1.1253	0.0003
80/20	1.1313	1.1302	0.0004
70/30	1.1358	1.1352	0.0008
50/50	1.1459	1.1451	0.0003
30/70	1.1543	1.1550	0.0005
20/80	1.1595	1.1600	0.0003
10/90	1.1646	1.1649	0.0004
0/100	1.1699	—	0.0003



Figure 9 Yield stress of the blends against composition.

miscibilization may be responsible in these blends for the density and modulus behavior.

The yield stress values are shown in Figure 9. As usual, the yield stress follows a behavior comparable to that of the modulus. Despite the values slightly below those of the rule of mixtures in very rich phenoxy compositions, a synergistic behavior is observed for the rest of the blends. This takes also place in the cocontinuous 30/70 blend in opposition to the behavior of the modulus of elasticity that is measured at a much lower strain. This behavior indicates once again a good phase adhesion between the phases of the blends, despite the almost full immiscibility. This more positive relative behavior with respect to the rule of mixtures of the yield stress compared to that of the modulus of elasticity also took place in other compatible and immiscible blends^{6,45,46} and is probably due to the higher effect of orientation on the yield stress, compared to that on the modulus.⁵³



Figure 10 Break stress of the blends against composition.



Figure 11 Break strain of the blends against composition.

Figures 10 and 11 show the evolution with composition of large strain properties—in this case, break stress and ductility. As can be seen, the values of both properties are fairly adequately described by the simple rule of mixtures. In the case of the tensile strength, this is a consequence of the post-cold drawing steady increase of stress with elongation in the tensile test and of the linearity of the plot of ductility. The ductility plot is not that expected for immiscible blends, which show, in most cases, clear negative deviations from the rule of mixtures^{7,8,42,44,45,51} due to the lack of interfacial adhesion. This behavior is not, however, entirely unexpected because it may be influenced by the rather similar Young's (Fig. 8) and Poisson's moduli (the experimental value of phenoxy was not available but the calculated⁵⁴ Poisson's moduli of PA 6 and phenoxy are 0.40 and 0.39, respectively). This promotes fairly similar elongations in the applied stress direction and similar contractions in the perpendicular direction that do not help debonding.

Additionally, as commented on before, the dispersed phases of the tensile specimens were elongated before testing [Fig. 4(e)]. Elongated structures have a larger deformation ability than that expected for immiscible blends.^{6–8} This is because they allow an increase in the amount of the interfacial area per unit volume of the dispersed phase and, as a consequence, an easier stress transmission from the matrix to the dispersed phase. This easier transmission increases the possibility of the dispersed phase to be further elongated during the tensile test and increases ductility in the flow direction (which, in this case, is also the testing direction). These structures explain the good break properties observed for the PA 6/phe-



Figure 12 Impact strength of the blends against composition: (a) notch radius = 0.25 mm; (b) notch radius = 1 mm. When the impact values are close to the detection limit of the apparatus, the error bars are not shown.

noxy blends. With respect to adhesion, debonding was produced (Fig. 6), but the elongated morphology of the blends of Figure 6 as compared to that before testing (Fig. 4) shows that the adhesion level, although probably low as shown by the fiber surface, is enough to elongate the dispersed phase. Finally, although the presence of an elongated dispersed phase is probably enough to explain the observed fracture behavior, it must be emphasized that the small dispersed-phase size should also play a role in the observed behavior. Thus, dispersed-phase sizes below or close to 1 μ m have also provided remarkable fracture properties in other almost fully immiscible blends such as polycarbonate/poly(methyl methacrylate)^{55,56} or partially miscible blends such as polyetherimide/polyacrylate.36,57

In Figure 12, the impact strength of the blends

is shown against the composition. The favorable tensile behavior is not observed in this case. This is because the impact strength values in Figure 12(a) are clearly below linearity and close in most compositions to that of the pure phenoxy. This may be due, besides to a different rate dependence, to (a) the notch sensitivity of phenoxy, (b) the plane strain conditions, and (c) the morphology. To test the possibility of notch sensitivity, impact tests were also performed on specimens with a greater notch tip radius (1 mm). The results are shown in Figure 12(b). As can be seen, the larger impact strength values indicate the clearly smaller notch effect. However, the dependence on composition does not change. This indicates that the notch sensitivity of both components of the blend is not the reason for the observed behavior. With respect to plane strain conditions, the sharp notch, high strain rate, and specimen thickness used in impact tests should give rise to conditions close to the plane strain which will be different from the probably mixed⁵⁸ conditions of the 2-mm thin tensile specimens. Plane-strain conditions suppress plastic deformation⁵⁹ and promote fast, unstable crack propagation through the phase boundary, resulting in low impact strength. These different deformation mechanisms can contribute to the different mechanical behaviors observed in tensile and impact tests.

Finally, with respect to the morphology, the dispersed-phase size of impact specimens (from close to 1 μ m in the extreme compositions to roughly 2 μ m in the surroundings of the phase inversion) was clearly larger than that of tensile specimens. Moreover, it was less deformed before testing, in part because the more deformed skin was removed by notching. Compression molding could provide information related to unoriented specimens, but the associated different cooling rates and specific volume would make comparison of the results difficult. The lower deformation seen in the dispersed phases of impact specimens [Fig. 7(a)], which appear approximately as deformed after testing, as do the cryogenically fractured tensile specimens [Fig. 4(e)], is due to the fact that the thickness of the molding is critical in achieving high molecular⁶⁰ and phase orientation. Both morphological differences are detrimental and point to morphological reasons as the main reason for the observed impact behavior.

CONCLUSIONS

PA 6/phenoxy blends with fine and homogeneously dispersed phases were obtained by direct injection molding. Two glass transitions were observed by DSC and DMTA near those of the pure components, indicating practically total immiscibility, with the exception of the phenoxy-rich phases that showed some PA 6 presence at high PA 6 contents. SEM showed biphasic structures with slightly elongated dispersed phases in tensile specimens before testing that, unlike impact specimens, became fibrilar after tensile testing. These oriented structures appear to be the main reason for the observed additive ductility values, in spite of the immiscibility. Small-strain mechanical properties showed a more complex behavior, which may be explained on the basis of blending induced free-volume variations. The defective impact strength is attributed mainly to the more coarse and probably less oriented morphology of the impact specimens.

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