

Polystyrene and Polyester Polyurethane Elastomer Blends Compatibilized by SMA

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ABSTRACT: Blends of polystyrene (PS) with polyester polyurethane elastomer (PU-es) were compatibilized by addition of poly(styrene-co-maleic anhydride) (SMA) containing 7 wt % of maleic anhydride. Binary nonreactive (PS/PU-es) blends, binary reactive (SMA/PU-es) blends, and ternary reactive blends (PS/SMA/PU-es) were prepared with 10 and 20 wt % of PU-es. The maleic anhydride content in the ternary reactive blends was varied through addition of different SMA amounts from 0.5 to 5 wt %. Polyurethane in the blends was crosslinked by using dicumyl peroxide or sulfur to improve its mechanical properties. The experimental processing conditions, such as temperature and rotor speed in an internal mixer, were analyzed before blend preparation by processing the individual polymers, PS and SMA, and the PS/PU-es nonreactive blend (90/10), to prevent the degradation of the polymer during melt mixing and to assure

macroscopic homogeneity. The torque behavior during the mixture indicated a grafting copolymerization, which was responsible for the significant drop of the PU-es domain size in the glassy matrix, as observed by scanning electronic microscopy (SEM). The miscibility of the glassy matrix, which was shown to be dependent on the composition and the phase behavior of ternary blends, became very complex as the SMA concentration increased, as concluded from dynamical-mechanical analysis. Blends containing 20 wt % of PU-es presented an increase up to a factor of 2 in the deflection at break in relation to PS. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2297–2304, 2004

Key words: blends; reactive processing; mechanical properties

INTRODUCTION

In polymer blends, immiscibility of the components results in incompatibility of the phases. The first term is a thermodynamic parameter and is responsible for phase segregation, whereas the second one is mainly related to the technological properties of the blends.¹ Incompatible blends generally present coarse morphology and poor physical properties. Compatibility and adhesion between different polymeric phases can be improved by addition of suitable block or graft copolymers that act as interfacial agents. These block or graft copolymers can, in principle, be added to polymer blends. However, because of the lack of economically viable routes for the synthesis of suitable copolymers, these were not used as extensively as their potential utility might suggest. An alternative is to generate these copolymers *in situ* during blend preparation through polymer-polymer graft reactions by using functionalized polymers.^{2,3}

Poly(styrene-co-maleic anhydride) (SMA) was used as a successful reactive compatibilizer in several incompatible polymer blends. Immiscible blends of poly(styrene-co-acrylonitrile) (SAN) and thermoplas-

tic polyurethane (TPU) obtained by melt mixing were compatibilized by the addition of SMA. The best compatibility was attained for the TPU/SAN/SMA (70/30/5) blend.⁴ SMA was demonstrated to be a highly effective compatibilizer for immiscible and incompatible blends of polyamide-6 (PA6) and poly(phenylene oxide) (PPO). The overall improvement in mechanical properties was drastic after compatibilization.⁵ The addition of SMA copolymer in blends of amorphous polyamide (a-PA) and SAN led to the enhancement of interfacial adhesion and the tensile properties were improved up to 10 wt % SMA content.⁶ PA6 and poly(methyl methacrylate) (PMMA) blends were satisfactorily compatibilized by SMA containing 20 wt % of maleic anhydride.⁷ Blends of SAN with poly(ethene-co-1-octene) rubber (EOR) were investigated by Mader et al.⁸ An improved toughness-stiffness balance was achieved when oxazoline-functionalized EOR and SMA were added to the mixture. SMA was used in blends containing poly(ethylene-co-vinyl alcohol) (EVAL) prepared by melt mixing.⁹ The reaction between the hydroxyl group of EVAL and the maleic anhydride groups of SMA leads to the formation of branched and crosslinked molecules, which can cause morphology stabilization of the immiscible blend.

The present work is part of a study of PS/PU immiscible blends containing SMA as a compatibilizer. Initially, we studied the formation of a graft copolymer during the processing of the PS/SMA/PU blends,

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TABLE I
Characteristics of the Starting Polymers

Polymer	\bar{M}_w (g mol ⁻¹)	\bar{M}_w/\bar{M}_n	T_g (°C) ^a	Flexible segment	Source
PS	293,000	1.9	112	—	CBE ^b
SMA	283,000	2.0	127	—	Aldrich
PU-es	107,000	1.9	-22	Polyester adipate based	Uniroyal Chemical

^a T_g values obtained by DSC.

^b Companhia Brasileira de Estireno.

using as dispersed phase polyurethane elastomer containing flexible polyester or polyether segments.¹⁰ The graft copolymer formed *in situ* was responsible for reduction of the domain size of the dispersed phase and by its better distribution in all composition ranges studied. In the present work, the influence of SMA content on the morphology, dynamic mechanical properties, and flexural properties of the blends was studied.

EXPERIMENTAL

The properties of PS, SMA containing 7 wt % of maleic anhydride, and polyurethane elastomer (PU-es) used to prepare the blends are summarized in Table I. The molecular weight and polydispersity of polymers were obtained by gel permeation chromatography with a Waters GPC (Milford, MA), equipped with polystyrene gel columns (Ultrastyrigel). The detector was a refractive index type (Waters 410) and the carrier solvent was THF. PS standards were used for calibration.

The glass-transition temperature (T_g) was obtained by differential scanning calorimetry (DSC) in a MDSC 2910 (TA Instruments, New Castle, DE) in a dry nitrogen atmosphere by using the following methods: initial temperature: 150°C; cooling rate of 10°C/min to -120°C; heating rate of 20°C/min to 250°C.

Indium was used for calibration, and the T_g was obtained from the half-height of the slope change of the heat capacity plot.

Experimental processing conditions of the polystyrene (PS), SMA, and PS/noncrosslinked PU-es (90/10) blend were determined by evaluating the torque of the

melt mixing in a Haake Rheometer 600 (Karlsruhe, Germany) internal mixer, at different rotor speeds (30, 60, 90, and 120 rpm) at 190°C. After these initial tests, the experimental conditions chosen for blend processing were 12 min, 30 rpm, and 190°C.

Binary blends, PS/PU-es and SMA/PU-es, and ternary blends, PS/SMA/PU-es, containing 10 and 20 wt % of PU-es were prepared. The content of the maleic anhydride in the glassy phase varied from 0.5 to 5 wt %, by addition of different SMA amounts to the ternary blends, as shown in Table II. According to the supplier's recommendations,¹¹ after 2 min of mixing, 0.4 wt % of dicumyl peroxide or 2 wt % of sulfur was added to the blends to promote PU-es crosslinking. The blends were compression-molded into plates of 1.35 mm thickness by using a hot press at 200°C, under 4.4 MPa for 3 min.

The morphology of the binary and ternary blends was analyzed by scanning electron microscopy (SEM). Blends were cryogenically fractured, and the PU-es phase was extracted from the fractured samples by refluxing in an ethanolic KOH solution (0.5 mol/L) for 3 h, because polyester is quickly hydrolyzed in alkaline solution. The extracted surface was coated with a gold layer and then the morphology of the PS/SMA/PU-es blend containing up to 1 wt % of anhydride was examined with a JEOL JSTM-300 (Tokyo, Japan) instrument. All other blends were examined with a FE-SEM JSM-6340F (Tokyo, Japan) instrument.

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

TABLE II
Anhydride, PS, and SMA Contents in the Binary and Ternary Blends

Anhydride (wt %)	PS (wt %)	SMA (wt %)	Blend
0	100	—	Binary blend
0.5	93	7	Ternary blends (PS/SMA/PU-es)
1.0	86	14	
3.0	56	44	
5.0	28	72	
7.0	0	100	Binary blend (SMA/PU-es)

Dynamic mechanical analysis (DMA) was carried out by means of a DMA-983 (DuPont Instruments, New Castle, DE) at a frequency of 1 Hz from -150 to 200°C , with a heating rate of $2^{\circ}\text{C}/\text{min}$. Samples having $40.0 \times 10.0 \times 1.30$ mm dimensions were submitted to sinusoidal deformation with 0.20 mm of amplitude.

Flexural tests were performed on a universal test machine, EMIC 2000 (São José dos Pinhais, Brazil), in accordance with ASTM D790, using a crosshead speed of 1 mm/min and samples with dimensions of $58.0 \times 12.8 \times 1.30$ mm.

RESULTS AND DISCUSSION

PS, SMA, and the PS/noncrosslinked PU-es (90/10) blend were processed at different rotor speeds at 190°C to establish conditions that assured the minimum polymer degradation during blend processing. Degradation of the polymer chains results in a material with poor mechanical properties and should be avoided. PS and SMA were processed individually to identify their rheological behavior, as they were the majority components in blends. PS/PU-es (90/10) blend was chosen because it is a nonreactive system and its profile was not masked by intentional grafting reactions.

Decreasing the torque with an increase of processing time at constant rotor speed can be associated with the reduction of viscosity of the polymer due to the scission of their chains. On the other hand, an increase of torque during the processing can be related to a rise in viscosity, which is attributed to the increase of molecular weight resulting from crosslinking reactions.¹² Curves of torque versus time at different rotor speeds for PS, SMA, and the PS/PU-es (90/10) blend are shown in Figure 1. The scale of torque in this figure was omitted because the curves for the different polymers were displaced for better visualization. The torque curves of PS and SMA show similar profiles. The drop of the torque with the processing time at constant rotor speed is indicative of polymer degradation. The drop of torque is more accentuated for SMA than for PS, which can be attributed to the presence of anhydride groups in the copolymer resulting in the formation of higher concentrations of free radicals during the processing, accelerating the scission of chains.¹³ The torque also decreased with the increase of the rotor speed, a consequence of the degradation as well as the rheological behavior of the polymers. It is important to note how the increase of the processing time and the rotor speed differently affects the torque behavior. The changes observed with the increase of processing time is mainly related to the degradation, while higher rotor speed implies lower viscosities for these polymers, which is a rheological characteristic.

On the other hand, the torque curve for the PS/PU-es (90/10) blend shows an increase of torque at higher processing times, indicating that reactions re-

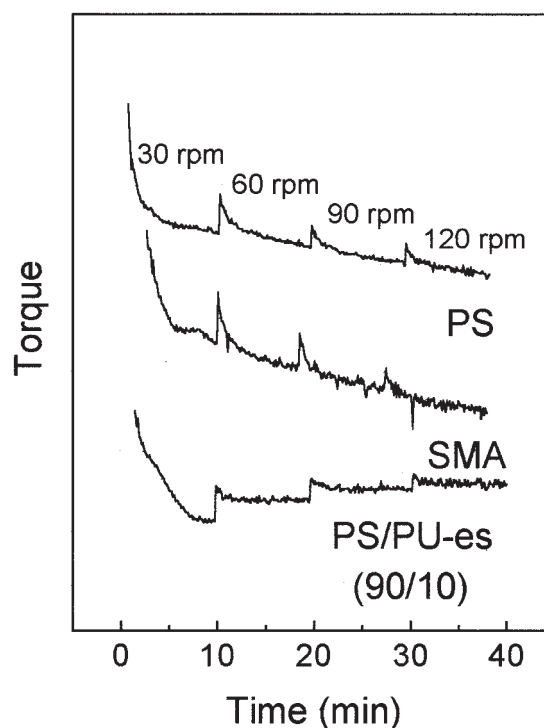


Figure 1 Torque curves at different rotor speeds for PS, SMA, and PS/noncrosslinked PU-es (90/10) blend.

sulting in an increase of viscosity, such as crosslinking, took place during the mechanical mixing. The influence of rotor speed on the torque of the PS/PU-es blend was also different from that observed for PS at a similar processing time. Only 10 wt % of PU-es was able to drastically change the rheological behavior of PS in the blends, whose viscosity increased with increasing rotor speed.

To prevent an extensive degradation of polymers during melting mixing, 30 rpm was adopted as a condition to prepare all blends, as at this rotor speed all the samples were macroscopically homogeneous.

Blends prepared without crosslinkers for PU-es were tacky, a characteristic of noncrosslinked PU-es. To avoid this characteristic, PS/PU-es and SMA/PU-es binary blends and PS/SMA/PU-es ternary blends were prepared in the presence of either dicumyl peroxide or sulfur as crosslinkers. In ternary blends, the content of the maleic anhydride reactive group was varied through the addition of different amounts of SMA to the blends. SMA/PU-es binary blends contained the higher maleic anhydride content (7 wt %) (Table II), while PS/PU-es binary blends were a nonreactive system, as in these blends there was no maleic anhydride.

From the torque versus time curves, it was possible to infer about the formation of a graft copolymer during blend processing when maleic anhydride is present. In Figure 2, the torque versus time curves for PS and SMA processed at conditions indicated above

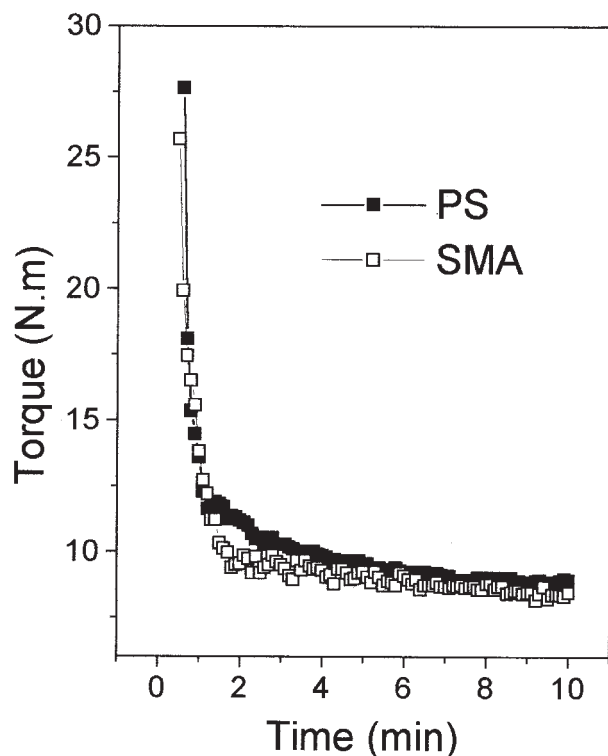


Figure 2 Torque curves for PS and SMA at 30 rpm and 190°C.

are shown and it can be observed that torque values are practically the same for both polymers. Therefore, the viscosity of these polymers is very similar in the experimental processing conditions used. This fact allowed the utilization of torque curves to monitor the variation of viscosity in blends during melt mixing.

Figure 3 shows torque versus time curves for the PS/PU-es (90/10) nonreactive blend and for the SMA/PU-es (90/10) reactive blend. It can be observed that the torque curve of the SMA/PU-es blend exhibits higher torque value than the PS/PU-es blend over the whole time range, even though the individual polymers, PS and SMA, show similar torque curves. The higher torque value found for the SMA/PU-es blend indicates that, in this system, reactions occurred, such as grafting between PU-es and SMA. In a prior work, we suggested that the grafting occurs through a transesterification reaction between anhydride, ester, and carbamide groups of polyester-polyurethane.¹⁰ Despite the grafting reactions, the torque curve of the SMA/PU-es (90/10) blend did not present a peak, common for many reactive mixtures. The absence of a peak confirms that this grafting reaction is very fast, occurring at the beginning of the processing. A similar behavior was observed by Triacca et al.¹⁴ in polyamide 6 and poly(styrene-co-acrylonitrile) compatibilized by SMA containing 25 wt % of maleic anhydride. Apparently, the graft reaction is accompanied by degradation as the torque of the mixture diminishes with processing time.

The formation of a graft copolymer during melt mixing was confirmed by a selective solubilization test as described previously¹⁰ and plays an important role in the morphology. A drastic decrease of the PU-es domain size is observed when SMA is used as the matrix (Fig. 4).

The morphology of the immiscible blends is determined by the rheological properties of the polymers and by the interfacial tension. Although the polymers PS and SMA present similar rheological properties, for the blends PS/PU-es and PS/SMA, these properties are different. The viscosity of the reactive blends is higher (Fig. 2) because of the formation of the grafting copolymer, which acts as a surfactant, decreasing the interfacial tension. In this case, decreasing the interfacial tension is a predominant factor determining the morphology of the reactive blends, because a decrease was observed in the elastomer domain size as the anhydride content and the resulting grafting copolymer content increased. A similar morphology was observed for blends of PS and SMA containing polyether-polyurethane as a dispersed phase.¹⁵ Figure 5 shows the average diameter size of the PU-es phase as a function of maleic anhydride content in the blend matrix. The bar on each point is related to the maximum and minimum domain size found for each blend. The domain size, as well as the domain size distribution, showed an accentuated reduction with an increase in the anhydride content, becoming very

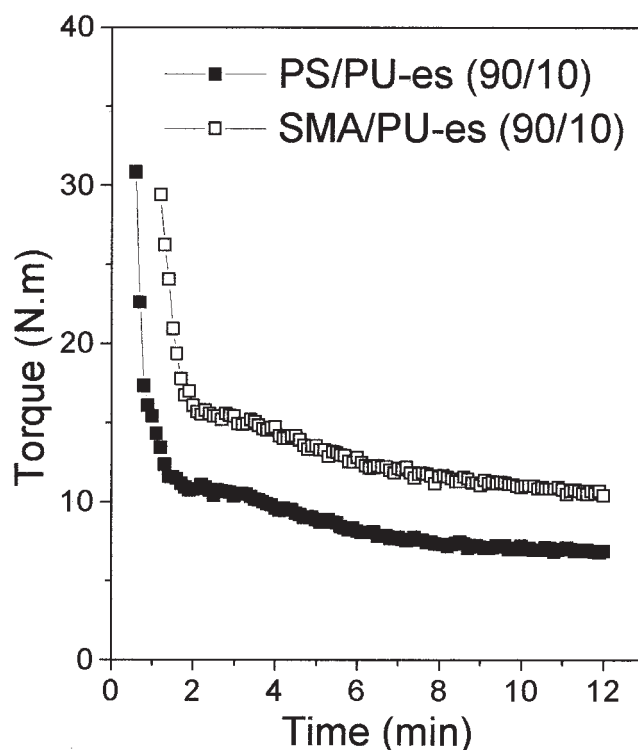


Figure 3 Torque curves for the nonreactive binary blend PS/PU-es (90/10) and the reactive binary blend SMA/PU-es (90/10) at 30 rpm and 190°C.

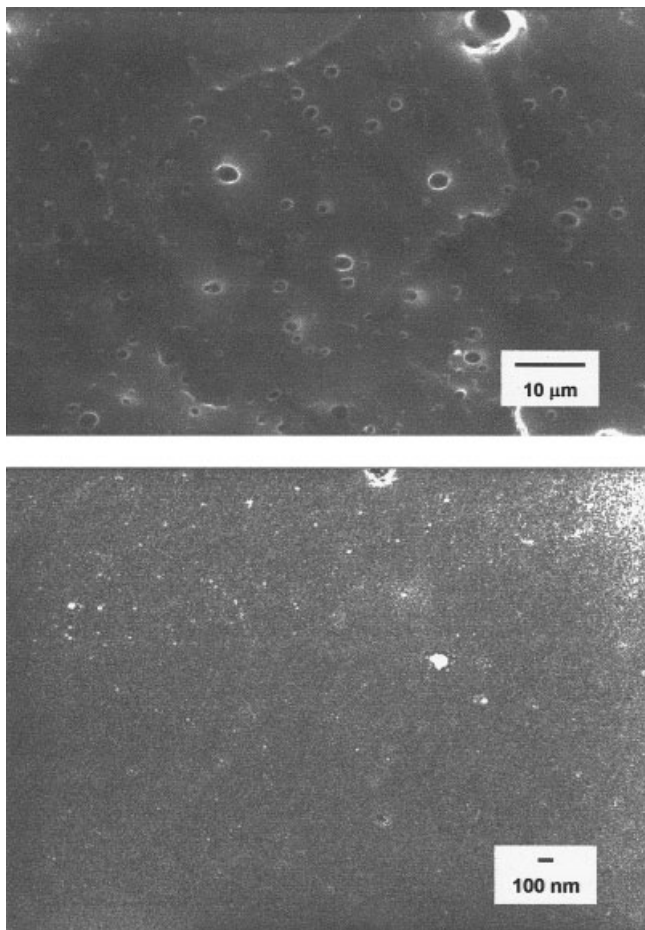


Figure 4 SEM micrographs of the binary blends containing 10 wt % of PU-es crosslinked with dicumyl peroxide: (a) PS/PU-es ($\times 1500$) and (b) SMA/PU-es.

close at high concentrations of anhydride (5 and 7 wt %). The narrowness of the domain size distribution could be associated with the reduction of the coalescence process of the PU-es particles in the presence of the high graft copolymer concentration.^{1,6,15}

The crosslinking of the PU-es phase by dicumyl peroxide or sulfur practically does not affect the PU-es domain size, as can be seen in Figure 5(a, b).

The dynamic-mechanical behavior of the blends was evaluated. The loss modulus (E'') versus temperature (T) curves for PS and SMA are shown in Figure 6(a). The maximum of the E'' vs T curves at higher temperature is related to the glass transition occurring at 111°C for PS and at 124°C for SMA. Moreover, a large secondary relaxation for SMA can be observed, which occurs between -125 and 0°C with maximum at -55°C.

In Figure 6(b), curves of storage modulus (E') and the loss modulus as a function of temperature for PU-es are shown. The loss modulus curve exhibits two peaks with maximums at -86°C and -20°C. The former is due to the secondary relaxation of the PU-es groups, whereas the more intense peak at the higher

temperature is attributed to the glass transition of soft segments of PU-es chains.¹⁶ In the $E'xT$ curve after the glass transition, there is an elastic plateau, which begins at $\sim 0^\circ\text{C}$ and extends to 75°C, followed by the viscous flux above 75°C.

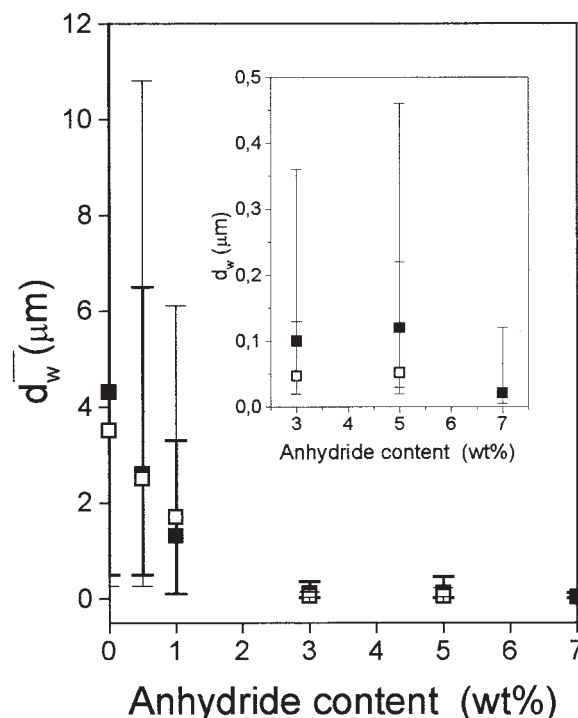
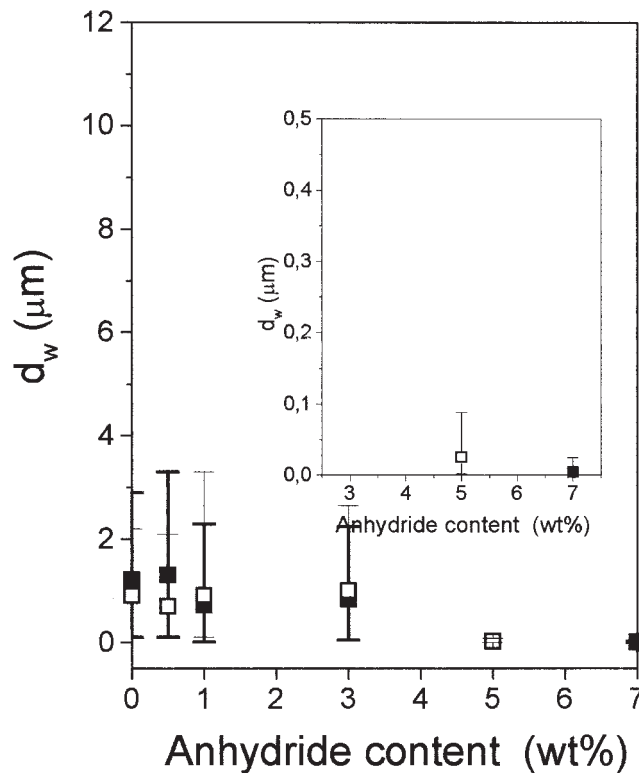


Figure 5 Average diameter of the dispersed phase in the blends containing: (a) 10 wt % of PU-es and (b) 20 wt % of PU-es. Crosslinking agents: (■) dicumyl peroxide and (□) sulfur.

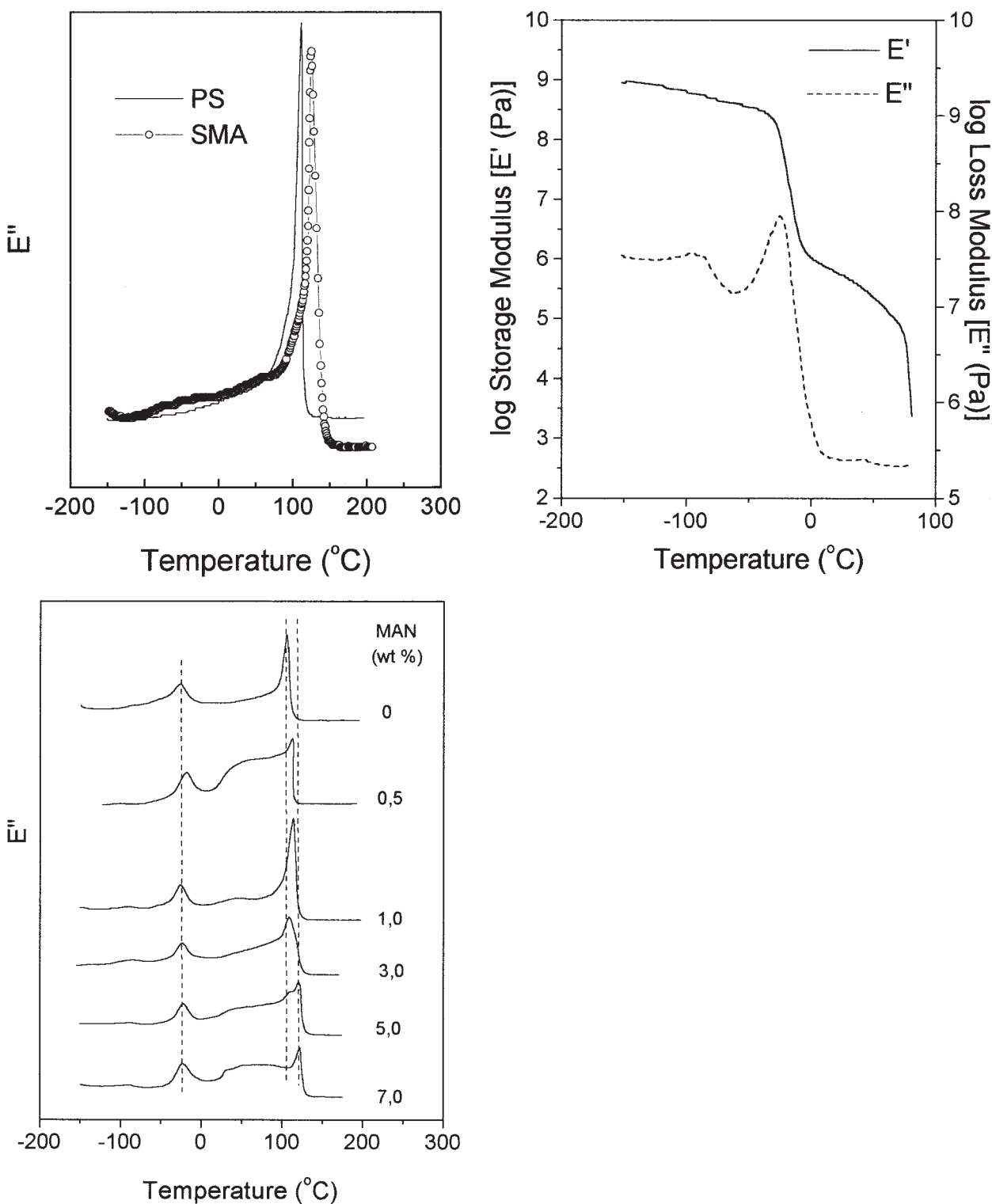


Figure 6 (a) Loss modulus (E'') as a function of temperature (T) for PS and SMA, (b) E'' and storage modulus (E') versus T for PU-es and (c) E'' versus T for PS/SMA/PU-es (80/20) blends crosslinked with sulfur.

Loss-modulus curves as a function of temperature for PS/SMA/PU-es (80/20) blends crosslinked with sulfur are shown in Figure 6(c). The loss-modulus curves were shifted from one another to allow better analysis. Relaxations related to elastomeric and glassy phases were observed, as expected, for an immiscible

mixture. A meticulous analysis of the loss modulus curves reveal a peak associated with the glass transition of PU-es at -20°C for all blends. In contrast, the glass transition of the matrix at higher temperatures was shown to depend on the matrix composition. Blends containing 7 and 14 wt % of SMA (0.5 and 1 wt

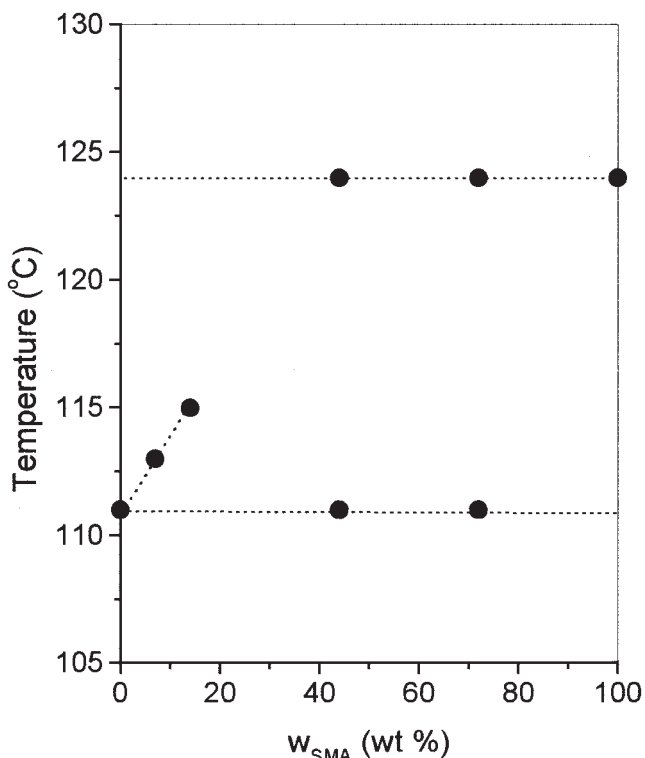


Figure 7 Glass-transition temperature as a function of the composition of the glassy matrix.

% of anhydride, see Table II) presented a peak corresponding to the glass transition at intermediate temperatures between the T_g of PS and SMA, indicating the miscibility of these polymers at these compositions. These blends can be described as two phase mixtures where one phase is PU-es and the other is a miscible mixture of PS and SMA. For all other blends, the phase behavior became very complex. Probably, there are at least three different phases, PU-es, PS, and SMA phases, as a peak and a shoulder were observed in the temperature range of the glass transition of the matrix and were related to the presence of PS phase and SMA phase. The T_g 's of the glassy phases as a function of their composition are shown in Figure 7.

The flexural modulus for the blends with different compositions is shown in Figure 8 as a function of the anhydride content. The addition of PU-es causes a slight reduction of the flexure modulus in comparison to PS, which is represented by the horizontal line in the graph. The crosslinking agent of the PU-es phase and the anhydride content in the blends practically do not affect the flexural modulus. Blends containing 20 wt % of PU-es presented lower flexural modulus than those containing 10 wt %. This behavior was expected because the flexural modulus reflects the stiffness of the material and the addition of a higher content of elastomer should reduce it.

The strain at break for the blends is shown in Figure 9. The increase of anhydride content in the PS glass

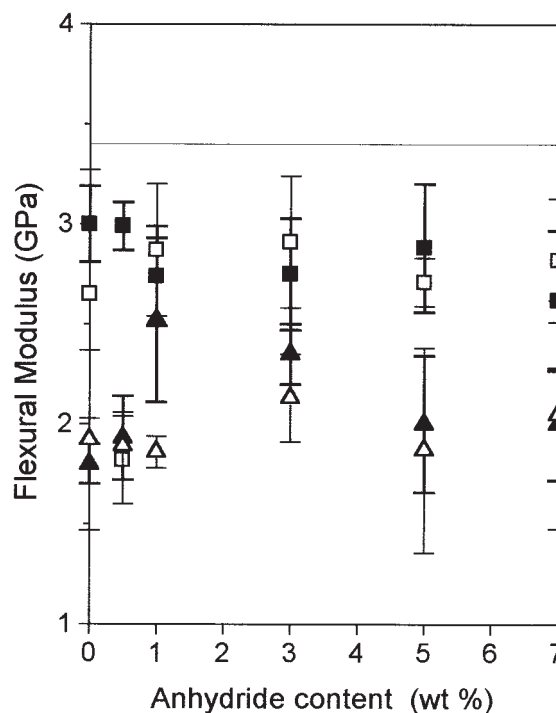


Figure 8 Flexural modulus as a function of the anhydride content for blends containing different concentrations of PU-es: 10 (■) and 20 (▲) wt % crosslinked with dicumyl peroxide, and 10 (□) and 20 (△) wt % of PU-es crosslinked with sulfur. The continuous line is related to the PS flexural modulus.

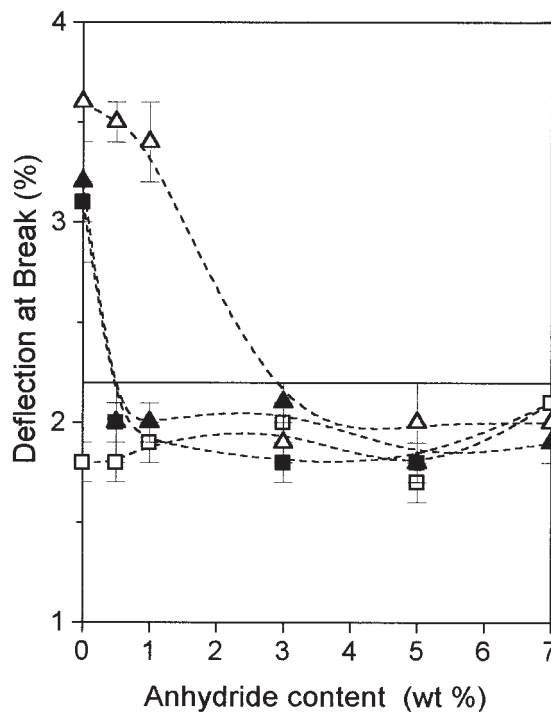


Figure 9 Deflection at break as a function of the anhydride content for blends containing different concentrations of PU-es: 10 (■) and 20 (▲) wt % crosslinked with dicumyl peroxide and 10 (□) and 20 (△) wt % crosslinked with sulfur. The continuous line is related to the PS deflection at break.

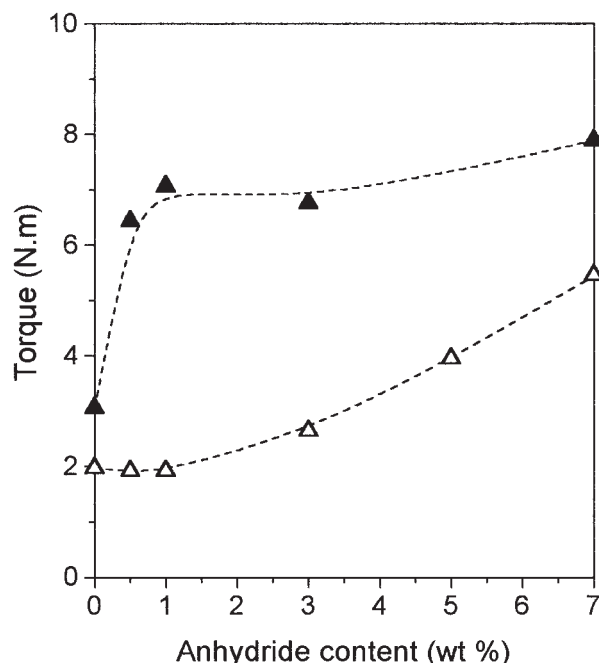


Figure 10 Torque as a function of the anhydride content for the blends containing 20 wt % of PU-es obtained at 11 min. Blends containing PU-es crosslinked with (-▲-) dicumyl peroxide and (-△-) sulfur.

matrix should cause an increase of stiffness,¹⁷ which should promote a sudden and accentuated drop of the strain at break. Meanwhile, addition of 20 wt % of the PU-es crosslinked with sulfur causes an increase by a factor of 2 in the strain at break, in relation to the PS for the blends containing up to 1 wt % of anhydride. PU-es crosslinked with dicumyl peroxide did not improve the strain at break of the ternary blends, independent of the elastomer content. This behavior could be related to the difference of crosslinking density caused by dicumyl peroxide and sulfur. The curves of torque at 11 min of mixing versus anhydride content for blends containing the PU-es crosslinked with dicumyl peroxide or sulfur are shown in Figure 10. The blends containing sulfur as crosslinking agent showed a constant and smooth increase of the torque with the increase of anhydride content, while in the blends containing dicumyl peroxide the torque values suddenly increased at small quantities of anhydride (up to 1 wt %) and then remained constant up to 7 wt % anhydride. This behavior indicates that a higher crosslinking density is promoted by dicumyl peroxide, with respect to sulfur at the same anhydride concentration. For the blends studied, the crosslinker and therefore the crosslinking density did not affect the

morphology. Again, the factor responsible for the morphology is undoubtedly the interfacial tension, which is apparently independent of the crosslinker for the elastomer.

CONCLUSION

The compatibilization of PS/PU-es blends was promoted by SMA addition. This compatibilization occurred by the formation of a graft copolymer during the melt mixing and was responsible for the decrease of the elastomer domain size in the glassy matrix. Apparently the predominant factor determining the morphology of these blends is the interfacial tension.

The phase behavior of the blends depended on the composition. Blends containing up to 1 wt % of anhydride (14 wt % of SMA) presented a miscible glassy phase, whereas blends containing higher SMA concentrations presented at least three phases, the PU-es, PS, and SMA phases.

The flexural mechanical properties of blends were changed by the addition of different SMA contents. The higher value of strain at break was obtained with the addition of low SMA copolymer concentration (up to 1 wt %), in blends containing 20 wt % of PU-es crosslinked with sulfur.

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