Polystyrene and Polyether Polyurethane Elastomer Blends Compatibilized by SMA: Morphology and Mechanical Properties

SILVANA NAVARRO CASSU, MARIA ISABEL FELISBERTI

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13.083-970, Campinas, SP, Brazil

ABSTRACT: Blends of polystyrene (PS) and the polyether polyurethane elastomer (PU-et) were prepared by melt mixing using poly(styrene-*co*-maleic anhydride) (SMA) containing 7 wt % of maleic anhydride as a compatibilizer. The polyurethane in the blends was crosslinked using dicumyl peroxide or sulfur. The content of maleic anhydride was varied in the blends through the addition of different SMA amounts. The morphology of the blends was analyzed by SEM and a drastic reduction of both the domain size and its distribution was observed with increase of the anhydride content in the blends. The morphology of the PU-et blends also showed dependence on the crosslinker agent used for the elastomer, and larger domains were obtained for the elastomer phase crosslinked with dicumyl peroxide. The mechanical properties of the blends were evaluated by flexural and impact strength tests. The blend containing 0.5 wt % of maleic anhydride and 20 wt % of PU-et crosslinked with sulfur showed the highest strength impact, which was three times superior to the PS strength impact, and the blends containing 20 wt % of PU-et crosslinked with dicumyl peroxide showed the highest deflection at break independent of the anhydride content. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 830–837, 2002

Key words: reactive compatibilization; PS/SMA/PU blends; mechanical properties

INTRODUCTION

Polymer blends have received attention in the last decades because the mixing process of different polymers results in a great number of new materials, which can show completely different characteristics of the starting polymers. Another and more recent reason for blending different polymers is the recycling of them. However, the immiscibility of most polymer pairs results in materials with a coarse morphology and poor physical properties. To overcome this problem and to improve the mechanical properties of immiscible blends, block or graft copolymers have been used as compatibilizers.[1,2] Compatibilizers act as emulsifiers, reducing the interfacial energy of the phases and the domain size.[3] It is also possible to generate a graft copolymer *in situ* by using the reactive blending technique. In this blending process, in general, one phase contains reactive groups inherent in the polymer chains while the other has no inherent functionality. Reactive groups can be incorporated into the second phase by adding to it a functionalized polymer miscible with it. In some cases, both phases have to be functionalized. The *in situ*-generated copolymer compatibilizer is located preferentially at the interface, reducing the size of the dispersed phase and improving the interfacial adhesion and the physical properties of the blends.[4]

Table I Characteristics of the Starting Polymer

Polymer	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	Flexible Segment	Source
PS	293,000	1.90	—	CBE[a]
SMA	283,000	1.96	—	Aldrich[b]
PU-et	201,000	1.90	Poly(tetramethylene oxide)	Uniroyal Chemical[c]

[a] Companhia Brasileira de Estireno, São Paulo, Brazil.
[b] St. Louis, MO.
[c] São Paulo, Brazil.

Poly(styrene-*co*-maleic anhydride) (SMA) has been used as an effective compatibilizer for immiscible and incompatible blends of polyamide-6 (PA6) and poly(phenylene oxide) (PPO). The overall improvement in the mechanical properties was drastic after compatibilization.[5] The addition of SMA into blends of amorphous polyamide (a-PA) and the styrene–acrylonitrile copolymer (SAN) leads to the enhancement of interfacial adhesion and the tensile properties were improved until 10 wt % of SMA content.[6] SMA has also been used in blends containing poly(ethylene-*co*-vinyl alcohol) (EVAL) prepared by melt mixing.[7]

The reaction between the hydroxyl group of EVAL and anhydride groups of SMA leads to the formation of branched and crosslinked molecules, which can cause stabilization of the morphology. In these blends, the content of hydroxyl and maleic anhydride groups was changed and the best combination of mechanical properties was observed for low concentrations of hydroxyl groups with respect to anhydride groups.

In this study, the SMA copolymer was used as a compatibilizer for immiscible blends of polystyrene (PS) and the polyether polyurethane elastomer (PU-et). The anhydride groups of SMA reacts with the PU-et, generating a graft copolymer, which reduces the interfacial energy, promoting a better domain distribution as well as a reduction of the domain size.[8] In the present work, the mechanical properties of the blends were analyzed and correlated to the morphological blend characteristics.

EXPERIMENTAL

The characteristics of the materials used to prepare the blends are summarized in Table I. The PU-et used contains as a hard segment toluene diisocyanate (TDI), containing 80% of the 2,4 isomer and 20% of the 2,6 isomer. The TDI concentration was approximately 4 wt %. PU-et also contains low concentrations of unsaturated groups.[9]

Melt Mixing

PS/PU-et and SMA/PU-et binary and PS/SMA/PU-et ternary blends containing 10 and 20 wt % of PU-et were prepared by melt mixing in an internal mixer, a Haake Rheometer 600, at 30 rpm and 190°C for 12 min, while the torque was recorded. After 2 min of mixing, dicumyl peroxide was added to the blends (1.2 wt % as recommended by the supplier[9]). Blends containing 2 wt % of sulfur were also prepared. Either dicumyl peroxide or sulfur was added to the blends to promote PU-et crosslinking, improving its mechanical properties. To study the effect of the compatibilizer content, ternary blends PS/SMA/PU-et were prepared with the content of maleic anhydride varying between 0.5 and 7 wt %. The desired maleic anhydride concentration in the blends was achieved by addition of different SMA amounts to the blends (Table II). The blends were compression-molded into plates of 1.35-mm thickness using a hot press at 200°C, under 4.4 MPa for 3 min.

Table II Anhydride Content in the Blends

Anhydride (wt %)	PS (wt %)	SMA (wt %)
0	100	—
0.5	93	7
1.0	86	14
3.0	56	44
5.0	28	72
7.0	0	100

Morphology

The morphology of the binary and ternary blends obtained by melt blending was analyzed by scanning electronic microscopy. Fractured samples of the PU-et blends were refluxed during 24 h in a 5% v/v phosphoric acid aqueous solution to promote the hydrolysis of the PU-et chains. The extracted surface was coated with a gold layer and then the morphology of the blends containing up to 1 wt % of anhydride was examined with a JEOL JSTM-300. All other blends were examined with an FE-SEM JSM–6340F microscope.

Image Pro-Plus—The Proven Solution software was used to determine the particle-size distribution and the average diameter ($\bar{M}_w$). Approximately 150 particles were analyzed for each blend.

Mechanical Tests

Flexural tests were performed in a universal test machine, EMIC 2000, in accordance with ASTM D 790 using a crosshead speed of 1 mm/min. The dimensions of the samples were 58.0 × 12.8 × 1.30 mm. Impact strength tests were carried out using Izod notched bars (ASTM D-256) (thickness, 3.175 mm) obtained by injection in a Mini-Max Atlas–LMM at 150°C.

RESULTS AND DISCUSSION

Morphology

The influence of the anhydride content on the morphology of the PS/SMA/PU-et blends containing 10 wt % of the elastomeric phase crosslinked with sulfur is shown in Figure 1. For all the blends, spherical particles of PU-et were dispersed in a rigid and continuous phase. A similar morphology was observed for the blends containing 20 wt % of the PU-et independently of the crosslinker agent used for the elastomer. In the blends with above 3 wt % anhydride content, some agglomeration can be seen [Fig. 1(d–f)], which are attributed to the PU-et phase not extracted by hydrolysis, because a fraction of the PU-et is chemically bound to the matrix, as proposed in a previous article.[8]

Figure 2 shows the average diameter size of the PU phase as a function of the anhydride content in the PS/SMA/PU blends. The bar at each point is related to the maximum and minimum domain size found for each blend. In the absence of anhydride groups, that is, in PS/PU blends, a broad distribution of the domain size was observed and the average size of the dispersed domains was 2.6 μm for the blends containing 10 wt % of PU-et, crosslinked with dicumyl peroxide. Meanwhile, when the anhydride was added to the blends, the domain size drastically decreased and seemed to reach a plateau for about 3 wt % of SMA. In the blends containing 7 wt % of anhydride (SMA/PU blends), the domain sizes were of the order of 0.050 μm. Moreover, the distribution of the domain sizes became narrower with increase of the anhydride content in the blends. Identical behavior was observed for PA6/SAN blends[6] and PA6/poly(phenylene oxide) blends,[5] both obtained by melt blending using the SMA copolymer as a compatibilizer.

Cho et al.[6] also observed the reduction of the domain size and of the distribution size in the PA6/SAN blends with increase of the SMA content. The first one was attributed to the reduction of the interfacial tension due to the presence of the in situ-formed graft copolymers at the interface. However, the breadth decrease of the domain-size distribution with an increase of the SMA content could not be explained by the reduction of interfacial tension alone. The authors[6] attributed this behavior to phase coalescence, which is also an important factor in determining the final blend morphology in the melt blending.

In blends obtained without the SMA copolymer, very small domains may result from the breakup process in the high shear regions, while increased coalescence due to interactions of the domains will result in very large domains. However, in the blends containing the SMA copolymer, the coalescence is prevented because the in situ-formed graft copolymers at the interface stabilizes the morphology. As a result of increasing SMA content in the blends, the breadth of the domain-size distribution became narrower due to the suppression of the phase coalescence between the small domains.[6] This can be clearly observed for PS/SMA/PU-et blends containing above 3 wt % of anhydride [Fig. 1(d–f)].

The crosslinker agent used also affected the domain size. In the PU-et blends containing up to 1 wt % of anhydride, the size of the elastomer particles crosslinked with dicumyl peroxide was at least twice larger than were those obtained with sulfur. This behavior should be related to the reaction mechanisms that occur in each case. The crosslinking mechanism of an unsaturated elastomer with sulfur is not completely understood. However, it is believed that sulfur must be preferentially bonded to unsaturated groups.[10] On
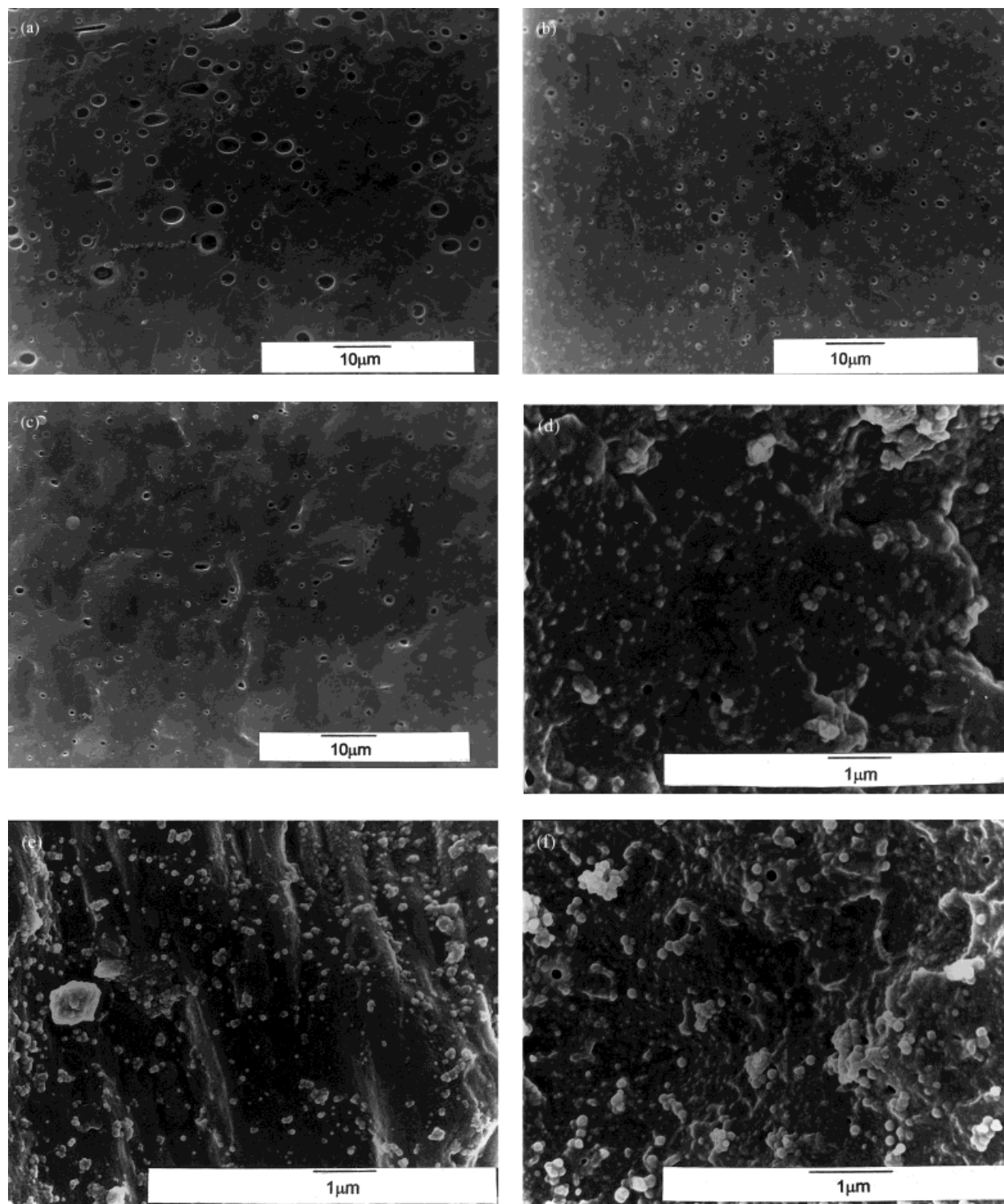
Figure 1   SEM micrographs of the blends containing 10 wt % of PU-et crosslinked with sulfur and different anhydride contents: (a) 0 wt % (×1500), (b) 0.5 wt % (×1500), (c) 1.0 wt % (×1500), (d) 3.0 wt % (×15,000), (e) 5.0 wt % (×10,000), and (f) 7.0 wt % (×20,000).

the other hand, free radicals generated from the thermal decomposition of the dicumyl peroxide are able to attack other groups besides unsatur-

ated groups.[11,12] Therefore, the density of the crosslinking achieved in the PU-et domains in blends containing dicumyl peroxide should be
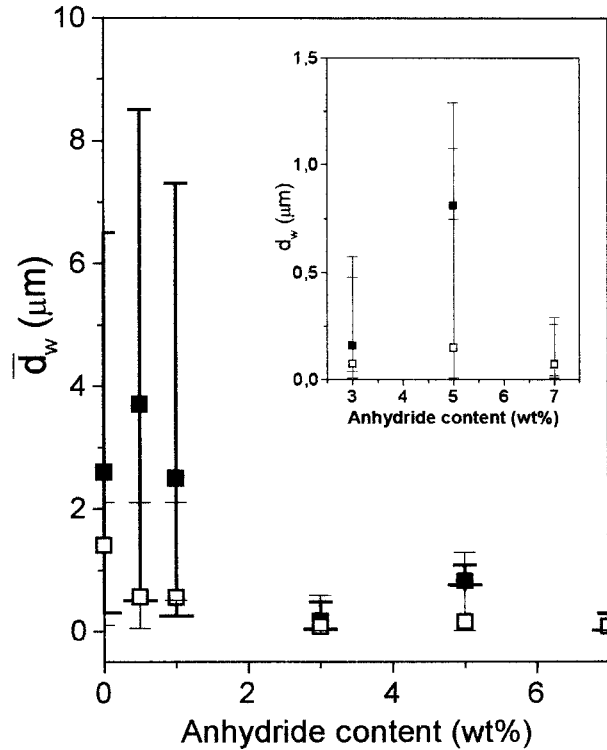
Figure 2 Average diameter of the dispersed phase in the blends containing 10 wt % of PU-et. Crosslinker agents: (■) dicumyl peroxide; and (□) sulfur.

higher than in blends obtained with sulfur, since the polyurethane used in this study possesses a low concentration of unsaturated groups. This effect can be seen in the torque versus time curves for the PS/PU-et blends containing different crosslinker agents, dicumyl peroxide and sulfur, and no crosslinker agent [Fig. 3(a)]. The torque at the equilibrium of the PS/PU-et blends without a crosslinker agent was the lowest, followed by the torque of PS/PU-et blend containing sulfur. The highest torque was observed for the PS/PU-et blend with dicumyl peroxide, showing that this blend possesses the highest viscosity, which made the dispersion of the PU-et phase more difficult and, consequently, larger domains were obtained. When SMA was used as the matrix [Fig. 3(b)], the lowest torque was also observed for the blend without crosslinker agents. However, when dicumyl peroxide or sulfur were added to the SMA/PU-et blend, there was an increase of the torque value and it was very close to both cases. This fact can explain the domain size found for the blends containing a concentration above 3 wt % of anhydride, where the dispersed phase size is similar in the blends containing sulfur or dicumyl peroxide. In these cases, the effect of the crosslinker agent

on the elastomer dispersion must be overlapped by the higher concentration of the *in situ*-formed graft copolymer.
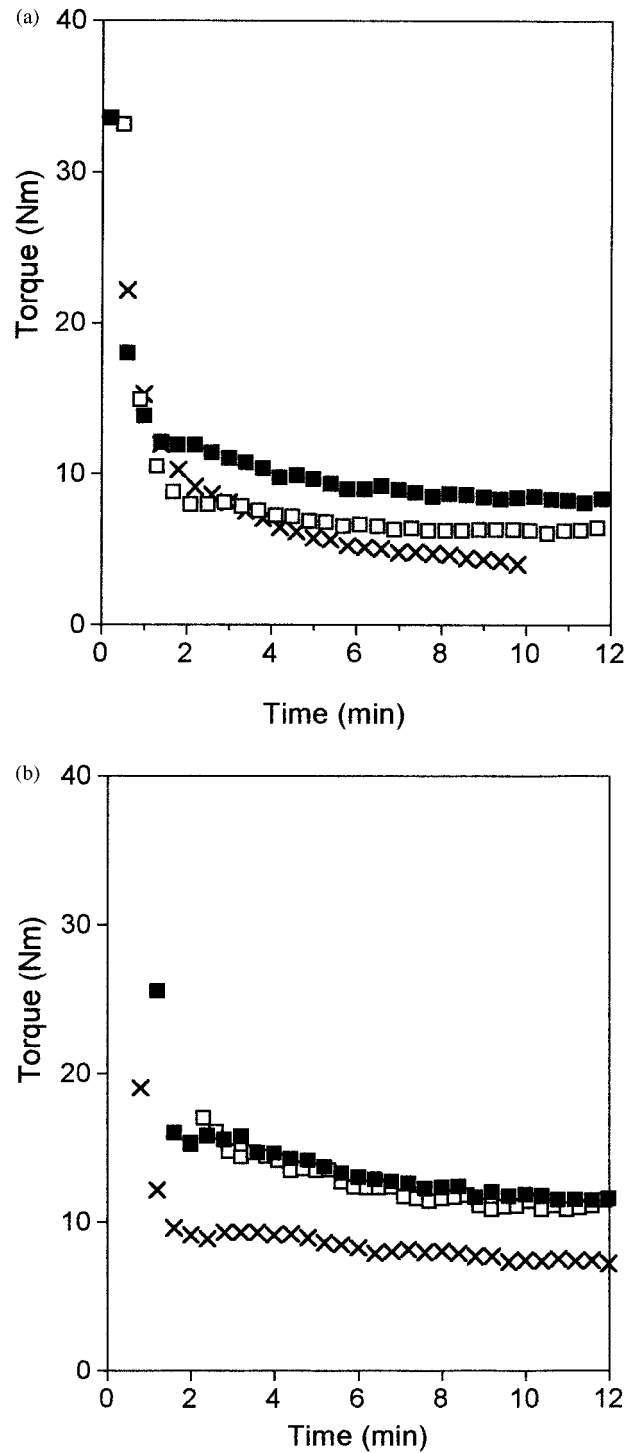

Figure 3 Torque versus time curves of the blends containing 10 wt % of PU-et: (a) PS/PU-et, (b) SMA/PU-et. (—✕—) Blends without crosslinker agents; (—□—) elastomer crosslinked with sulfur; (—■—) elastomer crosslinked with dicumyl peroxide.
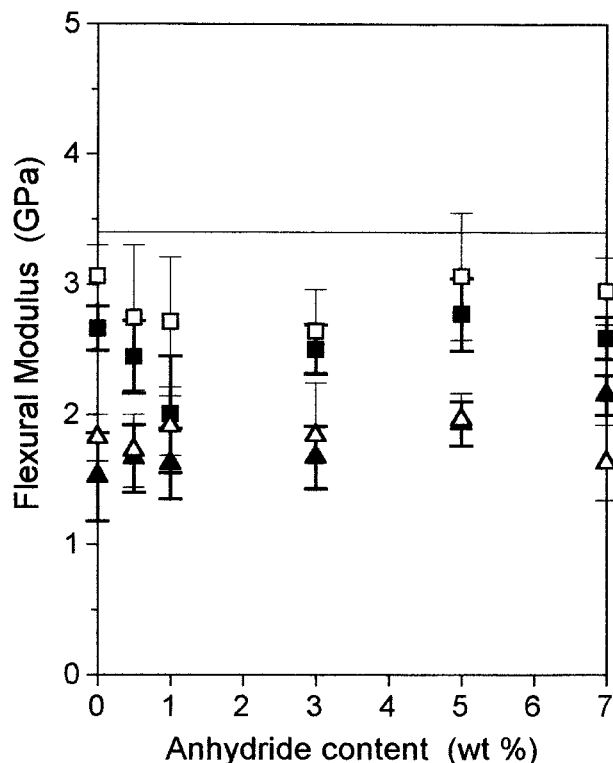
Figure 4 Flexural modulus as a function of the anhydride content for the blends containing PU-et. Blends containing (—■—) 10 and (—▲—) 20 wt % of the PU-et, crosslinked with dicumyl peroxide. Blends containing (—□—) 10 and —△—) 20 wt % of the PU-et crosslinked with sulfur. The continuous line is related to the PS flexural modulus.

Mechanical Properties

The flexural modulus as a function of the anhydride content for the blends with different compositions is shown in Figure 4. In general, the addition of PU-et causes a reduction of the modulus in relation to the homopolymer PS, which is represented by the horizontal line in the graphic. The crosslinking of the PU-et phase and the anhydride content in the blends have a small influence on the flexural modulus.

The deflection at break as a function of the anhydride content for the blends is shown in Figure 5. The deflection at break for the blends is higher than for pure PS. However, for all blends, the deflection at break diminished as the anhydride content increased, independently of the crosslinker agent. This behavior reflects mainly an increase of the stiffness of the matrix with an increase of the anhydride content.[13] The blends containing 20 wt % of PU-et and up to 1 wt % of anhydride crosslinked with dicumyl peroxide

showed the highest deflection-at-break values, which were approximately three times superior to the PS ones.

The impact strength as a function of the anhydride content for the blends is shown in Figure 6. PU-et at 10 wt % in the blends did not cause the improvement of the impact strength with respect to PS, independent of the anhydride content or the crosslinker agent. Meanwhile, blends containing 20 wt % of PU-et showed an impact strength higher than those observed for PS, and the blends with PU-et crosslinked with sulfur containing 0.5 wt % of anhydride showed an impact strength of 60 J/m, which is approximately three times superior to the PS impact strength and half the value found for HIPS [100–120 J/m].[14] Blends with a concentration of anhydride above 1 wt % crosslinked with sulfur showed an impact strength approximately twice higher ($\cong$35J/m) than that of the PS ones. The highest impact strength of the PS/SMA/PU-et blends containing
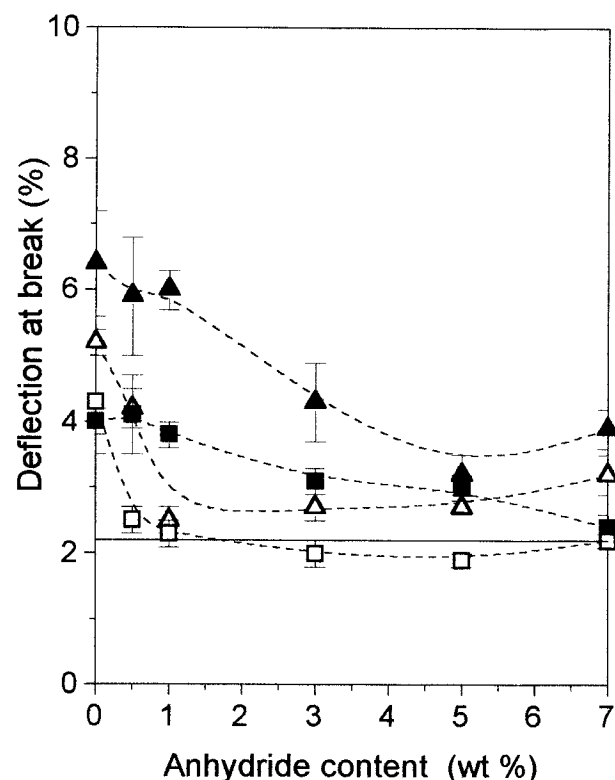

Figure 5 Deflection at break as a function of the anhydride content for the blends containing PU-et. Blends containing (—■—) 10 and (—▲—) 20 wt % of the PU crosslinked with dicumyl peroxide. Blends containing (—□—) 10 and (—△—) 20 wt % of the PU crosslinked with sulfur. The continuous line is related to the PS deflection at break.
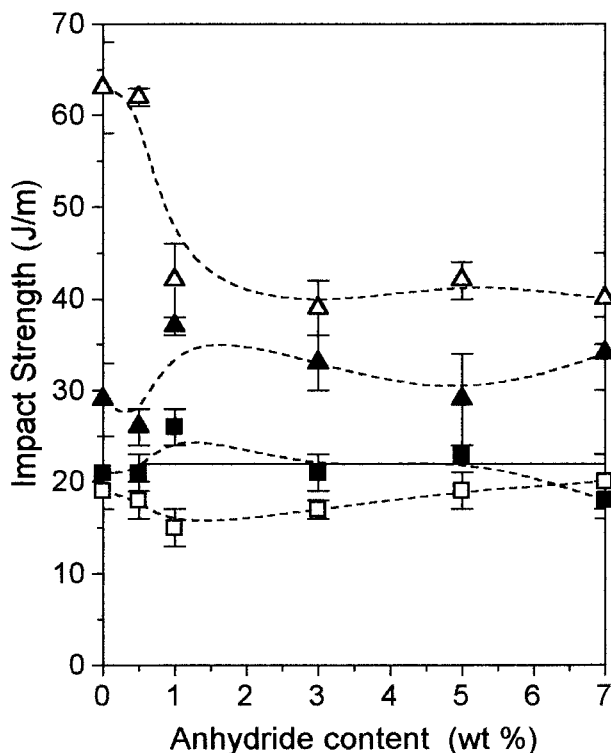
Figure 6 Impact strength as a function of the anhydride content for the PS/SMA/PU-et blends.

than the minimum craze thickness.[14,15] However, it is accepted that small particles (<1 μm) reinforce PS to a much lesser degree than do large particles (2–5 μm) at a constant rubber content.[15] Particles whose diameters are significantly greater than an optimum domain size (2–5 μm to PS) are less effective for craze initiation. The stress-concentration zone is much broader than is the optimum thickness of crazes.[16] These considerations are in accordance with the improvement in impact strength obtained for PS/SMA/PU-et blends containing 20 wt % of the PU-et crosslinked with sulfur with respect to those containing PU-et crosslinked with dicumyl peroxide, which must possess much larger domains to promote the PS toughness.

Even though the domain sizes of the blends containing 10 wt % of PU-et and an anhydride content up to 1.0 wt %, which were crosslinked with dicumyl peroxide, were approximately equal (2.6 μm) to the domain sizes obtained for the blends containing 20 wt % of PU-et crosslinked with sulfur, the impact strength was not improved. This fact must be related to the critical interparticle distance, which was probably not attained in 10 wt % of PU-et.
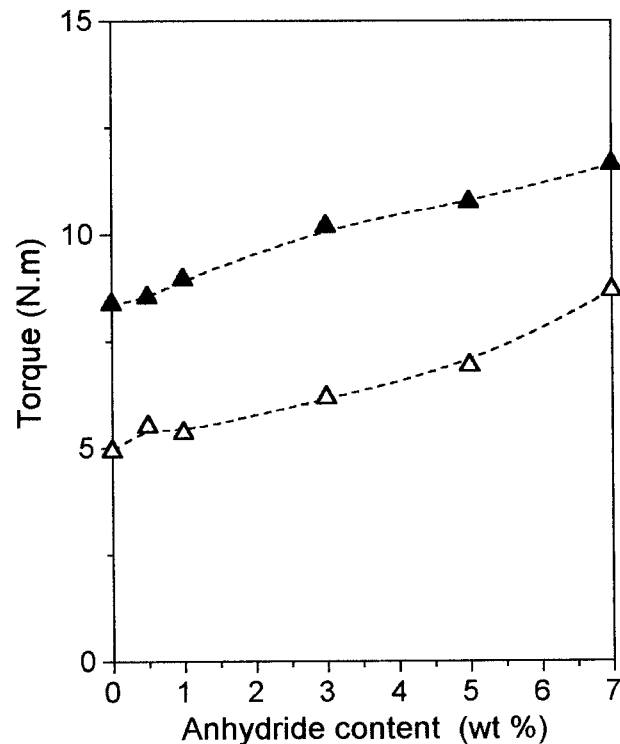
20 wt % of the PU-et crosslinked with sulfur could be related to the size of the dispersed phase. Considering that the domain size increases proportionally to the increase of the PU-et volume fraction, it was expected that the dispersed phase size should vary within 5 and 7 μm for blends crosslinked with dicumyl peroxide, while blends crosslinked with sulfur should have domain sizes varying between 1 and 3 μm.

The domain size must reflect the rheological properties of the mixture. The torque at 7 min of mixing as a function of the anhydride concentration for the blends containing 20 wt % of the elastomer phase crosslinked with different agents is shown in Figure 7. The blends crosslinked with dicumyl peroxide show torque values approximately 1.3 times higher than those of the respective blends crosslinked with sulfur, independent of the anhydride content. Therefore, the viscosity of the former blends is higher, making the dispersion of the PU-et phase more difficult, resulting in larger domain sizes, as predicted.

It is known that the particle size plays an important role in polymer toughening. A minimum effective particle diameter of 0.040 μm for the toughening of PS was established, because the stress-concentration zone must not be smaller

Figure 7 Torque as a function of the anhydride content for the blends containing 20 wt % of the PU-et obtained at 7 min. Blends containing PU-et crosslinked with (—▲—) dicumyl peroxide and (—△—) sulfur.

CONCLUSIONS

The addition of SMA to blends of PS and polyether polyurethane caused a decrease in the diameter of the dispersed phase and the reduction of the distribution of the domain sizes due to the presence of an *in situ*-formed graft copolymer. The diameter of the dispersed phase was also dependent on the crosslinker agents used, dicumyl peroxide or sulfur, and larger domains were obtained with dicumyl peroxide.

The best mechanical properties were reached with the addition of 20 wt % of PU-et and small amounts of the SMA (to 1 wt % of anhydride). The mechanical properties of the blends were also influenced by the crosslinker agent used. Blends containing 20 wt % of PU-et crosslinked with dicumyl peroxide showed the highest deflection at break values, independent of the anhydride content, probably due to the PU-et elastic strength, while the highest impact strength values were obtained to respective blends crosslinked with sulfur, which was related to the more appropriated domain size obtained in these blends.

REFERENCES

1. Sakellariou, P. Polymer 1993, 34, 3408.
2. Xu, S.; Chen, B.; Tang, T.; Huang, B. Polymer 1999, 40, 3399.
3. Fox, D. W.; Allen, R. B. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwits, J. I., Eds.; Wiley: New York, 1988; Vol. 3, p 758.
4. Liu, N. C.; Baker, W. E. Adv Polym Technol 1992, 11, 249.
5. Chiang, C.-R.; Chang, F.-C. Polymer 1997, 38, 4807.
6. Cho, K.; Hoon, K.; Ahn, T. O. J Appl Polym Sci 1998, 68, 1925.
7. Teselios, C. H.; Bikiaris, D.; Prinos, J.; Panayiotou, C. J Appl Polym Sci 1997, 64 983.
8. Cassu, S. N.; Felisberti, M. I. J Appl Polym Sci, to appear.
9. Uniroyal Chemical Co Inc. Catalogue: Adiprene FM.
10. Coran, A. Y. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwits, J. I., Eds.; Wiley: New York, 1988; Vol. 17, p 666.
11. Gaylord, N. G.; Elayaperumal, P. J Polym Sci Polym Lett 1983, 21, 781.
12. Gaylord, N. G.; Mehta, R. J Polym Sci. Polym Chem 1988, 26, 1189.
13. Moore, E. R.; Traugott, T. D. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwits, J. I., Eds.; Wiley: New York, 1988; Vol. 16, pp 1–97.
14. Piorkowska, E.; Argon, A. S.; Cohen, R. E. Polymer 1993, 34, 4435.
15. Schneider, M.; Pith, T.; Lambla, M. J Mater Sci 1997, 32, 5191.
16. Micheler, G. H.; Starke, J.-U. In Toughened Plastics II—Novel Approaches in Science and Engineering; Riew, C. K.; Kinloch, A. J., Eds.; American Chemical Society: Washington, DC, 1996; Series 252, p 251.