JOURNAL OF MATERIALS SCIENCE 32 (1997) 971–977

Acrylonitrile–butadiene–styrene-toughened polysulphone of bisphenol A blends: influence of processing temperature and composition

B. E. RUIZ DE GAUNA, M. GAZTELUMENDI, J. NAZABAL*
Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química (E.H.U./U.P.V.), P.O. Box 1072, 20080-San Sebastián, Basque Country, Spain

---

Polysulphone of bisphenol A (PSU)/acrylonitrile–butadiene–styrene (ABS) blends have been obtained by direct injection moulding at different temperatures and for compositions in the PSU-rich range. Direct injection moulding provided a mixing level similar to that of kneading. The blends were almost fully immiscible with the exception of the polybutadiene (PBD) phase where some PSU appeared to be present. Only a very small amount of ABS was required to greatly improve the tracking index of PSU. The mechanical properties, however, were those of a compatible material, and did not depend on the injection temperature. Moreover, with the exception of the ductility, they were in fairly good proportion to the blend composition, and provided the most balanced set of properties at an ABS content near 5%.

---

1. Introduction

In the wide field of polymer blends, those having as the second component a rubber-like polymer, constitute a distinct and commercially successful group, that has specific production technology, deformation mechanisms and denomination: rubber-toughened blends. The addition of small amounts, usually in the range of 5%–20%, of a second rubber-like component that disperses in the matrix, gives rise to a remarkable improvement in fracture properties, impact resistance mainly, producing a new material with a more balanced set of properties.

The obvious candidates to be rubber toughened were brittle materials, such as polystyrene or thermoset polymers, but nowadays the technology has been successfully extended to fairly inherently tough polymers, such as, for instance, polycarbonate (PC) and polypropylene (PP). One of the most successful blends of this type is polycarbonate/acrylonitrile–butadiene–styrene (PC/ABS) that has been commercialized under the trade names of Bayblend, Cycoloy and Pulse among others, and that has been the subject of a number of investigations [1–6]. This may be due to the wide applications of PC and to the versatility of ABS that may change its nature both by means of the rubber content and by the copolymer composition. In this way, not only the compatibility with the matrix may be controlled by means of the copolymer composition, but also the elastic moduli difference between those of the matrix and the dispersed phase, by means of the rubber content. As a consequence, one of the most important parameters that controls the deformation mechanisms may be chosen within limitations.

Polysulphone of bisphenol A (PSU) is an engineering thermoplastic with chemical nature similar in part to that of PC and with applications competing with those of PC and in electrical parts. However, despite the clear interest of PC/ABS blends and the recent commercialization of PSU/ABS blends [7], no work, to our knowledge, has been carried out on PSU/ABS blends.

There are many parameters to be fixed when toughened blends are being developed. Besides the components, two of the more important ones are composition and processing parameters, mainly temperature. This is because both are fundamental in determining the structure and its characteristics, i.e. dispersed particle size, main distance between particles, particle distribution, etc. Hence, in this work, PSU/ABS blends were obtained in the melt state by direct injection moulding. Both the effects of the mixing temperature and of the composition were studied. The effects of the processing temperature were studied at the 75/25 composition and the chosen temperatures were close to that of the most suitable processing temperature. The effects of the composition were studied at 260 °C and in the ABS minority range, where the highest improvement in properties has been obtained in similar systems [4, 8]. To ensure that a suitable mixing level was attained by direct injection moulding, the mixing level of the injection-moulded blends was compared with that of blends obtained by a more usual method, kneading. The comparison was made by measuring the change of T_g in the two mixing methods. Given the wide use of PSU in electrical applications [9], one of the most representative

---

*Author to whom all correspondence should be addressed.

electrical properties, the tracking resistance of the blends was measured. The nature and morphology of the blends were studied by dynamic mechanical thermal analysis (DMTA) and SEM and were related to the most relevant mechanical properties measured by means of both the tensile and impact tests.

2. Experimental procedure

PSU (Udel P-1700 Amoco) and ABS (Novodur PK Bayer) were dried before processing at conditions recommended by the manufacturers (3.5 h at 135 °C for the PSU and 6 h at 80 °C for the ABS).

PSU/ABS blends were obtained by direct injection moulding (IM) in a Battenfeld BA 230E machine that provided tensile and impact specimens. The effects of injection temperature was studied in the 75/25 blend and the injection temperatures used were 250, 260 and 270 °C. The injection temperatures for the pure materials (320 °C for PSU and 250 °C for ABS) were different to allow correct injection and to prevent degradation of the ABS. For the study of the effects of composition, PSU/ABS blends with 0%, 5%, 15%, 25% and 35% ABS by weight were obtained at an injection temperature of 260 °C.

Kneading was also carried out to verify that suitable mixing was attained in the injection machine. It was carried out in a Brabender mixer at 30 r.p.m. in the PSU/ABS 75/25 blend and pure ABS at 240, 250, 260 and 280 °C, and also at 260 °C for different compositions. The mixing operation was maintained for 12 min. Compression moulded (CM) sheets (thickness 1 mm) were then obtained, at the same temperatures as were used for kneading, in a Schwabenthan-Polystat 200-T press. The sheets were cooled in air.

Dynamic-mechanical thermal analysis was carried out in specimens obtained from CM sheets and from the tensile specimens obtained by IM that were machined to a thickness of 1 mm. This was performed in a Polymer Laboratories DMTA which provided the storage, E', and loss, E'', moduli and the loss tangent, δ, as a function of temperature. A constant heating rate of 4 °C min^{-1} was employed at a frequency of 1 Hz.

The comparative tracking indexes (CTI) of IM specimens (thickness 3.2 mm) were determined in a Tracking Test Apparatus (ASTM D 3638). The index is defined as the numerical value of that voltage which will cause failure by tracking when the number of drops of contaminant required to cause failure is equal to 50. This value was obtained from a plot of the number of drops to failure by tracking, versus the applied voltage. The contaminant used was a 0.1% solution of ammonium chloride in water.

Tensile tests of IM specimens (thickness 2 mm) (ASTM D638 type IV) were carried out in an Instron 4301 tensile frame in conjunction with an Instron series IX computer data acquisition. The crosshead speed and the temperature were 10 mm min^{-1} and 23 °C, respectively. Young's modulus, yield stress, nominal stress at break and ductility, as measured by the nominal strain at break, were measured from the force–displacement curves. A minimum of eight specimens was tested for each reported value.

Izod impact tests were carried out in notched specimens (ASTM D-256, thickness 6.3 mm) using a CEAST 6548/000 pendulum. The notches (depth 2.54 mm, radius 0.25 mm) were machined after IM. A minimum of eight specimens was tested for each determination.

The fracture surfaces of IM specimens were observed after gold coating using a scanning electron microscope (SEM) Hitachi S-2700, operated at 15 kV.

3. Results and discussion

3.1. Processing temperature

The 75/25 blend in the melt as well as in the solid state after injection moulding (IM) was opaque. This proves the expected immiscibility and the presence of two phases. Additional information concerning the chemical nature of the phases was attained by means of the DMTA results. Four clear peaks were seen in the tan δ plot of the blends; their temperature and strength corresponded to the T_g's of PSU, polybutadiene (PBD) and styrene-acrylonitrile (SAN) and to the low-temperature secondary transition of PSU.

The values of the T_g's of the IM blends processed at different temperatures, as well as those of the pure components, are collected in Table I. With the aim of comparison with a recognized mixing method, the T_g's of kneaded and compression-moulded (CM) 75/25 blends were also measured and are shown in Table II. As can be seen, the T_g values of both IM and CM blends are very similar. This proves that the attained mixing level in this 75/25 blend, whatever the temperature, is very similar both in IM and in CM blends and indicates that direct IM, as in other polymer blends [10], may be successfully used in this blend. As can be seen in both Tables I and II, with small variations, the T_g of SAN remains unchanged after blending, but a slight decrease is seen in the T_g of PSU and a fairly clear slip towards higher temperatures in that of PBD. Thus, although immiscibility is clear, it is dubious to consider all the phases as being chemically pure, especially in the case of PBD.

A progressive increase in T_g with increasing processing temperatures, such as that which took place in PBD, could also be due to degradation by reticulation [2]. However, in CM blends, for instance, at the minimum processing temperature of 240 °C, there is a T_g change of 10 °C. Moreover, a temperature change of 20 °C at 280 °C is so high that it could not only be due to degradation. The presence of oligomers [11] may also be partially responsible for the shift in the T_g's, so that the shift of the T_g of the PSU phase is not significant enough. However, taking into account the comparatively large T_g change, the presence in the PBD phase of a low content of another component, probably PSU, has to be taken into account.

In order to elucidate the origin of the increase in T_g of the PBD, pure ABS was processed by kneading at the same processing parameters as those used for the blends. It was supposed that the PSU presence will

TABLE I T_gs of the IM blends processed at different temperatures (T_{proc}). T_{g_1}, T_{g_2} and T_{g_3} are the T_gs of the phases rich in PBD, SAN and PSU, respectively

PSU/ABS	T_{proc} (°C)	T_{g_1} (°C)	T_{g_2} (°C)	T_{g_3} (°C)
100/0	320			197
75/25	250	− 51	119	188
75/25	260	− 40	120	188
75/25	270	− 39	118	189
0/100	250	− 62	116	

TABLE II T_gs of the CM blends processed at different temperatures (T_{proc}). Symbols as in Table I

PSU/ABS	T_{proc} (°C)	T_{g_1} (°C)	T_{g_2} (°C)	T_{g_3} (°C)
100/0	260			197
75/25	240	− 57	117	193
75/25	250	− 52	113	190
75/25	260	− 55	115	190
75/25	280	− 47	116	190
0/100	260	− 67	115	

TABLE III T_gs of the neat ABS processed at the same conditions as those of the blends of Table II and change of T_g due to the presence of PSU (ΔT_{g_1}). Other symbols as in Table I

T_{proc} (°C)	T_{g_1} (°C)	ΔT_{g_1} (°C)	T_{g_2} (°C)
240	− 68	11	116
250	− 67	15	115
260	− 67	12	115
280	− 62	15	115

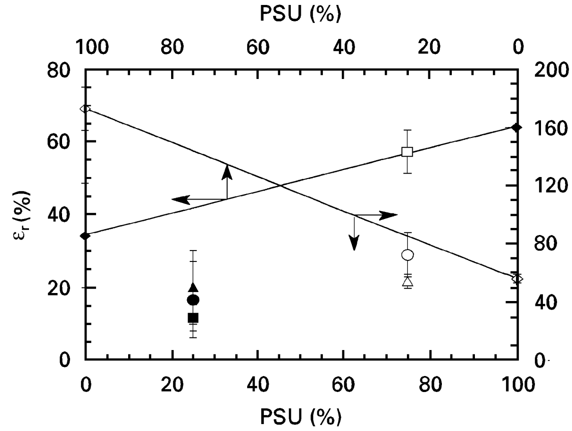


Figure 1 (■, ●, ▲, ◆) Break strain and (□, ○, △, ◇) impact resistance of 75/25 IM blend obtained at (■, □) 250 °C, (●, ○) 260 °C and (▲, △) 270 °C and (◆, ◇) those of their components.

not have an important effect on the possible degradation of the much less viscous ABS. The values of T_g's in DMTA are collected in Table III. As can be seen, leaving aside the constancy of the T_g of the SAN phase, and with the exception of 280 °C where the small increase is very probably due to degradation, the T_g of PBD remains constant. This clearly denies a possible degradation and the presence of SAN in the PBD-rich phase of the PSU/ABS blends as reasons for the observed T_g increase. Thus, it indicates that it appears to be due to the presence of a slight amount of PSU in the PBD phase.

If the content of the minority component was calculated for both IM and CM blends by means of the Fox equation [12]

$$\frac{1}{T_g} = \frac{w_a}{T_{g_a}} + \frac{w_b}{T_{g_b}} \tag{1}$$

where T_g is the T_g of the blend, T_{g_a} and T_{g_b} are the T_g's of the pure materials and w_a and w_b are their corresponding weight fractions, and taking into account the contribution of the degradation of ABS at a processing temperature of 280 °C, the PBD content in the PSU phase would be negligible (1%–1.5%) but the PSU content in the PBD-rich phase would be roughly between 9% and 13%.

The processing temperature appears to have little effect on the amount of PSU in the PBD-rich phase. This is because, as seen in Tables I and III, its effect, i.e. the difference of T_g of PBD in the blend and in neat ABS, is fairly similar whatever the processing temperature. This is not what takes place in other polymer blends [10], although the slight tendency towards miscibility in this PSU/ABS blend may account for this different behaviour.

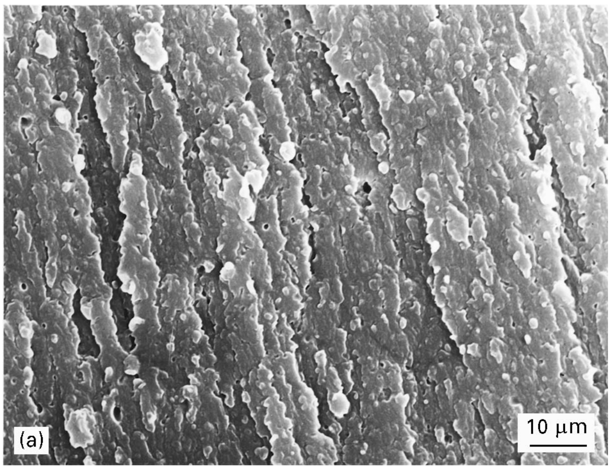
Most of the mechanical properties of the IM blends were almost independent of the moulding temperature in the range studied. This agrees with the observed similar increase in T_g because of the presence of PSU. Most of the mechanical properties were also very close to the additive values obtained from the composition of the blend and the properties of the two components. Thus, in the case of the modulus of elasticity and the yield and break stresses, the deviations from additivity of these properties at the different injection temperatures were clearly smaller than the typical standard deviation of the measurement. With respect to the fracture properties, in Fig. 1 the ductility and impact resistance of the blends against composition are shown. As can be seen, in the case of ductility, large changes with processing temperature were not seen, but the most clear negative deviations from additivity were observed in this property.

The impact resistance, Fig. 1, clearly changed with processing temperature, giving, in contrast to that seen in ductility, values not far from additivity and even a positive deviation at the minimum processing temperature. This is surprising, because the plane strain conditions characteristic of the impact tests are prone to produce brittle responses [13] even in ductile polymers such as PC [5]. It is helped, however, by the fact that an interfacial minimum adhesion typical for Van der Waals interactions is enough to provide good impact properties in rubber-toughened blends [14]. It is also known [1] that the particle size and, as a consequence, the distance between particles, has a relevant influence in the impact resistance. Thus, the morphology is an important parameter when fracture properties are discussed. This is why the broken surfaces of the tensile and impact specimens were observed by SEM.

The morphology of the tensile fractured specimens (Fig. 2a) was difficult to observe. This was because the fracture was mainly cohesive and, as a consequence, few particles could be observed. However, in cryogenic conditions (Fig. 2b), debonding of particles was general, and as a consequence, the structure was clearly denoted. The blends injected at the other two temperatures showed similar morphologies and size. As can be seen, the dispersed phase is small, roughly 1 μm. This indicates that the attained mixing level in IM in this case, as took place in other blends [10], is comparable to that obtained in mixing machines. The morphology of the impact specimens (Fig. 3), however, also fairly independent of injection temperature, was much coarser than that of the tensile specimens. The parameters of the injection machine and the moulding conditions, (cooling water temperature for instance), were the same. Thus, the differences may be due to the geometry of the specimens, thicker in the case of the impact specimens. The slower cooling rate to which it gives rise, may allow particles to coarsen. Coarsening was also observed in the blends when the particle size of kneaded blends before CM was compared with that of CM blends.

These different morphologies must influence the mechanical response in tensile and impact tests. It is known that a fine particle size or low interparticle distance, when below the critical interparticle distance [14] (which is a property of the matrix) or below the critical matrix ligament thickness [15], is positive because it toughens the matrix. This is the opposite to that which takes place in this case, where coarser morphologies in impact specimens produced remarkable impact resistance, but fine tensile morphologies produced bad ductility. However, it must be taken into account that impact tests in unnotched specimens place a great emphasis upon ductility prior to crack initiation; but this is not the case in sharply notched specimens where the resistance to crack propagation, i.e. when fracture has begun, is the most important measured parameter. Additionally, besides particle size, the mechanical response closely depends on the mode and rate of deformation, which are very different in tensile and impact tests. All these facts must also be taken into account when these two fracture properties, ductility and impact resistance, are compared and related to structure.

Thus, 75/25 PSU/ABS blends are basically immiscible blends. Among the small T_g changes observed, only that of the PBD may be related to the presence of other components, PSU in this case. The observed T_g changes and the mechanical stress properties of the blends are practically independent of the injection temperature. The small-strain mechanical properties are close to additivity. The different behaviours with respect to the additive values of ductility, which is below, and the impact resistance, which is very close, are attributed to the different mode and rate of deformation characteristic of each test.



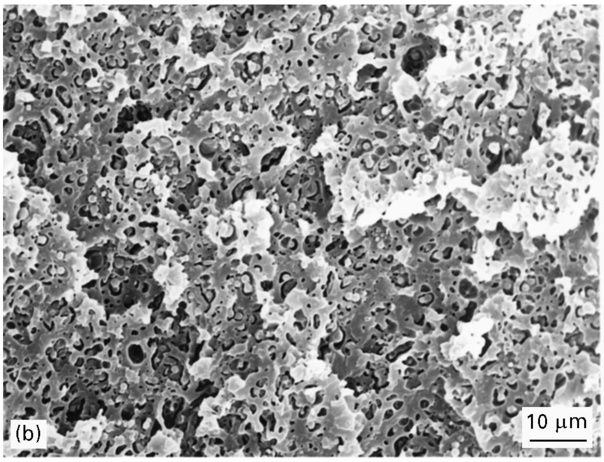


Figure 2 Scanning electron micrographs of tensile specimens of the 75/25 IM blend obtained at 260 °C: (a) fracture surface, and (b) cryogenic fracture surface.

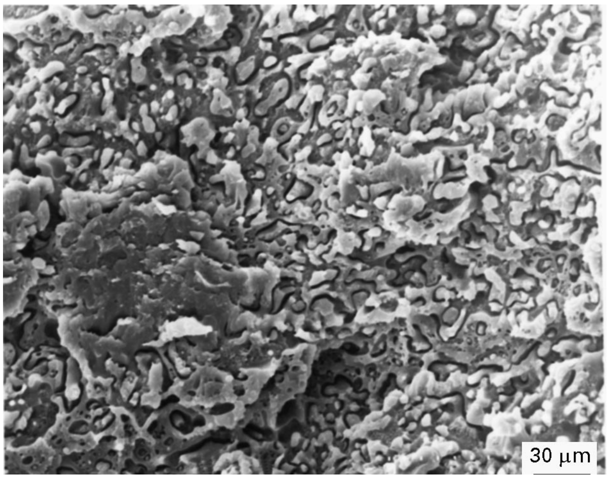


Figure 3 Scanning electron micrographs of the fractured impact specimens of the 75/25 IM blend at 250 °C.

3.2. ABS content

In an attempt to determine the composition range with the most favourable balance of properties, PSU/ABS blends with ABS contents of 5%, 15%, 25% and 35% were obtained by IM at 260 °C. ABS clearly improved the processability of PSU because ABS contents of 15% and 25%, for

TABLE IV T_gs of the IM blends. Symbols as in Table I

PSU/ABS	T_{proc} (°C)	T_{g_1} (°C)	T_{g_2} (°C)	T_{g_3} (°C)
100/0	320			197
95/5	260		117	195
85/15	260	− 41	117	191
75/25	260	− 40	120	188
65/35	260	− 50	119	184
0/100	250	− 62	116	

TABLE V T_gs of the CM blends. Blending and moulding temperature 260 °C. Symbols as in Table I

PSU/ABS	T_{g_1} (°C)	T_{g_2} (°C)	T_{g_3} (°C)
100/0			197
95/5		117	194
85/15	− 48	115	193
75/25	− 55	115	190
65/35	− 57	114	189
0/100	− 67	115	

instance, decreased by roughly 30% and 50%, respectively, the kneading torque of PSU. In all the compositions and whatever the moulding method, the blends were opaque, indicating, as is well known, immiscibility. The nature of the phases of the blends was studied by DMTA. As can be seen in Tables IV and V, where the T_gs of the IM and CM blends, respectively, are shown, the T_g values of the IM and CM blends are very similar, whatever the composition. This indicates the good mixing level attained in direct IM at all the ABS contents studied.

As seen in Tables IV and V, the T_g of the SAN phase did not change with the composition in either the IM or CM blends, but as seen before, both the T_g of the PSU and mainly that of the PBD phase slip towards the T_gs of PBD and PSU, respectively. The change of T_g of PSU was seen not to be significant enough, and thus, the possible presence of other components negligible. However, the change in the T_g of PBD, as took place in the 75/25 blend, is significant. Moreover, it takes place at a constant processing temperature, and depends on the composition, so that it is typical for blends with the presence of one component in the other. Thus, this is additional support for the stated slight presence of PSU in the PBD-rich phase.

Before discussing the mechanical properties, the effect of adding ABS on the tracking resistance of PSU was tested. This is interesting due to the wide use of polysulphones because of their relevant electrical properties [9]. In Fig. 4 the comparative tracking indexes of the blends are shown plotted against composition. As can be seen, the indexes remain constant with composition, but a remarkable increase with respect to the index of PSU is seen when even very small amounts of ABS (5%) are present in the PSU matrix. This is an important practical fact, but not unexpected given the high CTI of ABS that exceeds 600 V, which is the maximum value that the technique can provide.

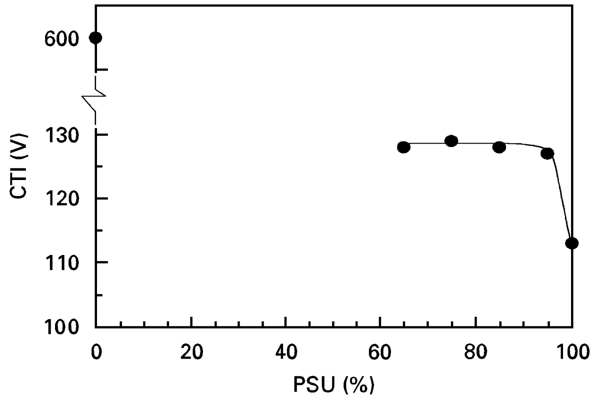


Figure 4 Comparative tracking index of the IM blends obtained at 260 °C as a function of composition.

Thus, when ABS content increases, the CTI remains constant. This is a fairly surprising result because it is supposed that in the path where tracking occurs, that is roughly 2 mm wide, the amount of ABS should be important. A tentative possibility is that a concentration of the less viscous ABS in the skin of the specimens could have occurred during moulding. Given that tracking is a totally surface process, this would give rise to CTI values almost independent of composition. For this reason, the skin of the specimens was carefully observed, but no ABS concentration was found there. Thus, this indicates that only small amounts of a second tracking-resistant component are enough for a significant increase in CTI to be obtained.

With respect to the mechanical properties, when the ABS content changed, both the modulus of elasticity and the yield stress showed a fully additive response between those of the pure components (2000 and 1270 MPa for the moduli of elasticity and 68 and 26 MPa for the yield stress of PSU and ABS, respectively). Thus, the rest of the compositions follow the trends observed in the 75/25 blend. The ABS presence in PSU changed the shape of the tensile curves. This is because the stress drop after the yield stress that was vertical in the case of PSU, appeared progressively smoother as the ABS content increased. This indicates that ABS takes part actively in the mechanical response of the blends and that the dominant deformation mechanism changes. This is in accordance with the localized yielding of PSU which became more diffuse as the ABS content increased.

The ductility of the blends, which is shown plotted against composition on the left side of Fig. 5, was again far from the additive values. The impact resistance, however, was fairly additive, even with a small synergism at an ABS content of 5%. Thus, taking into account the overall linearity of the other properties, the blends poor or very poor in ABS and showing a slight synergism in impact strength with the minimum ductility decrease, appear to be those which offer the best balance of properties among the compositions studied. The structure of the broken surface of the cryogenically fractured tensile specimens was fairly fine (1 μm) with the exception of the 65/35 blend,

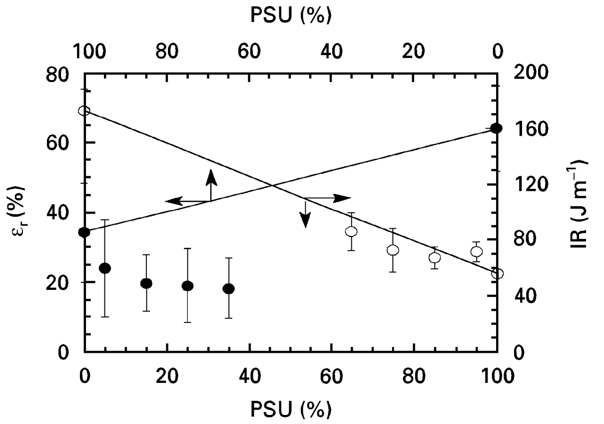


Figure 5 (●) Break strain and (○) impact resistance of the IM blends obtained at 260 °C as a function of composition.

where larger particles (roughly 3 μm) were observed. The fine structures, however, were not able to give rise to additive ductility values. The coarse structures (roughly 3 μm) of the impact specimens, however, gave additive values. This behaviour agrees with that observed when the processing temperature was changed and indicates again that the toughening effect is not accompanied by a similar positive effect on ductility.

As seen before, the different mode and rate of deformation and the notch presence must account for this different behaviour of ductility and impact resistance. The subject, however, is far from fully understood. For instance, a similar behaviour was found in kneaded and CM PC/ABS blends [3] where, despite the appearance, albeit small, of a decrease in ductility, a maximum in impact strength was seen in the ABS-poor composition side. However, PC/ABS blends [4] after IM gave fairly additive and even synergistic values of the two properties in the ABS minority range. The different PBD content of ABS may partially account for the different responses observed. The opposite behaviour to that seen here was shown when toughening was carried out by the dispersion of a brittle phase in a tough matrix. Thus, phenoxy/SAN blends [16] of low phenoxy contents gave synergistic break strains, while impact strength was low. IM PSU/SAN blends also gave rise [17] to a very slight (5–7 °C) T_g change in the SAN phase and to an opposite break behaviour to that shown here. This is because ductility was even above additivity while impact resistance was poor. This was despite the morphology that was, as in these PSU/ABS blends, fine in tensile specimens (0.5 μm roughly) and coarse in selected areas of the impact specimens. Finally, other almost fully immiscible polymer blends, composed of two tough polymers, have also shown remarkable ductility [18], but incompatibility is the usual rule. This is especially true in CM blends where the lack of orientation avoids the compatibilization of the blend [19].

Thus, PSU modified with minority ABS contents, despite the almost full immiscibility of the components, show an overall positive balance of properties. This is because, besides the generally found additivity of the small strain properties and the improved processing, the fracture properties are not those proper to an immiscible blend but they show a tolerable decrease in the case of ductility and a remarkable and practically relevant impact resistance.

4. Conclusions

PSU/ABS blends are almost immiscible blends. The observed PSU phase is almost pure but a small presence of PSU in the PBD phase is indicated because of the comparatively large T_g change. IM gives rise to fine structures that show a great tendency to coalesce. This is because of the increased particle size during CM and because of the larger particle size of the IM impact specimens compared with that of tensile ones.

Changes in the injection temperature, in the range that allows suitable mixing, do not show a notable influence either in the structure or in the small-strain mechanical properties of the 75/25 blend. However, ductility slightly, and mainly impact resistance, were affected.

The CTI of the blends clearly increased when only 5% ABS was added. Larger ABS contents did not increase the CTI. This is not due to the morphology of the blends, so it indicates that, provided a minimum amount of second phase is present, the CTI is independent of the blend composition.

The small strain properties remain additive whatever the ABS content. Ductility is fairly low, but impact resistance shows an overall additive behaviour. Thus, low ABS contents, close to 5%, are the most beneficial for fracture properties giving rise, with the exception of ductility, to values close to additivity or even synergistic in such an important property as impact strength. This allows PSU/ABS blends to be presented as a new family of rubber-toughened polymer blends.

Acknowledgement

The financial support of the Basque government (Project number P193/102) is gratefully acknowledged.

References

1. J. H. CHUN, K. S. MAENG and K. S. SUH, *J. Mater. Sci.* **26** (1991) 5347.
2. J. I. EGUIAZÁBAL and J. NAZÁBAL, *Polym. Eng. Sci.* **30** (1990) 527.
3. W. CHIANG and D. HWUNG, *ibid.* **27** (1987) 632.
4. B. S. LOMBARDO, H. KESKKULA and D. R. PAUL, *J. Appl. Polym. Sci.* **54** (1994) 1697.
5. M. ISHIKAWA and I. CHIBA, *Polymer* **31** (1990) 1232.
6. M. P. LEE, A. HILTNER and E. BAER, *Polym. Eng. Sci.* **32** (1992) 909.
7. A. K. KULSHRESHTHA, *Polym. Plast. Technol. Eng.* **32** (1993) 551.
8. A. K. GUPTA, A. K. JAIN, B. K. RATNAM and S. N. MAITI, *J. Appl. Polym. Sci.* **39** (1990) 515.
9. J. A. BRYDSON, "Plastics Materials" (Butterworth Scientific, London, 1982).

10. R. ERRO, M. GAZTELUMENDI and J. NAZÁBAL, *J. Appl. Polym. Sci.* **45** (1992) 339.
11. T. A. CALLAGHAM, K. TAKAKUWA and D. R. PAUL, *Polymer* **34** (1993) 3796.
12. T. G. FOX, *Bull. Am. Phys. Soc.* **1** (1956) 123.
13. K. J. PASCOE, in "Failure of Plastics", edited by W. Brostow and R. D. Corneliussen (Hanser, Munich, 1986) p. 150.
14. S. WU, *Polymer* **26** (1985) 1855.
15. *Idem*, *J. Appl. Polym. Sci.* **35** (1988) 549.
16. S. M. LEE, C. H. CHOI and B. K. KIM, *Eur. Polym. J.* **30** (1994) 993.
17. B. E. RUIZ DE GAUNA, M. GAZTELUMENDI and J. NAZÁBAL, *ibid.* in press.
18. A. ARZAK, J. I. EGUIAZÁBAL and J. NAZÁBAL, *J. Appl. Polym. Sci.* **58** (1995) 653.
19. J. I. EGUIAZÁBAL and J. NAZÁBAL, *Plast. Rubb. Proc. Appl.* **14** (1990) 211.

Received 16 February
and accepted 31 July 1996.