

Compatibilization of Polystyrene and Polyamide 6 Mixtures with Poly(Styrene-co-Sodium Acrylate)

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ABSTRACT: In this work, the compatibilization of polystyrene-and-nylon 6 mixtures with the ionomer, poly(styrene-co-sodium acrylate), is investigated. The ionomer was synthesized by emulsion polymerization. Scanning electron microscopy reveals that an appreciable size reduction of the dispersed phase is achieved in the whole composition range, when small amounts of the ionomer were added. IR spectroscopy and water absorption tests disclose that a chemical

reaction occurs between the carboxylic group of the ionomer and the terminal amine group of the polyamide 6, which allows the compatibilization process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1736–1745, 2004

Key words: compatibilization; ionomers; morphology; blends

INTRODUCTION

Polymer mixtures or blends with improved physical, optical, and mechanical properties are commonly made by using compatible parent polymers or by adding small amounts of a third component (*compatibilizer*) to induce compatibility. Compatibility can be also produced by an *in situ* chemical reaction between the chemical groups of the polymers in the mixture.¹

Typically, a mixture of two immiscible polymers produced by melt mixing exhibits low deformation capacity and poor ultimate properties. This is because a main dominant phase (polymer matrix) and another poorly dispersed phase result. Frequently, when a polymer mixture is subjected to a stress, the stress concentrates at the interface, which, for incompatible polymer pairs, is weak and unable to transfer the stress between the phases.² Hence, one of the crucial roles of a compatibilizer is to transfer the stress between the continuous and the disperse phases. Other roles are to allow the formation of an extremely fine dispersion of one phase into the other by an emulsifying-like effect and to increase the interfacial adhesion.¹ As a result, an increase in the strain rate transfer between the continuous and dispersed phases is pro-

duced, which improves the mechanical properties of the blend^{3–5} and promotes much more stable morphologies where the dispersed phase becomes finer and whose tendency to coalescence is significantly reduced.^{6–9}

Among the numerous and well-known commercial blends, the polystyrene–polyamides mixtures have been scarcely studied.¹⁰ In earlier reports, it was attempted to obtain polystyrene-based mixtures with diverse rubbers with similar properties to those of high-impact polystyrenes (HIPS).^{11–12} In commercial mixtures containing polyamides, on the other hand, the tenacity of the polyamide matrix was increased by the incorporation of a rubber-like dispersed phase.¹³ Also, the permeability properties of polyamide 6/polyolefins blends have been studied.¹⁴

The extensive use of polyamides in binary mixtures is a consequence of the capacity of their terminal amine groups to react with functional groups of other polymers in a mixture, which is very important for allowing compatibility.¹ For instance, it is known that the terminal amine groups are capable of reacting with carboxylic groups to form chemical linkages.¹⁵ This property of the polyamides has been used in mixtures with polystyrene¹⁵ or with polyethylene to produce blends with enhanced properties.¹⁶ Moreover, the addition of a copolymer of styrene and methacrylic acid to polystyrene and polyamide 6 mixtures yields an important improvement in the dispersing capacity of one polymer into the other because a chemical reaction is carried out between the terminal amine groups and the carboxylic groups of the styrene–methacrylic

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acid copolymer.¹⁵ Chen et al.¹⁷ reported that a copolymer of styrene and maleic anhydride is a better compatibilizer than a copolymer of styrene-methacrylic acid for mixtures of polystyrene and polyamide 6 because of the presence of the more reactive groups (with the amine group) in the former compatibilizer.

In this work, we report that the addition of small amounts of the ionomer poly(styrene-co-sodium acrylate) (PSSAc) to mixtures of commercial Nylon 6 (PA6) and polystyrene (PS) induces an important decrease of the dispersed-phase size in the whole composition range. Experimental evidence indicates that a chemical reaction between the amine terminal groups of the PA6 and the carboxylic groups of the ionomer produces the compatibilization.

EXPERIMENTAL

Polystyrene (Resirene HF-777 from Resistol, Leyma, Mexico) was used as received. The number-average (M_n) and the weight-average (M_w) molar masses of this polymer, measured by GPC (using polystyrene standards for calibration), were 160,000 and 190,000 g/mol, respectively. The nylon 6 (3100 from Celanese, Octolan, Mexico) was subjected to a thermal treatment for 12 h at 60°C in an oven to remove humidity before any test or mixing. The average molar mass of this polymer, measured by viscosimetry (with acid formic 88 wt % used as solvent from Merck, Rahway, NJ), was 30,000 g/mol.

The PSSAc was made by emulsion polymerization at 60°C for 3 h in a glass reactor with sodium dodecyl sulfate (99% pure from Tokyo Kasei) as the emulsifier and potassium persulfate (KPS) as the initiator. The initial weight ratio of styrene to sodium acrylate was 90/10. The conversion was followed by gravimetry. The final conversion was ~84%. M_w of the PSSAc, measured by GPC, again by using polystyrene standards for calibration and THF as the mobile phase, was 2.8×10^6 g/mol. The PSSAc at the end of the reaction contained only 2% sodium acrylate. Details on the synthesis and characterization of this ionomer are given elsewhere.^{18,19}

PS/PA6 mixtures with different compositions (10, 30, 50, 70, and 90 wt % PA6) were prepared in a Haake Rheomix 600 internal mixer with a roller blade geometry operating at a chamber temperature of 250°C, rotor speed of 40 rpm, and blending time of 7 min. For the mixtures with PSSAc (PA6/PS/PSSAc = 90/7/3; 70/27/3; 50/47/3; 30/67/3; 10/87/3 by weight), master batches of PS and the PSSAc were prepared before adding the PA6. The shear viscosities of PS, PA6, PSSAc, and the mixtures with or without compatibilizer were measured as a function of shear rate at 250°C in a Rosand RH2200 capillary rheometer. This

instrument automatically makes the Bagley and the Rabinowitsch corrections.

The morphologies of the freeze-fracture polymer samples with and without ionomer were examined in a JEOL JSM-5400 LV scanning electron microscope (SEM) equipped with a quantum superdry detector. Potentials of 15 to 20 kV were employed. Samples were immersed in liquid nitrogen and then fractured and placed in a Baltec CE SCD004 golden evaporator to deposit a gold layer by electrodeposition. The size distribution of the dispersed phase in each mixture was determined from the SEM micrographs with an image-Pro Express analyzer (Media Cybernetics). The number-average (D_n) and volume-average (D_v) diameters were calculated from:

$$D_n = \frac{\sum n_i d_i}{\sum n_i}$$

$$D_v = \frac{\sum n_i d_i^4}{\sum n_i d_i^3}$$

Here n_i is the number of particles with diameter d_i . For these calculations, at least 300 particles were measured. A correction was applied to the size distribution according to the Saltikov method.^{20,21}

To determine whether there is a chemical reaction or only strong interactions (for example, hydrogen bonding) between PA6 and PSSAc, 50/50 (w/w) blends of these two polymers were subjected to a treatment in a Soxhlet apparatus to remove PS residual from the synthesis of the ionomer and *nonreacted* PA6. The latter was removed with formic acid, whereas the PS was extracted with toluene. In both cases, the extraction lasted 8 h. The same extraction treatment was performed on a ternary mixture made of 3 wt % PSSAc, 47 wt % PS, and 50 wt % PA6. The residues from both extraction processes were filtered, dried, weighed, and analyzed by FTIR spectroscopy in a Perkin-Elmer Spectrum One spectrometer. FTIR analysis was performed on pellets of FTIR-grade KBr (Aldrich) with small quantities of the sample.

The melting temperature (T_m) of the PA6 and the glass transition temperature (T_g) of the PSSAc were obtained in a Perkin-Elmer DSC-7 differential scanning calorimeter at heating and cooling rates of 10°C/min. Reported values were from the second heating-and-cooling scan.

For the water absorption tests, mixtures of PS/PA6 with and without compatibilizer were prepared by thermocompression for 28 min following a force ramp in an Schwabenthan Polystat 200T press at 210°C. Polymer probes with dimensions of $2 \times 1 \times 0.2$ cm were obtained. To facilitate sample removal from the mold, a silicone-demolding agent (DMD 100 from

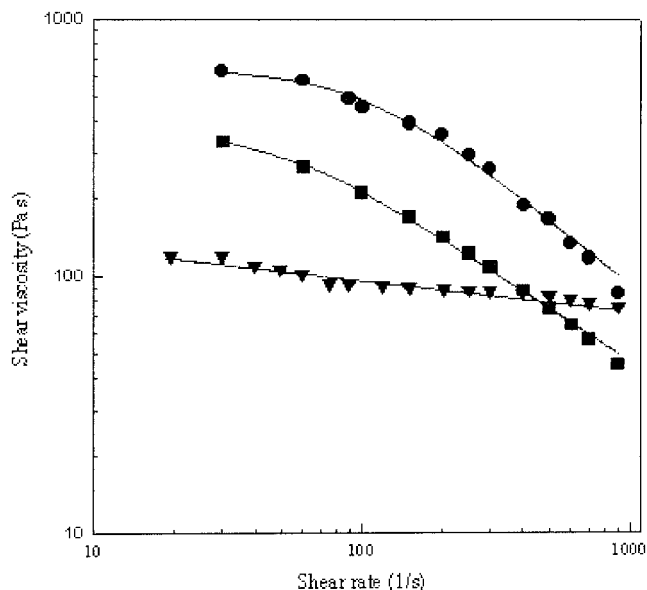


Figure 1 Shear viscosity as a function of shear rate for the pure materials at 250°C. (▼) PA6; (■) PS; (●) PSSAc.

Continental Polímeros) was employed. Next, samples with and without PSSAc were dried in an oven at 60°C for 24 h and weighed (w_{dry}). Then, these samples were placed in a controlled temperature chamber where doubly distilled water was boiled continuously. Two hours later, the samples were drawn and introduced in a recipient with distilled water at room temperature. After 15 min, the samples were dried off with a flannel and immediately weighed (w_{wet}). The relative amount of water absorbed by the samples was calculated as

$$H_2O_{\text{abs}} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}$$

RESULTS

Figure 1 shows the viscosity as a function of shear rate for PS, PA6, and the ionomer. Measurements were done at 250°C because the parent polymers (the melting temperature of PA-6 used here was 212°C, which is lower than the reported value of 230°C,¹⁰ because of its low molar mass) and mixtures are in the melted

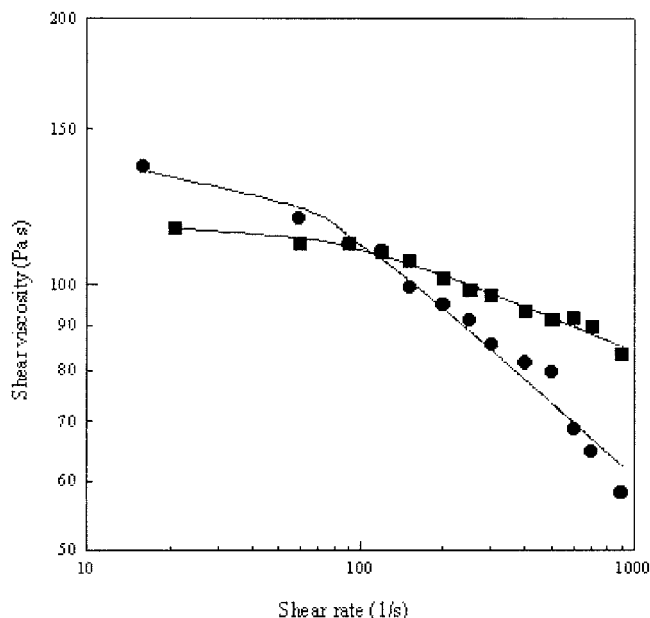


Figure 2 Shear viscosity as a function of shear rate for two mixtures of PS and PA6 with and without the compatibilizer (PSSAc) at 250°C. (●) PS/PSSAc/PA6 (7/3/90); (■) PS/PA6 (10/90).

state. Both PS and PSSAc exhibit the typical shear thinning behavior of linear polymer melts. The viscosity of the ionomer is larger than that of PS at all shear rates because of its larger molar mass and the ionic interactions between ion pairs. PA6, in turn, displays a near-Newtonian behavior and much lower viscosities because of its low molar mass. The lines in this figure are the best fit of the Carreau model.²² The values of the fitting parameters of this model are reported in Table I.

Figure 2 displays the viscosity as a function of shear rate for PA6/PS (=90/10) and PA6/PS/PSSAc (=90/7/3) mixtures. Again, the solid lines in this figure correspond to the best fit of the Carreau model. The values of the parameters of this model are reported in Table I. In the absence of the compatibilizer, the rheological behavior of the mixture is similar to that of PA6, except at the higher shear-rate range, where an incipient shear thinning region is observed (cf. Figs. 1 and 2). By contrast, the mixture containing the com-

TABLE I
Parameters of Carreau Model $\{\eta = \eta_0[1 + (\lambda\dot{\gamma})^2]^{(n-1)/2}\}$

Parameters	PS	PA6	PSSAc	PS/PA6 (10/90)	PS/PSSAc/PA6 (7/3/90)
η_0	368	155	1048	116	136
λ	0.02	0.55	0.32	0.01	0.02
n	0.31	0.88	0.55	0.87	0.72

patibilizer shows shear-thinning behavior at all shear rates without a Newtonian region.

Figure 3 displays a series of SEM photographs of PS/PA6 mixtures without (Series A) and with (Series B) PSSAc. The morphologies of the mixtures with high content of PS without PSSAc can be seen in A.1 (PS/PA6 = 90/10) and A.2 (PS/PA6 = 70/30). In both pictures, segregation in a two-phase morphology is disclosed. Both pictures reveal a matrix of the major component (PS) and a dispersed second phase of the minor component (PA6). To reduce the superficial contact between PS and PA6, the mixture forms spheroid microregions. Because of the brittle behavior of the PS at ambient temperature,²³ sharp pleats (indicated by arrows in A.1) form when the blends containing PS as the main component are fractured. The average size of the dispersed microregions increases upon increasing the PA6 content in the mixture (cf. A.1 and A.2).

The morphologies of mixtures rich in PS containing PSSAc, B.1 (PS/PSSAc/PA6 = 87/3/10), and B.2 (PS/PSSAc/PA6 = 67/3/30) are shown in Figure 3. Even though phase segregation is also observed with the same basic features as those shown in A.1 and A.2 (i.e., spheroid microdomains and sharp contours at the borders), the size of the spheroid microdomains decreases substantially. This is particularly noticeable for the PS/PSSAc/PA6 (=87/3/10), where the microdomains were the smallest in the whole composition range.

In mixtures with equal or similar PS and PA6 content without (PS/PA6 = 50/50) (A.3, Fig. 3) or with PSSAc (PS/PSSAc/PA6 = 47/3/50) (B.3, Fig. 3), the spheroid microdomains (dispersed phase) are the largest compared to those detected at other compositions. Nevertheless, the sizes of the microdomains in the mixtures containing the compatibilizer (B.3) are smaller than those in the mixtures without the compatibilizer (A.3). To determine which polymer forms the matrix, PS/PA6 (=50/50) and PS/PSSAc/PA6 (=47/3/50) samples were treated with toluene or formic acid. Because only one of these solvents can dissolve PS or PA6 from these samples, this extraction test indicates which polymer forms the matrix. The samples treated with formic acid collapsed and only powder remained. By contrast, the samples treated with toluene maintained its form and shape, indicating that the matrix in both cases is composed of PA6.

Because of the nature of the polyamide, the mixtures with higher content of PA6 are less brittle. Here, the sharp borders are no longer observed [A.4 for PS/PA6 (=30/70) and A.5 for PS/PA6 (=10/90) in Fig. 3]. Again, two phases are detected, spherical PS-rich microdomains dispersed in a PA6-rich matrix. The size of the dispersed phase diminishes upon decreasing the PS content in these mixtures (cf. A.4 and A.5). Again, in mixtures with high content of PA6, the compatibilization action of the PSSAc is extremely

important for the stabilization and reduction in size of the dispersed phase (cf. A.4 with B.4 and A.5 with B.5 in Fig. 3).

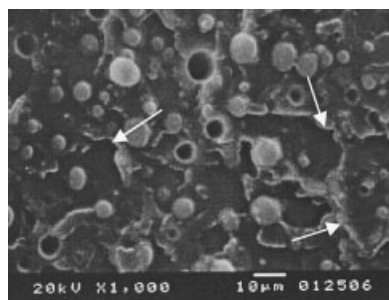
The number-average size (D_n) and the polydispersity (D_w/D_n) of the spheroid microdomains in the mixtures with and without PSSAc are reported in Table II. At all compositions, D_n and D_w of the mixtures containing PSSAc are substantially smaller than those of mixtures free of the compatibilizer. The average sizes of the microdomains increase as the content of the dispersed phase is increased up to the 50/50 (w/w) mixture, where the largest microdomains are seen without or with the compatibilizer, and then, the size of the dispersed microdomains diminishes again as the second component concentration is increased. Nevertheless, the size polydispersity, D_w/D_n , is very similar at all compositions in blends with or without ionomer (Table II).

Figure 4 shows IR spectra of PA6 [Fig. 4(A)], PSSAc [Fig. 4(B)], and an insoluble material obtained after a Soxhlet extraction with toluene and formic acid of a blend of PSSAc/PA6 (50/50 w/w) [Fig. 4(C)]. A very similar spectrum (not shown here) of the insoluble material from the ternary blend [PA6/PSSAc/PS (50/3/47)] was obtained.

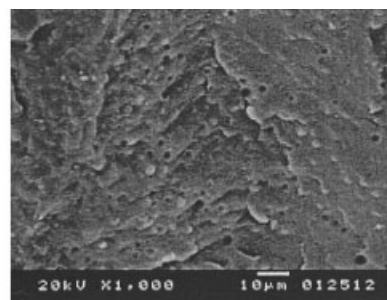
In the spectrum of PA6 [Fig. 4(A)], the three following bands stand out: (1) the wide band at 1641 cm^{-1} , which corresponds to the stretching vibration of the C=O group, typical of the amide group²⁴; (2) the wide and less intense band at 1540 cm^{-1} caused by the combination of the bending vibration of the N—H bond and the stretching vibration of the C—N bond of the amide group²⁵; and (3) the strong and wide band at 3305 cm^{-1} caused by inter- and intramolecular hydrogen bonding in —COOH and —NH₂ groups of the polyamide.^{24,25} It is important to point out that the terminal amine group of the PA6 exhibits a weak flexion peak of the N—H group between 1580 and 1490 cm^{-1} and another one between 3300 and 3000 cm^{-1} due to tension of the N—H group.^{24,26} However, these peaks are not clearly resolved here because of the overlapping with the more intense absorption peak of the amide groups at these wavelength ranges.

For the high content of polystyrene in the PSSAc ionomer, the spectral contributions of the PS dominate in the spectrum of the ionomer, shown in Figure 4(B). Here the band at 1601 cm^{-1} stands out. This band is produced by superposition of two bands, mainly a sharp peak at 1600 cm^{-1} due to C=C stretching of the aromatic ring of the polystyrene segments²⁷ and a very wide band at 1575 cm^{-1} due to resonance symmetric and antisymmetric of the COO⁻ group of the (sodium acrylate) units in the ionomer.¹⁹

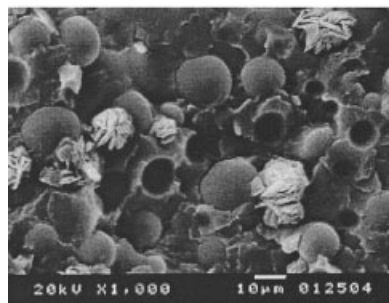
The spectrum of the insoluble material (PA6-PSSAc) is not a simple superposition of the spectra of PA6 and PSSAc. In Figure 4(C), the almost complete disappear-



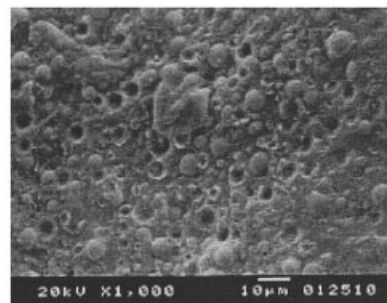
(A.1)



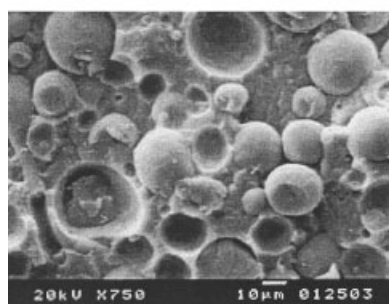
(B.1)



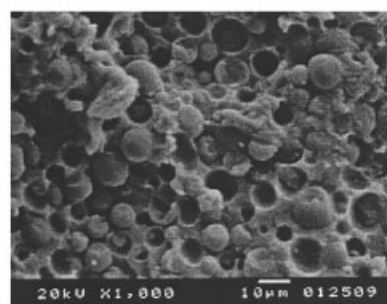
(A.2)



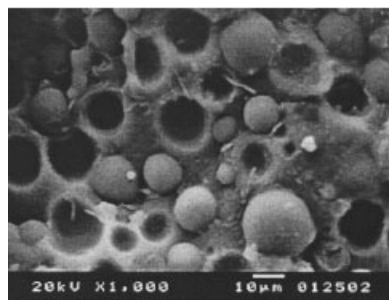
(B.2)



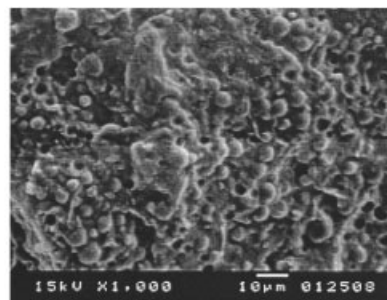
(A.3)



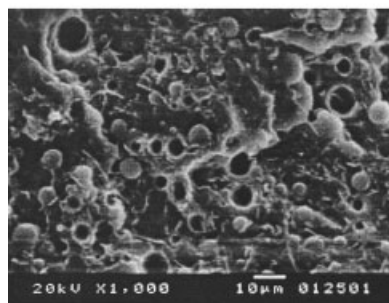
(B.3)



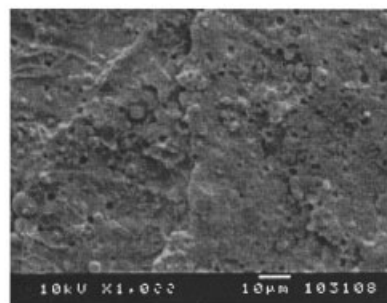
(A.4)



(B.4)



(A.5)



(B.5)

ances of the wide band of the —COOH and —NH_2 groups are evident. Now, only a weak band at 3299 cm^{-1} appears. This band and another very weak band at 3163 cm^{-1} are characteristic of the N—H stretching for associated amide type $\text{R}_1\text{—CO—NH—R}_2$ with NH in the *trans* position. Both bands are present in the spectrum of PA6 [Fig. 4(A)] but they are hidden by the strong band of the —COOH and —NH_2 groups.^{25,26} On the other hand, the combination of bands of C—O stretching and O—H flexion (1417 cm^{-1} weak and 1263 cm^{-1} strong)²⁵ present in the spectrum of PA6 [Fig. 4(A)] disappeared in the spectrum of PA6-PSSAc [Fig. 4(C)]. This means that there are no —COOH groups in the PA6-PSSAc mixture. In the range of 1500 to 1700 cm^{-1} , there are spectral contributions of the PSSAc and PA6, and so, the stretching vibration of the C=O group and the flexion vibration of the N—H group combined to tension of the C—N group appear at 1641 and 1542 cm^{-1} , respectively. Both peaks are associated with the PA6. Also, the band due to superposition of the vibrations of C=C group and the carboxylate group in the PSSAc appears at 1601 cm^{-1} . Notice that the bands of the amide group (1641 and 1542 cm^{-1}) are less intense than those of the methyl and methylene groups at 2924 and 2850 cm^{-1} , respectively, in the insoluble material of PA6-PSSAc [Fig. 4(C)], contrary to what is observed in the PA6 spectrum [Fig. 4(A)]. This indicates that there are less amide groups in the insoluble material compared to those in the pure PA6.

The large intensity decrease of the strong band in the proximity of 3000 to 3750 cm^{-1} indicates the virtual disappearance of the —COOH and —NH_2 groups in the PA6/PSSAc mixture [Fig. 4(C)]. This suggested that a chemical reaction has occurred between the terminal amine group of the PA6 and a carboxylate group of the PSSAc. Also, the disappearance of the C—O stretching and O—H flexion bands (1417 cm^{-1} weak and 1263 cm^{-1} strong, respectively) indicates the neutralization of the residual —COOH groups of the PA6 with Na^+ cations liberated in the chemical reaction between PSSAc and PA6 [Fig. 4(C)]. Therefore, these groups are in salt form. These reactions occur in ternary blend PS/PSSAc/PA6 as well.

Mass balance calculations from the known weight of the insoluble residue (PSSAc-PA6) obtained from the extraction of a known amount of the ternary mixture of PA6/PS/PSSAc, mentioned above, indicates that most of the PSSAc reacts with the terminal amine groups of the PA6 to promote compatibility.

TABLE II
 D_n and Size Polydispersity for Mixtures PS/PA6 without and with PSSAc

PA6 (wt %)	Mixtures without PSSAc		Mixtures with PSSAc	
	D_n (μm)	D_v/D_n	D_n (μm)	D_v/D_n
10	7.2	1.1	2.9	1.1
20	9.8	1.1	5.0	1.0
30	19.8	1.1	7.2	1.1
50	22.5	1.2	11.1	1.2
70	15.2	1.2	5.7	1.2
90	6.0	1.2	2.4	1.2

Table III reports the amount of absorbed water against composition for mixtures with and without PSSAc. Clearly, the amount of absorbed water increases upon increasing the PA6 content in both types of mixtures, as expected due to the hygroscopic character of this polymer. Nevertheless, the amount of absorbed water is somewhat smaller (in the whole interval of compositions) in mixtures with PSSAc.

DISCUSSION

PSSAc is a polymer with a small amount (2%) of neutralized acid groups in the form of sodium salt. This ionomer was synthesized in a direct way, that is, starting from their monomers (styrene and sodium acrylate), which is not commonly in the synthesis of this type of materials.²⁸ Usually, ionomers are prepared by partially neutralizing the acid groups of a polymer or copolymer with different type of bases to form salts with different cations.²⁹

Nuño-Donlucas et al. reported that the PSSAc is a copolymer with a PS-rich block and a second random block with units of sodium acrylate and styrene.^{18,19} In fact, a strong T_g at 101°C and another weak T_g at 187°C were detected, which confirm the diblock structure.¹⁹ That the structures of PS and PSSAc are very similar strongly suggest that they are compatible. However, due to the proximities of the T_g of PS and the lower T_g of PSSAc, it makes it difficult to prove miscibility by techniques such as DSC or dynamic mechanical analysis (DMA). Hence, we proposed that PSSAc is potentially attractive for the compatibilization of mixtures where polystyrene is one of the components and another polymer with proton acceptor functional groups.

Figure 3 Pictures obtained by SEM of PS/PA6 mixtures without (series of photos A) and with (series of B photos) the ionomer PSSAc. The compositions mass percentages are as follows: (A.1) 90/10; (A.2) 70/30; (A.3) 50/50; (A.4) 30/70; (A.5) 10/90; PS/PA6, respectively, and (B.1) 87/3/10; (B.2) 67/3/30; (B.3) 47/3/50; (B.4) 27/3/70; (B.5) 7/3/90 PS/PSSAc/PA6, respectively.

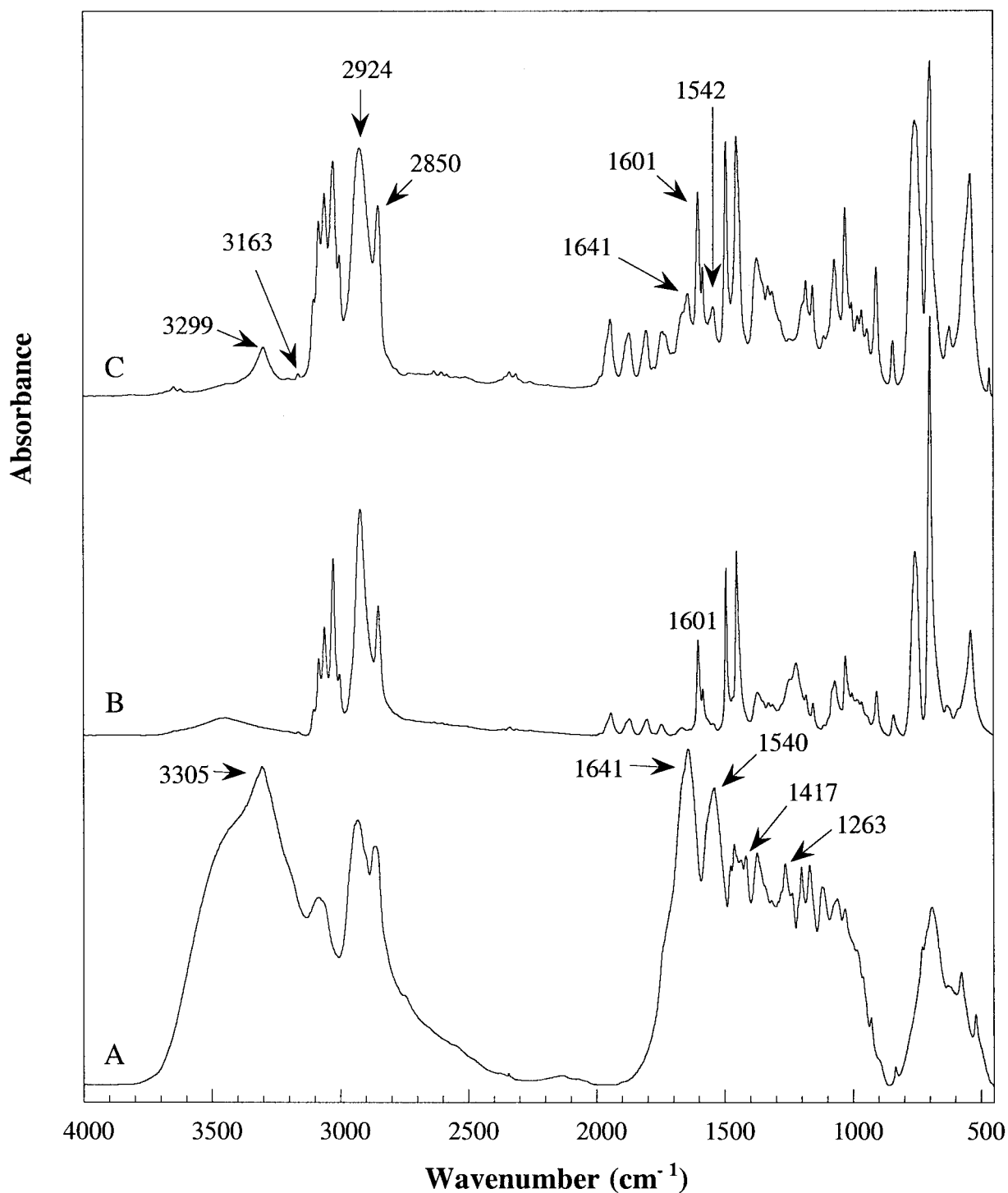


Figure 4 IR spectra of PA6 (A), PSSAc (B), and insoluble material of PSSAc/PA6 (50/50 w/w) blend (C).

Binary mixtures of polystyrene and polyamide 6 are immiscible but commercially attractive.^{10,30} This has motivated studies to reduce the size of the dispersed phase and to promote miscibility by using various compatibilizers.^{15,17} These reports indicate that the mechanical properties of PS/PA6 mixtures

improve when these compatibilizers are added.^{15,17} Mixtures of PS and nylon 6,6 without compatibilizer are characterized by a two-phase morphology, where the major polymer component forms the matrix in which the minor polymer component is dispersed in the form of spheroid microregions.³¹ This

TABLE III
 H_2O_{abs} as Function of the Composition (PA6 wt %) for
 Mixtures PS/PA6 without and with PSSAc

PA6 (wt %)	H_2O_{abs} mixtures without PSSAc	H_2O_{abs} mixtures with PSSAc
10	0.014	0.001
20	0.022	0.017
30	0.032	0.024
50	0.036	0.032
70	0.049	0.045
90	0.059	0.055

is frequently observed in other binary immiscible mixtures.³²

Here, the addition of small amounts of PSSAc induces a notable reduction in the size of the dispersed phase (Figs. 3 and Table II) in the whole composition range. This happens even when the overall amount of PSSAc in the mixtures is quite small (~ 3 wt %). The capacity of PSSAc to reduce microdomain size and to promote compatibility in PS/PA6 mixtures could be due to several factors, as follows: (i) the relative low molar mass of PA6, (ii) the high molar mass of PSSAc, and (iii) the occurrence of a chemical reaction between the PSSAc and the PA6.

It has been documented that the probability for the occurrence of a chemical reaction in mixtures where a polyamide is one of the components is strongly related to the number of terminal amine groups.¹⁵ Inasmuch as the number of terminal amine groups in polyamides increases with the reduction of their molar masses, the low molar mass PA6 used in this work facilitates the occurrence of chemical reactions with other functional groups, such as the carboxylic groups of the PSSAc.

Noolandi and Hong, on the other hand, have pointed out that compatibilizers with high molar masses induce an increase in the thickness of the polymer pair interphase, which apparently causes a decrease in the mixing enthalpy.³³ Inasmuch as the entropy of mixing of polymers is always positive,³⁴ this should lead to a reduction in the free energy of mixing, favoring the formation of more stable morphologies.

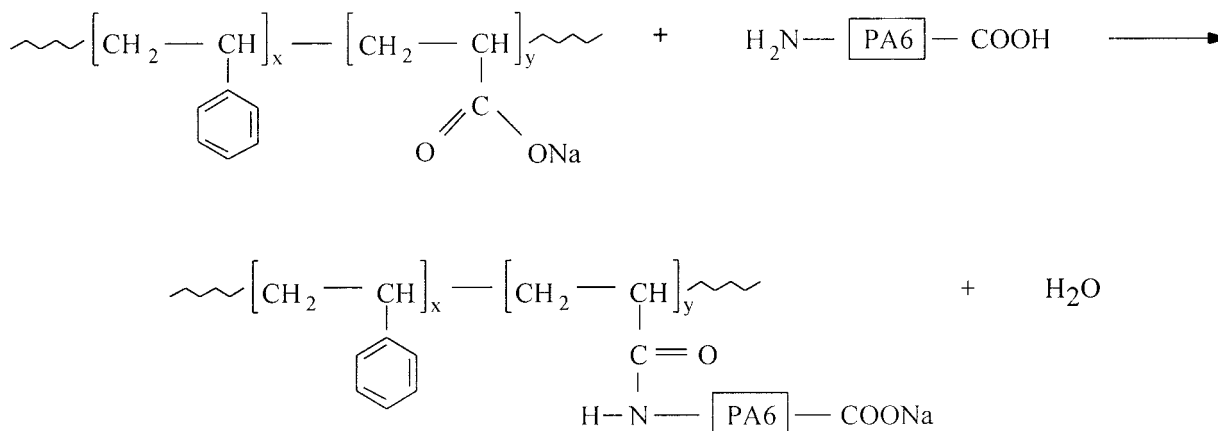
The compatibilizing effect of the PSSAc is demonstrated in the rheological response of the melt polymer mixtures. In the absence of PSSAc, a PA6-rich mixture has a similar shear viscosity than pure PA6, despite the fact that PS has a much higher molar mass and viscosity (cf. Figs. 1 and 2). By contrast, by adding small amounts of PSSAc, the behavior changes from a near-Newtonian fluid with relatively low shear viscosity to a shear-thinning fluid with a much higher shear viscosity at low shear rates and lower viscosities at high shear rates. That the value of the zero-shear

viscosity, η_0 , is higher in the mixture containing the compatibilizer (Table I) can be explained via the interfacial modification introduced by the ionomer. Willis et al. studied the emulsifying effect of a polyethylene-based ionomer on the phase size versus composition relationship for polypropylene/PA6 mixtures and explained that the localization of the ionomer at the interface decreases the interfacial mobility at all dispersed phase contents.³⁵ Chang and Hwu showed that a higher viscosity of the PS/nylon 6,6 mixtures with a compatibilizer [copolymer of styrene and maleic anhydride (SMA)] compared to that without the compatibilizer indicates a better miscibility and a molar mass increase due to the copolymer formation of SMA-nylon 6,6.³¹

The analysis of the IR spectra (Fig. 4) discloses important differences between the residue obtained after the astringent extraction process of either of the parent polymers from a PA6 and PSSAc (or PA6, PSSAc, and PS) mixture. The coexistence of the characteristic bands of the PA6 and of the PSSAc in the spectrum of the insoluble residue [Fig. 4(C)] supports the finding that a chemical reaction has occurred between the terminal amine groups of the PA6 and the carboxylic groups of the PSSAc. This is confirmed by the large intensity reduction of the terminal amine band in 3305 cm^{-1} of the PA6 [cf. spectra of Fig. 4(A, C)]. In this respect, it is possible to propose Scheme 1 for this reaction.

In this scheme, two chemical bonds (the C—O bond of the carboxylic group of the PSSAc and the N—H bond of the terminal amine group of the PA6) break and two chemical bonds (the union of the hydrogen from the N—H bond to the ^-ONa group to liberate Na^+ and of the nitrogen of the amide group of PA6 to the carbon of the carboxylic group of PSSAc) form. Then, the Na^+ neutralizes the terminal carboxylic group of the PA6 and a molecule of water is formed. As a result, the PA6 chains incorporate to the acrylate moieties of the PSSAc skeleton with the formation of H_2O . Similar schemes have already been documented. Raval et al. reported that in mixtures of low-density polyethylene grafted with butyl acrylate (LDPE-*g*-BuA) with PA6, a chemical reaction takes place where the nitrogen of the PA6 bound to the carbon of the carbonyl group of the butyl acrylate grafted to LDPE³⁶; in this reaction, one molecule of C_4H_9OH forms. Sathe et al. reported that in mixtures of polypropylene grafted with maleic anhydride (PP-*g*-MAH) with PA6, a chemical reaction is also carried out where a nitrogen bonds to a carbon of the carboxylic group of the grafted maleic anhydride with the formation of water.³²

Even though no internal standard was used in the IR spectra shown in Figure 4, a crude estimation of the



Scheme 1

amount of PSSAc that reacts with PA6 can be done. From the comparison of the highest absorbance peaks at 2924 and 1641 cm^{-1} in the spectrum of PA6 [Fig. 4(A)] (0.1684 and 0.3340, respectively, after subtracting adjacent bands effect) with the same peaks in the spectrum of PSSAc-PA6 [Fig. 4(C)] (0.3340 and 0.0913, respectively), it is possible to estimate the amount of PSSAc bonded to terminal amine groups of PA6. The absorbance of the peak at 1641 cm^{-1} (0.0913) of Figure 4(C) should correspond an absorbance of 0.046 in the peak at 2924 cm^{-1} . The difference, 0.288 (i.e., 0.3340 - 0.046), should correspond to the contribution of the PSSAc. If it is supposed that methyl and methylene groups of both components (PA6 and PSSAc) contribute to absorbance similarly, that means that 86.2% mol of the insoluble material is PSSAc. This result agrees with the mass balance calculations from the known weight of the insoluble residue (PSSAc-PA6) obtained from the extraction of a known amount of the ternary mixture of PA6/PS/PSSAc.

Finally, that the mixtures containing PSSAc absorb less water at all compositions that the mixtures without the ionomer (Table III) gives support to the hypothesis that a chemical reaction occurs between PA6 and the compatibilizer. On the other hand, another mechanism may explain the reduction of water absorption by the mixtures containing PSSAc. In this case, because of the reduction in size of the microdomain, the barrier properties change and hence, the water uptake.

CONCLUSION

The ionomer PSSAc is an effective compatibilizer of mixtures of PS/PA6 because it has the capacity to reduce the size of the dispersed rich phase at all mixture compositions. This decrease of the dispersed microdomains changes the rheological behavior of the mixtures. IR spectroscopy clearly shows that a chem-

ical reaction occurs between PA6 and PSSAc, in which the terminal amine groups of the PA6 join the carboxylate groups of the PSSAc ionomer. This reaction reduces the amount of absorbed water in the mixtures containing the ionomer, because the amount of the hygroscopic PA6 is reduced.

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