Compatibility in Immiscible Polysulfone/Poly(ethylene terephthalate) Blends

A. Retolaza, J. I. Eguiazábal, J. Nazábal

Departamento de Ciencia y Tecnología de Polímeros and Instituto de Materiales Poliméricos "POLYMAT," Facultad de Ciencias Químicas UPV/EHU, P. O. Box 1072, 20080 San Sebastián, Spain

Received 19 June 2003; accepted 27 March 2004 DOI 10.1002/app.20727 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polysulfone (PSU)/poly(ethylene terephthalate) (PET) blends were obtained by direct injection molding across the composition range. Their phase behavior, thermal properties, morphology, and mechanical properties were measured. The blends were composed of a pure PSU amorphous phase and either a pure PET phase in PSU-poor blends, or a PET-rich phase with some dissolved PSU in PSU-rich blends. The morphology of the dispersed phase was mostly spherical with some elongated particles in the PET-rich blends. A slight synergistic behavior was observed in the Young's modulus, mainly in the 90/10 blend, which is probably due to orientation effects. The presence of some broken particles indicated some interfacial adhesion. The ductility values were approximately linear with composition. This was generally the case in PSU-rich blends, and was attributed to the higher level of PSU in the PET-rich phase. Although embrittlement was seen in blends with 30% of the second component, the ductility of the two pure components did not significantly decrease after annealing due to the presence of low amounts (up to 10%) of another component of the blend. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2193–2200, 2004

Key words: poly(ether sulfones); polyesters; blends; miscibility; compatibility

INTRODUCTION

Blending of polymers is the most widely used method to obtain new polymeric materials.^{1,2} This is despite the fact that almost any two polymers are immiscible, and as a consequence, mechanically incompatible unless some compatibilization, for instance, by reaction leading to intermediate products, is produced. Thus, the research on new polymer blends either with some miscibility, or partially reacted, is attractive. This is especially true, for instance, when the main properties of one component of the blend compensate the deficiencies of the other, as in the case of amorphous/ semicrystalline pairs.

PSU is an amorphous thermoplastic, thermally stable, chemically inert, hydrolytically stable, and with good electrical properties. However, it has poor resistance to organic solvents. PSU has been blended with a great variety of polymeric materials such as poly-(ether ether ketone),^{3,4} phenolphthalein poly(ether ether ketone),^{5,6} poly(phenylene sulfide),^{7–11} poly(eth-ylene oxide),¹² poly(hydroxyether of bisphenol A),¹²

Contract grant sponsor: Spanish "Ministerio de Educación y Cultura"; project number: MAT2000–1742.

liquid crystalline polymers,^{13,14} and others.^{9,15,16} A PSU blend with polycarbonate (PC) is a commercial product (Mindel; Solvay Advanced Polymers, Alpharetta, GA) whose ability to be reprocessed has been studied.¹⁷ Recent patents refer to PSU/PC blends with excellent heat resistance,¹⁸ and to PSU/PC-carbon fiber composites with carbon black of high Izod impact strength and surface resistivity.¹⁹

PET is a widely used engineering thermoplastic. It presents good tensile and impact strength, stiffness, and a very good gas barrier performance. Studies of blends containing PET are numerous in the bibliography, for example, blends with PC,^{20,21} polyarylate (PAr),^{22–25} phenoxy,^{26–29} and polyether imide (PEI).^{30,31}

Thus, PSU and PET have complementary properties, so they may be a promising blend. However, to our knowledge, few works^{32,33} on PSU/PET blends have been published in the open literature. Compression molded PSU blends with PET showed synergistic Young's modulus, but very low ductilities (less than 5%).³² The compatibilization of polysulfones (PSU and poly(ether sulfone)) blends with PET, PBT, and other polyalkylene terephthalates by phenoxy has been studied.³³

In this work, the thermal properties, morphology, and mechanical properties of direct injection molded PSU/PET blends were studied by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMTA), density measurements, orientation measure-

Correspondence to: J. Nazábal (popnaetj@sq.ehu.es).

Contract grant sponsor: the University of the Basque Country.

Journal of Applied Polymer Science, Vol. 93, 2193–2200 (2004) © 2004 Wiley Periodicals, Inc.

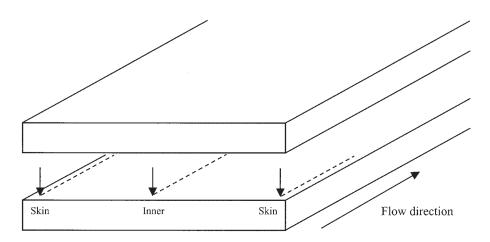


Figure 1 Schematic diagram of the samples preparation and probe points for the orientation measurements.

ments, scanning electron microscopy (SEM), and tensile and impact tests. The effects of annealing on the structure and ductility of the blends have also been studied.

EXPERIMENTAL

Polysulfone (PSU) (Udel P-1700) was supplied by Solvay Advanced Polymers (Alpharetta, GA). It had an M.F.I. of 8.8 \pm 1.0 g/10 min (ASTM D-1238, at 315°C with 5.0 kg load). Poly(ethylene terephthalate) (PET) was supplied by Brilen (Barbastro, Huesca, Spain). It had an intrinsic viscosity of 0.82 dL/g in o-chlorophenol at 30°C. PSU and PET were dried before processing at 135°C for 15 h, and at 120°C for 14 h, respectively. The pure PET and the blends were processed by direct injection molding in a Battenfeld BA 230E (Battenfeld GmbH, Kottingbrunn, Austria) reciprocating screw injection-molding machine (screw diameter = 18 mm and L/D = 17.8) at a barrel and nozzle temperature of 280°C, injection speed of 7.4 cm³/s, injection pressure of 2650 bar, and mold temperature of 18°C. The pure PSU was injected under the same conditions, but at a barrel and nozzle temperature of 310°C. Direct injection molding entails improvement in the economy of the process, and avoids an initial extrusion process, which might contribute to degradation.

The thermal behavior of the blends and of the pure components was studied by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-7 (Norwalk, CT) calorimeter. The samples were heated from 30 to 300°C at 20°C/min. The crystallization and melting temperatures and heats were determined respectively, at the maxima and from the areas of the corresponding peaks. The phase structure of the blends was studied by dynamic mechanical analysis (DMTA) using a TA Instruments Q 800 DMA (New Castle, DE). The samples were heated from 0 to 230° C at a heating rate of 4° C/min and at a frequency of 1 Hz.

The specific volume was measured in a Mirage SD-120-L densitometer (A&D Instruments, Oxford, United Kingdom) with a maximum typical deviation of 0.0008 cm³/g, using 1-butanol as immersion liquid.

Possible chemical reactions between PSU and PET were studied by Fourier Transform infrared spectroscopy (FTIR) using a Nicolet Magna 560 spectrophotometer (Nicolet Analytical Instruments, Madison, WI). An attenuated total reflection (ATR) objective attached to a Spectra Tech microscope (Shelton, CT) and a mercury-cadmium telluride detector were used. The orientation of the blends and of the pure components was also measured by FTIR in tensile specimens cut along the flow direction using a Leica 1600 microtome (Nussloch, Germany). Two measurements were carried out in each specimen in the three points indicated in Figure 1. The polarized ATR spectra were carried out at a 45° angle of incidence using a Nicolet Magna-IR 560 spectrophotometer equipped with an ATR accessory. The resolution was 8 cm⁻¹ and each reported value is the average of the six points. The dichroic ratio D was the ratio of the intensities of the absorption bands of a characteristic group measured for parallel (A_{\parallel}) and perpendicular (A \perp) polarization with respect to the injection direction.

$$D = \frac{A_{\parallel}}{A_{\perp}} \tag{1}$$

The average orientation is expressed as the orientation parameter (f) that is related to the dichroic ratio as

$$f = \frac{(D-1)(D_0+2)}{(D+2)(D_0-1)}$$
(2)

where $D_o = 2\cot^2 \alpha$, and α is the angle between the chain axis and the transition moment. Although α is

not accurately known, 90° can be used as a first approximation for all the perpendicular bands, because this angle would give rise to the minimum orientation value.

The tensile tests were carried out using an Instron 4301 (Canton, MA) at a cross-head speed of 10 mm/ min and at 23 \pm 2°C on injected ASTM D-638 type IV (1.8 mm thick) specimens. The Young's modulus, E, and yield stress, $\sigma_{y'}$, were determined from the load-elongation curves. The ductility was measured by means of the reduction of transversal area (d) by means of the expression:

$$d = \frac{A_0 - A}{A_0} \tag{3}$$

where d is the ductility, and A_0 and A are the initial and final transversal areas, respectively.

Scanning electron microscopy (SEM) was carried out on both etched and unetched surfaces of cryogenically fractured specimens, after gold coating. A Hitachi S-2700 (Ibaraki, Japan) electron microscope was used at an accelerating voltage of 15 kV. Etching with N,N-dimethylformamide was used to remove the PSU phase.

RESULTS AND DISCUSSION

Phase structure

The phase structure of the blends was first studied by DMTA. The glass transition temperatures (T_g) of the blends by DSC, when observed, were in accordance with those observed by DMTA. The T_g of PSU in the blends remained practically constant at 194°C, whatever the PET content. The T_g of PET at 84°C was also constant in the 10/90 and 30/70 blends, but it increased with the PSU content up to a maximum of 98°C in the 90/10 blend. These results indicated that the blends were composed of a pure PSU amorphous phase, and either a pure PET phase in PSU-poor blends, or a PET-rich phase with some PSU in PSU-rich blends. In other PSU/PET blends,³² the T_g values did not follow a consistent trend.

The approximate amount of PSU in the PET-rich phase of this work can be estimated by means of the Fox equation:³⁴

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g_1}} + \frac{\omega_2}{T_{g_2}}$$
(4)

where T_g is the glass transition of the blend, T_{g1} and T_{g2} those of the two components, and ω_1 and ω_2 the weight fractions of PET and PSU, respectively. The calculated PSU contents in the PET-rich phase of the 50/50, 70/30, and 90/10 blends were 4, 8, and 16%, respectively.

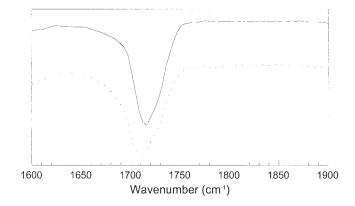


Figure 2 Experimental (–) and weighted addition (––) FTIR spectra of the 50/50 blend.

The PSU present in the PET-rich phase can be either miscibilized, reacted, or both. To test which of these possibilities was true, the occurrence of chemical reactions during processing was studied by FTIR. In Figure 2 the FTIR spectrum of the 50/50 blend is compared with that obtained from the weighted addition of the spectra of PSU and PET. As can be seen in the experimental spectrum, there is a displacement of the carbonyl group of the PET of the blend with respect to the calculated one. This indicates the existence of chemical reactions and the presence of reacted copolymers in the blends. An attempt was made to further elucidate the nature of the chemical reactions. However, the procedures used to separate both phases of the blends were unsuccessful. On the other hand, as the FTIR results are not quantitative, the additional presence of mixed PSU in the PET-rich phase cannot be inferred.

The possible effects of the presence of PSU on the crystallizability and crystallinity of PET were studied by DSC. The first DSC heating scans of pure PSU and PET, and of the blends versus temperature are shown in Figure 3. As can be seen, both PET and most of the blends showed a crystallization exotherm, indicating that they were not fully crystallized in the mold. The melting temperature (T_m), and crystallization temperature (T_c) of PET when observed, remained practically constant in the blends. These results indicated that the presence of PSU did not affect the crystallization of PET.

With respect to the crystallinity of PET, it was very low (roughly 6%), probably because of the low mold temperature, and barely changed with PSU content. The lack of change of both the T_m and the crystalline content in the blends indicated the formation of block copolymers, which are almost as crystallizable as pure PET.

Morphology

The morphologies of the cryofractured surfaces of the 70/30 and 30/70 blends are shown in Figures 4A and

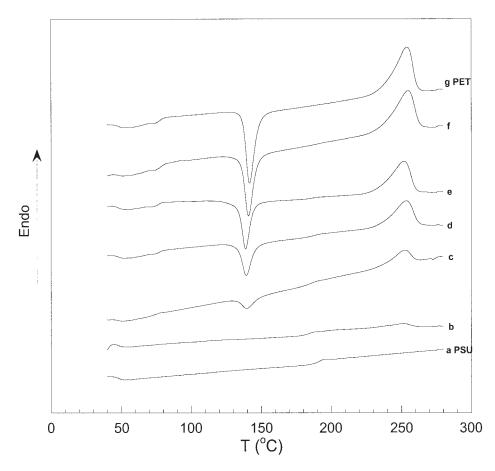


Figure 3 First DSC heating scans of pure PSU and PET, and PSU/PET blends.

4B, respectively. When the 90/10 blend was observed, small PET particles (typically 0.4 μ m) were homogeneously distributed in the PSU matrix. The morphology of the 70/30 blend shown in Figure 4A was difficult to discern, due to the topology of the matrix. For this reason, this blend was etched with N,N-dimethylformamide to remove the PSU matrix and better observe the morphology of the PET phase. The PET particles were spherical, with a particle size mostly between 0.5 and 2 μ m. They were apparently larger particle size than in Figure 4A, probably due to observation of the whole particle, instead of the smaller sections, corresponding to fracture in planes other than that crossing through the center of the particle.

The morphology of the 50/50 blend presented a partially oriented dispersed phase, with practically undeformed and elongated dispersed phases, not very different from that of Figure 4A. The nature of the dispersed phase was not clear; hence, it was studied both by means of the composition at which phase inversion should take place, and by etching. To find out the phase inversion composition, the viscosities of the components were measured by means of the torque in the melt state in the Brabender kneader. The lower viscosity of PET at 280°C suggested that phase

inversion should take place in PSU-rich blends, and as a consequence, the dispersed phase of the 50/50 blend should be PSU. With respect to etching, the solvent attacked the dispersed phase; thus, the matrix of the 50/50 blend was PET and phase inversion took place between 50/50 and 70/30 compositions.

The morphology of the 30/70 blend is shown in Figure 4B. Both this blend and the 10/90 blend presented both practically undeformed and rather fibrillar particles. Most PSU particles were small (mostly below 2 μ m). Some large particles (larger than 5 μ m) with PET particles inside were also observed. As can be seen, some particles were debonded, but others appeared broken, indicating some interfacial adhesion.

Mechanical properties

As-molded blends

The Young's moduli of both the pure components and the blends are shown in Figure 5 as a function of the PET content. Both the best approximation (continuous line) and the modified rule of mixtures (broken line) are drawn. As in a previous work,³² a small synergism

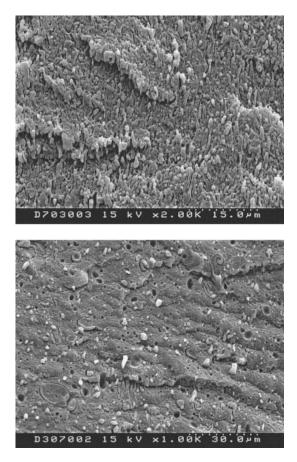


Figure 4 Morphologies of cryogenically broken surfaces of the PSU/PET 70/30 (A) and 30/70 (B) blends. The photographs were obtained by SEM at an angle of 30° from the perpendicular to the surface.

was observed at all blend compositions. Synergisms in the modulus are usual in miscible blends,^{35–37} in partially miscible blends,^{32,38,39} and also in reacted blends.^{24,40} However, some immiscible blends^{41,42} also showed synergisms in the modulus. This indicates that the adhesion level in the interface, when it exists, is not a relevant characteristic when discussing the modulus behavior. This is probably due to the very

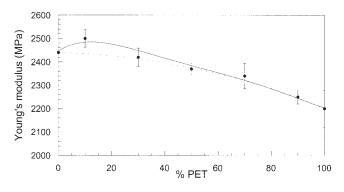


Figure 5 Young's modulus of the PSU/PET blends versus PET content.

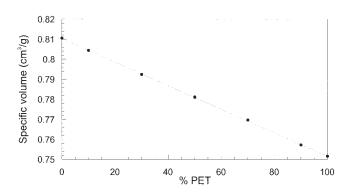


Figure 6 Specific volume of the PSU/PET blends versus PET content.

low strain at which it is measured, where debonding, and as a consequence lack of contribution to support the load, has not yet taken place.

Of the morphological features that may influence the modulus, the crystallinity level was the same in the blends and in pure PET. Therefore, it did not influence the modulus behavior. Mixing induced densification is often seen in miscible, and sometimes in partially miscible, blends. For this reason, the density of the pure components and the blends was measured. The corresponding specific volume plot is shown in Figure 6 against composition (density of pure PSU and PET respectively, 1.2338 and 1.3305 g/cm³). As can be seen, the plot closely followed the direct rule of mixtures. The crystallinity of PET was constant in the blends and in pure PET as was seen by DSC; therefore, the free volume of the amorphous phase did not change upon blending. The average orientation, expressed as the orientation parameter (f), is shown in Table I. As can be seen, the average orientation of the 10/90 blend was slightly lower than that of pure PET, and the average orientation of the 50/50 blend was almost the average of those of the pure polymers. However, in the 90/10 blend, the average orientation was almost that of pure PET, suggesting that the synergism in the modulus could be due to a greater orientation in the blend than expected.

The synergistic modulus behavior observed can be described (broken line) by means of the modified rule of mixtures proposed by Nielsen:⁴³

TABLE I Average Orientation of the Blends and the Pure Components

PSU/PET	Average orientation (f)		
100/0	0		
90/10	0.125		
50/50	0.0705		
10/90	0.136		
0/100	0.146		

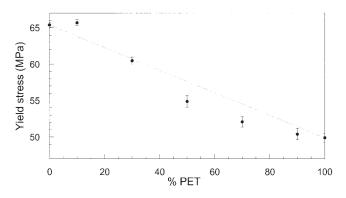


Figure 7 Yield stress of the PSU/PET blends versus PET content.

$$P = P_1 \phi_1 + P_2 \phi_2 + \beta_{12} \phi_1 \phi_2$$
 (5)

where P and ϕ are the studied property and the volume fraction, respectively; the subscripts 1 and 2 refer to the two components of the blend; and β_{12} is an empirical parameter that can be calculated as

$$\beta_{12} = 4P_{12} - 2P_1 - 2P_2 \tag{6}$$

where P_{12} is a property of the 50/50 blend. As can be seen, with the exception of the 90/10 blend that showed an absolute synergism, the continuous curve of Figure 5 that corresponds to Equation 5 reasonably fits the experimental data. The parameter β_{12} (200 MPa in this blend) quantifies the deviation and has been tentatively related to the compatibility of the blend.³⁶ Although a possible suppression of a low temperature secondary transition should also be taken into account,⁴⁴ the β_{12} values range between 200 and 2000 MPa in thermoplastic/thermoplastic blends both when the modulus synergism is attributed to volume contractions^{17,36,44} and when it is attributed to higher orientation of any of the components in the blends.⁴⁵ However, values of roughly 2500 MPa or higher are obtained in thermoplastic/liquid crystalline polymer (LCP)⁴⁶ and LCP/LCP blends,⁴⁷ due to the large orientation of the LCPs.

The yield stress of the blends versus PET content is shown in Figure 7. As can be seen, the synergism remained only in the 90/10 composition. As can also be seen, the tendency observed in the σ_y plot of Figure 7 mainly for the 50/50 and 30/70 blends, is different from that of Figure 5, where no negative value was seen. This could be due to the fact that the strain values at which both properties were measured, and as a consequence the mechanism involved, are different. This is despite parallel behavior of both short deformation properties to the usual rule.⁴⁸

The ductility of the blends is shown against PET content in Figure 8. It was measured by means of the reduction of transversal area, because breaking took place during the cold drawing process. This led to large ductility differences, which were not representative of the real ductility of the material when ductility was measured as the elongation at break. As can be seen, the 90/10 and 70/30 blends practically followed the rule of mixtures, whereas the 50/50 and 30/70 blends were below the tie line. The ductile behavior of these blends was opposite to that seen³² in Brabender mixed and compression molded PSU/PET blends where, probably due to the processing method, ductility values below 5% were obtained.

The better break performance of the PSU-rich blends is attributed to PSUs' partial miscibility. This is because the ductility behavior is often related to the miscibility level. Thus, although negative deviations can be observed due to a decrease in the free volume as a result of mixing,^{49,50} miscible and partially miscible blends usually present ductility synergistic^{51,52} or neutral^{40,53} values. Immiscible blends are expected to show negative deviations from the rule of mixtures⁵⁴ due to the lack of interfacial adhesion. Positive deviations in immiscible blends^{41,55,56} are attributed to additional parameters such as the lesser crystalline character of the components of the blend,⁴¹ the presence of highly oriented structures (fibrillar morphology),55 different Poisson's moduli of the components, and a small dispersed phase size.⁵⁶

Annealed blends

It is known that molded fully amorphous (and not fully crystallized) PET is able to crystallize after exposure to high temperatures decreasing its deformability. This change in PET from fully amorphous to partially crystalline determines its applications. Moreover, both PSU and PSU-based materials are often used in applications involving high temperatures for long periods of time. For these reasons, to find out the performance of the PSU/PET blends of this study at high temperatures, the blends were subjected to annealing, as were the pure components as a reference.

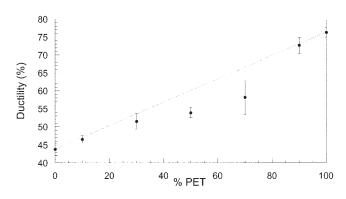


Figure 8 Ductility of the PSU/PET blends versus PET content.

Composition	Crystallinity (%)		Ductility (%)			
		After annealing			After annealing	
	As-molded	120°C	160°C	As-molded	120°C	160°C
100/0				44 (66)		46 (11)
90/10	6		21	47 (74)		39 (6.5)
70/30	6		24	52 (85)		1.2 (4.0)
30/70	6	23		58 (112)	1.4 (5)	
10/90	6	24		73 (210)	68 (11.5)	
0/100	6	24	24	76 (255)	71 (128)	69 (42)

 TABLE II

 rystallinity and Ductility of the As-molded and Annealed PSU/PET Blends

The values in parentheses correspond to ductility measured as the elongation at fracture. The main standard deviations of the ductility were 4% (6%) as-molded, 10% (10%) annealed at 120°C, and 6% (11%) annealed at 160°C.

Annealing was carried out in the case of PSU and PSU-rich blends at a temperature (160°C) close, but below, the T_g of PSU, and similar to the maximum continuous use temperature reported⁵⁷ for PSU. In the case of PET and PET-rich blends, annealing was carried out above T_g (120°C).

The possible changes in the crystallinity of PET after annealing were studied by DSC. The measured crystalline contents, as well as the ductility values that will be discussed later, are shown in Table II. As can be seen in Table II, annealing led to an increase in the crystalline content of PET up to its usual maximum value,^{58–60} whatever the annealing temperature.

The ductility of the blends after annealing is compared with that of the corresponding as-molded blends in Table II. As can be seen, in the case of the pure PSU, the decrease in ductility (a consequence of the decrease in free volume upon annealing) was very small. This was because reduction in the area at break did not change and because the decrease in elongation at break was only a consequence of the decrease in the ability to cold draw. In the case of the 70/30 blend, annealing led to a brittle behavior very different from that seen in annealed PSU. However, the presence of small PET levels (up to 10%) only worsened the performance at high temperature of PSU slightly. This was because the ductility values were comparable to those of pure PSU, indicating that the thermal resistance of the 90/10 blend is similar to that of neat PSU. The PET of the annealed blend was more crystalline and, therefore, less ductile. However, the ductility was constant, indicating that the higher crystalline content of the PET was not relevant when the fracture properties of the blends are concerned.

As can also be seen in Table II, although the ductility of neat PET measured by the elongation at break decreased, it remained ductile after annealing. The 30/70 blend embrittled after annealing. However, the 10/90 blend remained ductile as ductility measured by the reduction of the cross section was maintained, as in the 90/10 blend. Thus, the ductilities of the blends at low dispersed phase contents were rather similar to those of the pure components. This indicated that the possible negative effects on ductility of either the biphasic structure (PET-rich blends), or the combined effects of the biphasic structure and the increased crystallinity (PSU-rich blends) were not important enough to embrittle the blends. This was although their ability to cold draw decreased, as seen through the decrease in the elongation at break.

CONCLUSION

PSU-poor blends presented two pure PSU and PET amorphous phases. However, in PSU-rich blends some PSU was present in the PET-rich phase. Reaction occurred between PSU and PET. The crystallinity and crystallization ability of PET did not change as a consequence of the PSU presence. The dispersed phase was spherical with some elongated dispersed phases at PET contents above 30%. The observed synergism in the Young's modulus is attributed to higher orientation of the blends with respect to that expected for the average of the pure components. The linear behavior of ductility was in good agreement with the presence of some broken particles that indicated interfacial adhesion. The best ductility values took place, as expected, when the presence in one phase of the other component of the blend was maximum, but compatibility also extended to the compositions where full immiscibility was seen. Although the opposite was seen in blends with 30% of the second component, the presence of low amounts (up to 10%) of a second component barely modified the ability of the two pure polymers to resist high temperatures, as seen by the lack of significant decrease in ductility after annealing.

The authors gratefully acknowledge financial support of the Spanish "Ministerio de Educación y Cultura" (Project No. MAT2000–1742). A. Retolaza also gratefully acknowledges the University of the Basque Country for the award of a grant for the development of this work.

References

- 1. Shonaike, G. O.; Simon, G. P. Polymer Blends and Alloys; Marcel Dekker: New York, 1999.
- 2. Utracki, L. A. Polymer Alloys and Blends: Thermodynamics and Rheology; Hanser: New York, 1990.
- Arzak, A.; Eguiazábal, J. I.; Nazábal, J. J Appl Polym Sci 1997, 65, 1503.
- 4. Robeson, L. M.; Harris, J. E. Eur. Pat. 176988, 1985.
- Guo, Q.; Huang, J.; Chen, T.; Zang, H.; Yang, Y.; Hou, C.; Feng, Z. Polym Eng Sci 1990, 30, 44.
- 6. Guo, Q.; Huang, J.; Chen, T. Polym Bull 1988, 20, 517.
- 7. Cheung, M.-F.; Plummer, H. K. Polym Bull 1991, 26, 349.
- 8. Akhtar, S.; White, J. M. Polym Eng Sci 1991, 31, 84.
- 9. Zeng, H.; Mai, K. Makromol Chem 1986, 187, 1787.
- Cheung, M.-F.; Golovoy, A.; Plummer, H. K.; van Oene, H. Polymer 1990, 31, 2299.
- Cheung, M.-F.; Golovoy, A.; van Oene, H. Polymer 1990, 31, 2307.
- 12. Swinyard, B. T.; Barrie, J. A.; Walsh, D. J. Polym Commun 1987, 28, 331.
- Shumsky, V. F.; Lipatov, Y. S.; Kulichikhin, V. G.; Getmanchuk, I. P. Rheol Acta 1993, 32, 352.
- 14. Jung, H. C.; Lee, H. S.; Chun, Y. S.; Kim, S.-B.; Kim, W. N. Polym Bull 1998, 41, 387.
- 15. Goh, S. H.; Lau, W. W. Y.; Lee, C. S. Polym Bull 1991, 26, 319.
- 16. Chung, T.-S.; Glick, M.; Powers, E. J. Polym Eng Sci 1993, 33, 1042.
- Sánchez, P.; Remiro, P. M.; Nazábal, J. Polym Eng Sci 1992, 32, 861.
- Maeda, M.; Nagashima, T.; Nombra, H.; Nakamura, H. Eur. Pat. 0845501, 1998.
- 19. Nagashima, T.; Maeda, M.; Nakamura, H. US Pat. 6127492, 2000.
- García, M.; Eguiazábal, J. I.; Nazábal J. J Appl Polym Sci 2001, 81, 121.
- 21. Montaudo, G.; Puglisi, C.; Samperi, F. Macromolecules 1998, 31, 650.
- 22. Kimura, M.; Salee, G.; Porter, R. S. J Appl Polym Sci 1984, 29, 1629.
- 23. Robeson, L. M. J Appl Polym Sci 1985, 30, 4081.
- Martínez, J. M.; Eguiazábal, J. I.; Nazábal, J. J Appl Polym Sci 1992, 45, 1135.
- 25. Lee, S. S.; Jeong, H. M.; Jho, J. Y.; Ahn, T. O. Polymer 2000, 41, 1773.
- 26. Eguiazábal, J. I.; Iruin, J. J. Mater Chem Phys 1987, 18, 147.
- Cortázar, M.; Eguiazábal, J. I.; Iruin, J. J. Eur Polym J 1994, 30, 901.
- Seymour, R. W.; Zehner, B. E. J Polym Sci Polym Phys Ed 1980, 18, 2299.
- 29. Mascia, L.; Fekkai, Z. Polym Networks Blends 1992, 2, 197.

- Martínez, J. M.; Eguiazábal, J. I.; Nazábal, J. J Appl Polym Sci 1993, 48, 935.
- Martínez, J. M.; Eguiazábal, J. I.; Nazábal, J. J Appl Polym Sci 1996, 62, 385.
- Baranov, A. O.; Dubnikova, I. L.; Kompanietz, L. V.; Turusov, R. A.; Prut, E. V. Polym Polym Compos 1998, 6, 415.
- 33. Mascia, L.; Martin, L. H.; High Perform Polym 1996, 8, 119.
- 34. Fox, T. G. Bull Am Phys Soc 1956, 1, 123.
- 35. Avramova, N. Polymer 1995, 36, 801.
- Kleiner, L. W.; Karasz, F. E.; Macknight, W. J. Polym Eng Sci 1979, 19, 519.
- Joseph, E. A.; Lorenz, M. D.; Barlow, J. W.; Paul, D. R. Polymer 1982, 23, 112.
- 38. Bastida, S.; Eguiazábal, J. I.; Nazábal, J. Polymer 1996, 37, 2317.
- Sánchez, P.; Remiro, P. M.; Nazábal, J. J Appl Polym Sci 1993, 50, 995
- 40. Mondragón, I.; Nazábal, J. J Appl Polym Sci 1986, 32, 6191.
- 41. Erro, R.; Gaztelumendi, M.; Nazábal, J. J Polym Sci, Part B: Polym Phys 1996, 34, 1055.
- Jurado, M. J.; Gaztelumendi, M.; Nazábal, J.; Mondragón, I. J Polym Sci, Part B: Polym Phys 1990, 28, 1015.
- Nielsen, L. E. Predicting the Properties of Mixtures; Marcel Dekker: New York, 1978.
- 44. Gaztelumendi, M.; Nazábal, J. Polym Eng Sci 2000, 40, 430.
- Eguiazábal, J. I.; Nazábal, J. Plast Rubber Process and Appl 1990, 14, 211.
- García, M.; Eguiazábal, J. I.; Nazábal, J. Polym Eng Sci 2002, 42, 413.
- 47. Vallejo, F. J.; Eguiazábal, J. I.; Nazábal, J. Polym J 2001, 33, 128.
- Brown, N. In Failure of Plastics; Brostow, W.; Corneliussen, R. D., Eds.; Hanser Publishers: Munich, 1986, Chap 6.
- Vallejo, F. J.; Eguiazábal, J. I.; Nazábal, J. J Appl Polym Sci 2001, 80, 885.
- 50. Barlow, J. W.; Paul, D. R. Polym Eng Sci 1981, 21, 985.
- 51. Bastida, S.; Eguiazábal, J. I.; Nazabal, J. Eur Polym J 1996, 32, 1229.
- Guerrica-Echevarría, G.; Eguiazábal, J. I.; Nazabal, J. J Appl Polym Sci 2002, 37, 4529.
- Rodríguez, J. L.; Eguiazábal, J. I.; Nazabal, J. J Macromol Sci Phys B 1997, 36, 773.
- 54. Arzak, A.; Eguiazábal, J. I.; Nazábal, J. J Mater Sci 1991, 26, 5939.
- 55. Guerrica-Echevarría, G.; Eguiazábal, J. I.; Nazábal, J. J Appl Polym Sci 1999, 72, 1113.
- 56. Koo, K.; Inoue, T.; Miyasaha, K. Polym Eng Sci 1985, 25, 741.
- 57. Commercial information from Solvay Advanced Polymers.
- 58. Samios, C. K.; Kalfoglou, N. K. Polymer 1999, 40, 4811.
- 59. Kalfoglou, N. K.; Skafidas, D. S. Eur Polym J 1994, 30, 933.
- Kalfoglou, N. K.; Skafidas, D. S.; Kallitsis, J.; Lambert, J. C.; Van der Stappen, L. Polymer 1995, 36, 4453.