

Blends of i-PP and SBS. I. Influence of the *In Situ* Compatibilization on the Morphology

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ABSTRACT: This article concerns the *in situ* compatibilization of immiscible isotactic polypropylene/butadiene-styrene-butadiene triblock copolymer blends (i-PP/SBS) by means of a reactive mixture. For this purpose, maleated PP (PP-MAH) and SBS (SBS-MAH) were used as functionalized polymers and 4,4'-diaminediphenylmethane was used as a coupling agent between maleated polymers, resulting in a graft copolymer. Binary blends i-PP/SBS, nonreactive ternary blends i-PP/PP-MAH/SBS, and reactive ternary blends i-PP/PP-MAH/SBS-MAH with varying diamine and anhydride molar ratios were prepared. Torque measurements suggest a graft copolymerization during the melt blending for ternary reactive blends, but the extension of the grafting does not vary with the diamine and anhydride molar ratio, but with the elastomer concentration. The morphology of the blends was investigated by scanning electron microscopy. The morphology of binary and ternary nonreactive blends is similar, exhibiting elastomer domains disperse in the i-PP matrix, whose sizes increase with elastomer concentration. On the other hand, the elastomer domain size in the ternary reactive blends is practically independent of the blends composition and of the diamine and anhydride molar ratio. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 847–855, 2002

Key words: compatibilization; reactive mixture; polypropylene; SBS; morphology

INTRODUCTION

The poor impact strength of isotactic polypropylene (i-PP) at low temperatures is one of the deficiencies of this plastic in many applications. However, the ductility of i-PP can be modified by blending with elastomers such as ethylene-propylene copolymer (EPR),^{1–7} ethylene-propylene-diene terpolymer (EPDM),^{8–13} and styrene-butadiene block copolymer.^{14–18}

The mechanical properties of polymer blends are directly associated with its morphology. Among the parameters that influence the blend morphology are the ratio of the viscosities of the components, the interfacial tension, the nature of interactions or interfacial adhesion, the composition, and the elasticity of the polymers.

Generally, i-PP/elastomer blends are immiscible, exhibiting the morphology of a poorly dispersed elastomer phase with large domain sizes and size distribution in the i-PP matrix and very weak adhesion between the matrix and the disperse phase. As a consequence, the blends present poor mechanical properties such as low impact resistance and low tensile elongation.

A method frequently used to improve the phase adhesion consists of the addition of a compatibi-

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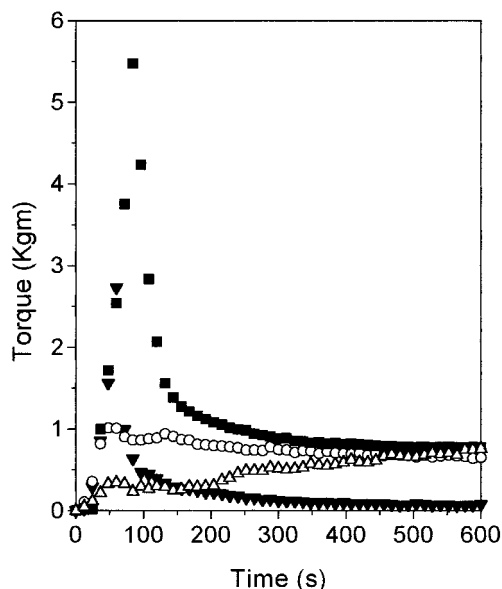


Figure 1 Torque–time curves at 190°C and 55 rpm: (■) i-PP, (○) SBS, (△) SBS-MAH, and (▼) PP-MAH.

lizer that acts as an interfacial agent containing segments capable of specific interaction or chemical reaction with the blend components. In the last case, block or graft copolymers can be generated *in situ* close to the interface during the polymers' mixing.^{19–25} As a consequence, a decrease of the interfacial tension and the stabilization of the phase dispersion against coalescence^{25–30} are verified. The smaller phase size plus the increased phase adhesion results in improved physical properties such as impact strength^{31–33} and tensile strength.³⁴ Sundararaj and Macosko²⁵ reported that block copolymers generated *in situ* are more efficient in stabilizing morphology than premade block copolymers.

The addition of a 50/50 diblock isotactic polystyrene (i-PS)-isotactic polypropylene to i-PS/i-PP blends at concentrations up to 10 wt % has a large compatibilizing effect on its morphology and properties, showing the importance of the adhesion between the components of a noncompatible blend. Not only is the phase size dramatically reduced, but also the phase dispersion and the interphase interaction are also significantly increased when the diblock compatibilizer is added.²⁴

Phan et al.¹⁹ studied the effect of the *in situ* generated compatibilizer in the mixture of maleated PP and maleated EPR by the addition of a third reactive phase, a polyetheramine, on the blends morphology. The compatibilized blends show a finer dispersion of rubber particles and a

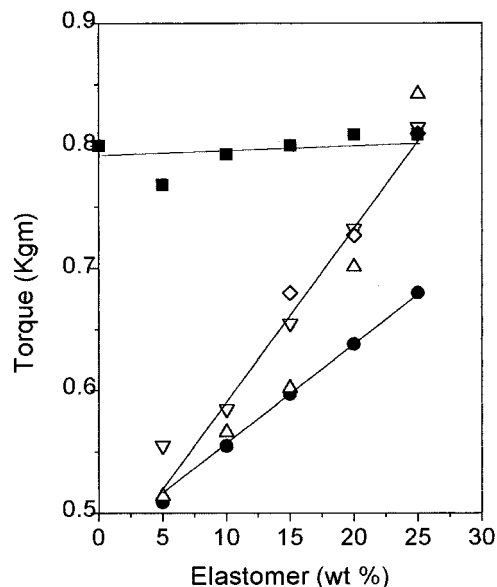


Figure 2 Torque at 400 s of mixing at 190°C and 55 rpm as a function of elastomer concentration: (■) i-PP/SBS, (●) i-PP/PP-MAH/SBS, (△) ternary reactive I, (▽) reactive II, and (◇) reactive III blends.

reduction in the particle size in comparison with the noncompatibilized blend.

Blends of i-PP and styrene-butadiene-styrene triblock copolymer (SBS) are immiscible and

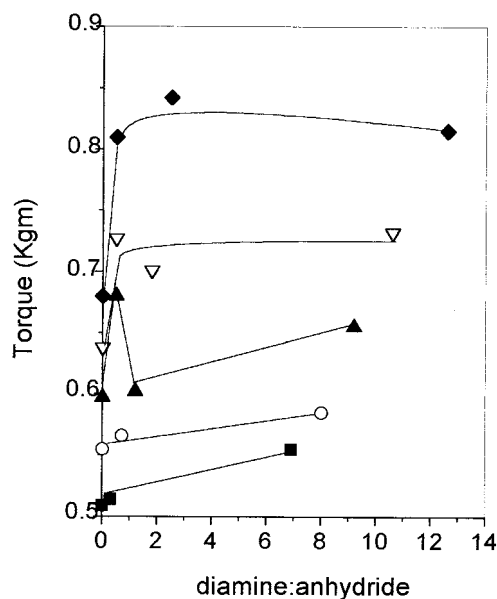


Figure 3 Torque at 400 s of mixing at 190°C and 55 rpm as a function of the diamine and anhydride molar ratio for the ternary blends: (■) 70/25/5, (○) 70/20/10, (▲) 70/15/15, (▽) 70/10/20, and (◆) 70/5/25.

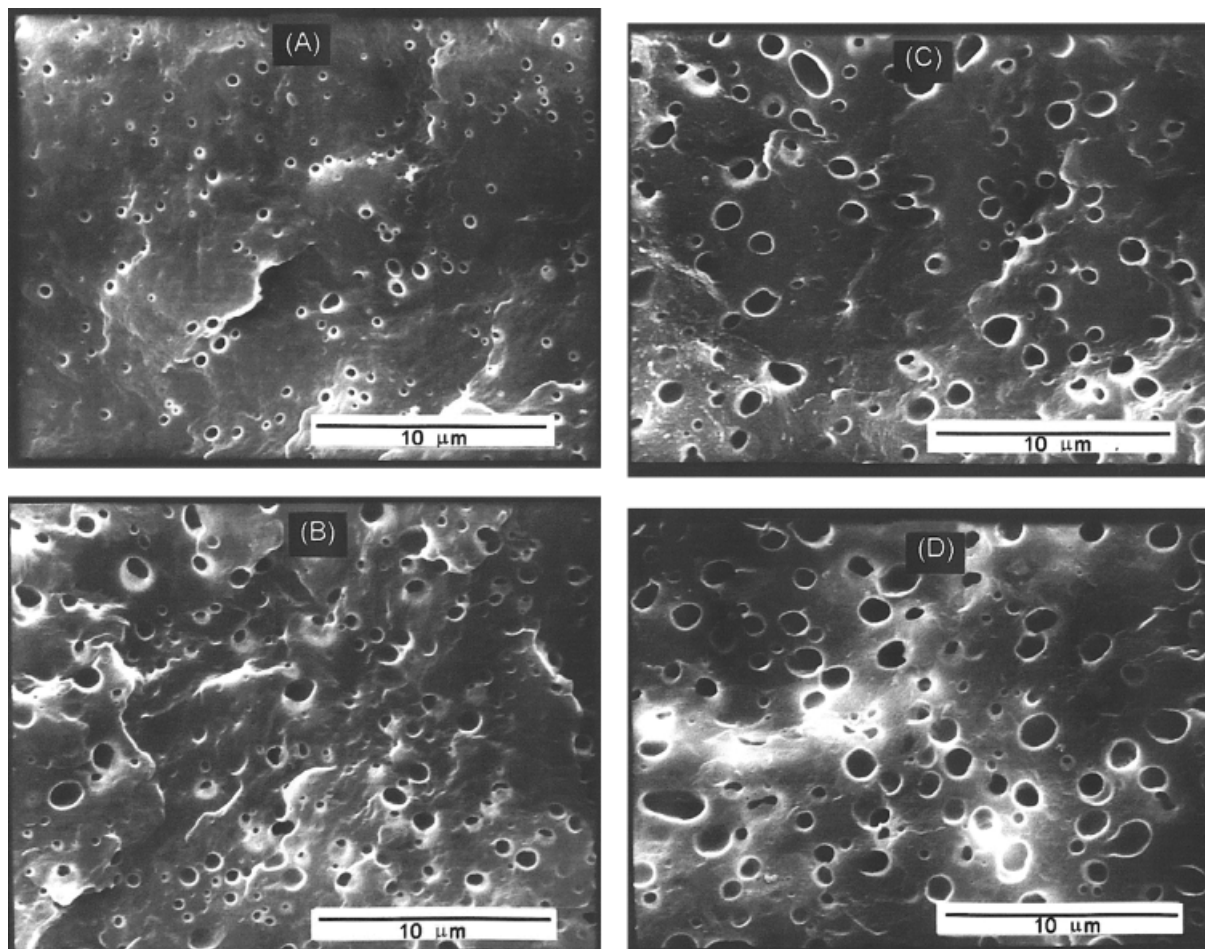


Figure 4 SEM photomicrographs of the i-PP/SBS blends at different compositions after SBS extraction with cold toluene: (A) 95/5, (B) 85/15, (C) 80/20, and (D) 75/25.

characterized by a sharp interface, coarse morphology, and poor physical and chemical interaction across the phase boundaries.^{18,35} In this work, the compatibilization of the i-PP/SBS blends by reactive mixture is proposed. The compatibilizer is generated *in situ* from the grafting reaction between maleated PP (PP-MAH) and maleated SBS (SBS-MAH) by means of 4,4'-diaminodiphenylmethane as a coupling agent between the functionalized polymers.³⁶

EXPERIMENTAL

Materials

i-PP (melt flow index: 3.5 g/10 min) was obtained from OPP SA (Triceno-RS, Brazil), SBS (33 mol % styrene content) was supplied by COPERBO Petroflex Ind. Com. SA. (Rio de Janeiro, Brazil),

SBS-MAH, containing 0.33 wt % of grafted maleic anhydride, was obtained as described in ref.³⁷, and a PP-MAH containing 0.56 wt % of maleic anhydride was supplied by Uniroyal Chemical.

Blends Preparation

The i-PP/SBS binary blends containing 5, 10, 15, 20, and 25 wt % of the elastomer were prepared by melt mixing at 190°C for 10 min and 55 rpm in a Haake Rheomix 600. Ternary nonreactive blends i-PP/PP-MAH/SBS were prepared in the same processing conditions. In these blends, the i-PP content was fixed at 70 wt % and the PP-MAH/SBS weight ratio was varied to perform a total content of 30 wt %.

Ternary reactive blends were obtained in the same compositions and conditions of the ternary nonreactive blends. However, in these blends, maleated SBS (SBS-MAH) replaced the SBS.

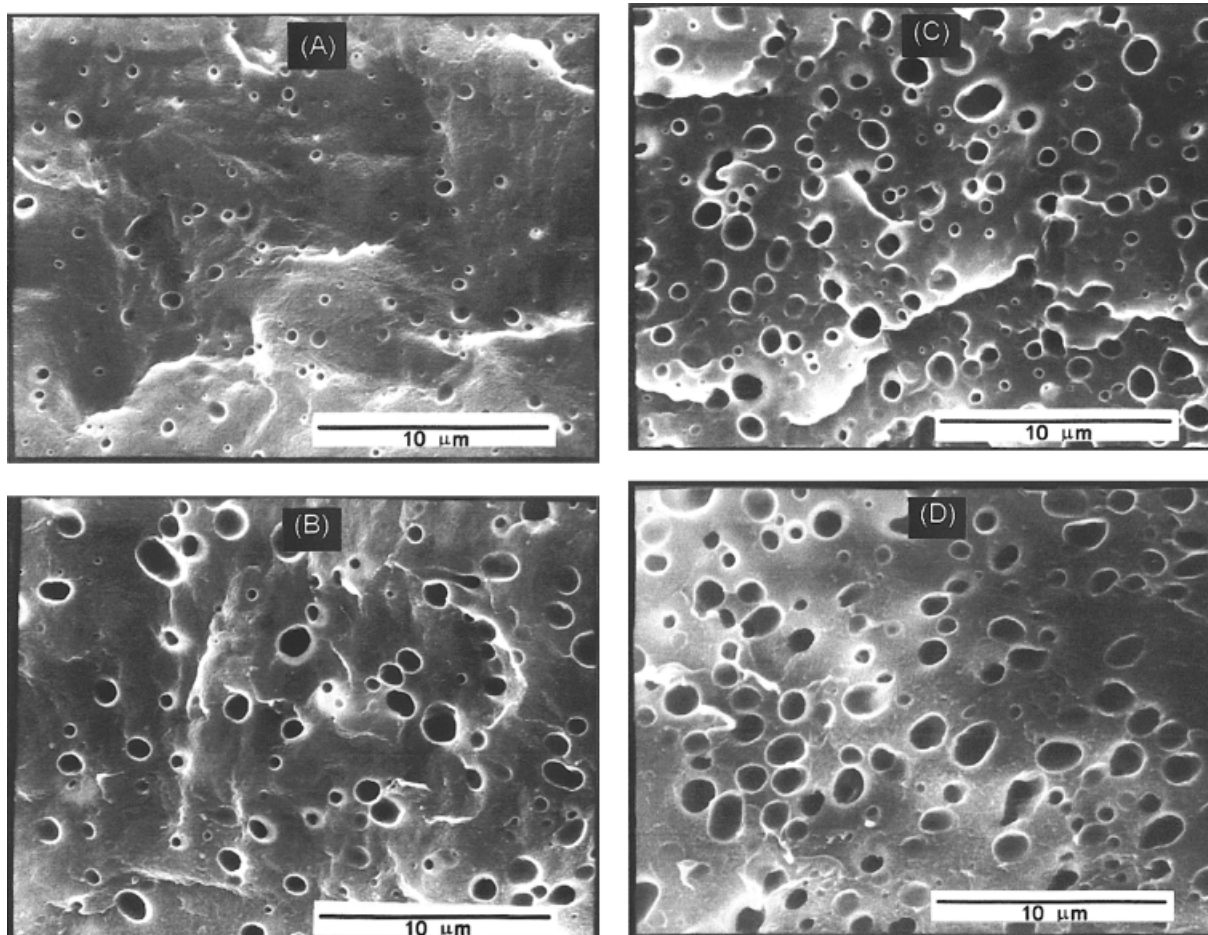


Figure 5 SEM photomicrographs of the ternary nonreactive blends iPP/PP-MAH/SBS at different compositions after SBS extraction with toluene: (A) 70/25/5, (B) 70/15/15, (C) 70/10/20, and (D) 70/5/25.

SBS-MAH contains residual free maleic anhydride and 4,4'-diaminodiphenylmethane used in the anhydride grafting reaction on the SBS.³⁷ Three groups of ternary reactive blends were prepared: the first group was obtained without addition of diamine, denominated ternary reactive I blends; the second group was obtained by the addition of 2 wt % of diamine, after 5 min at the beginning of the processing in the mixer, denominated ternary reactive II blends; and the third group, denominated ternary reactive III blends, was prepared by using the SBS-MAH previously purified, free from diamine and maleic anhydride. For ternary reactive III blends, the diamine was added in an amount to maintain a molar ratio of diamine and anhydride groups of 0.5/1 after 5 min at the beginning of the processing of these mixtures.

The stabilizer Irganox 1010 (Ciba-Geigy, São Paulo-SP, Brazil) was added to the blends at a concentration of 0.3 wt %.

The blends were milled in a Croton-type mill (Marconi, Model MA 580). Sheets of 1.10 mm thickness were prepared from the powdered blends by compression molding in a laboratory press (Marconi, Model MA 098/A) at 190°C and 2 MPa pressure using an appropriate mold. The mold was immediately cooled in water after molding.

Molded blends were cryogenically fractured in liquid nitrogen. The fractured samples were kept immersed in toluene for 3 weeks to remove the elastomer phase. The samples were then dried under vacuum. For morphological studies, the samples were sputter-coated with gold and photomicrographs were taken in a JEOL T-300 scanning electron microscope. The domain size was determined

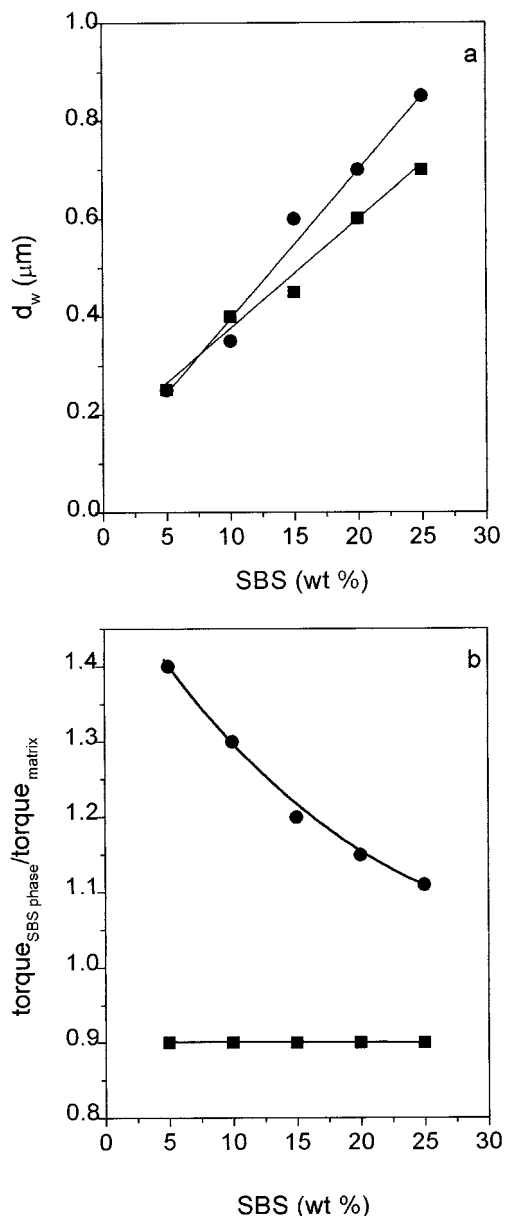


Figure 6 (a) Average particle diameter of the elastomer phase and (b) torque ratio of the blends components for: (■) i-PP/SBS and (○) i-PP/PP-MAH/SBS blends.

from the photomicrographs by using Image Pro Plus software. Several micrographs were taken for each blend and about 200 domains were taken for number-average domain diameter measurements.

RESULTS AND DISCUSSION

The torque–time curves for the pure components recorded during processing are shown in Figure 1.

The torque reaches a steady state after approximately 400 s of processing at 190°C and 55 rpm. In this case, PP-MAH presents the lowest torque, and therefore, the lowest viscosity among the blends components. On the other hand, SBS, SBS-MAH, and i-PP present close torque values at the same processing conditions after 400 s at the beginning of the processing.

The torque of the blends as a function of the elastomer contents in the blends at 400 s mixing is shown in Figure 2. The addition of SBS to i-PP has practically no influence on the torque of the mixtures (Fig. 2). However, the addition of PP-MAH to i-PP/SBS blends promotes a considerable decrease in the viscosity of the ternary reactive and nonreactive blends in comparison with the i-PP/SBS blends. This is attributed to the lower viscosity of PP-MAH, as shown in Figure 1. On the other hand, it was observed for ternary blends that the tendency of the torque is to increase as the elastomer concentration increases (Fig. 2). This behavior may be attributed to chemical reactions during melt blending between anhydride groups of SBS-MAH and of the PP-MAH and the amine groups of the coupling agent, resulting in a graft copolymer in the interface,³⁶ to crosslinking of SBS-MAH or PP-MAH and also to the decrease of PP-MAH concentration, the blend component with lower viscosity. However, the torque increase is more pronounced for ternary reactive blends than for ternary nonreactive blends, suggesting that a chemical reaction takes place in the first case.

Figure 3 shows the influence of the diamine and anhydride molar ratio on the torque. Each curve corresponds to the blend containing the same elastomer concentration and the diamine and to the varying anhydride molar ratios as the blend change from binary to ternary nonreactive, reactive I, II, and III blends. The torque behavior must reflect the extension of the grafting and crosslinking reactions, which are determined by diamine and anhydride molar ratio. For the analyzed blends, an increase of the torque for diamine and anhydride molar ratio up to 0.5/1 was observed, and then the torque remained practically constant, independent of the elastomer content. These results suggest that the increase of the diamine and anhydride molar ratio does not influence the crosslinking and grafting degree, and therefore, the blends viscosity.

The influence of the graft copolymer on the morphology of the blends was investigated by scanning electron microscopy (SEM). Figures 4

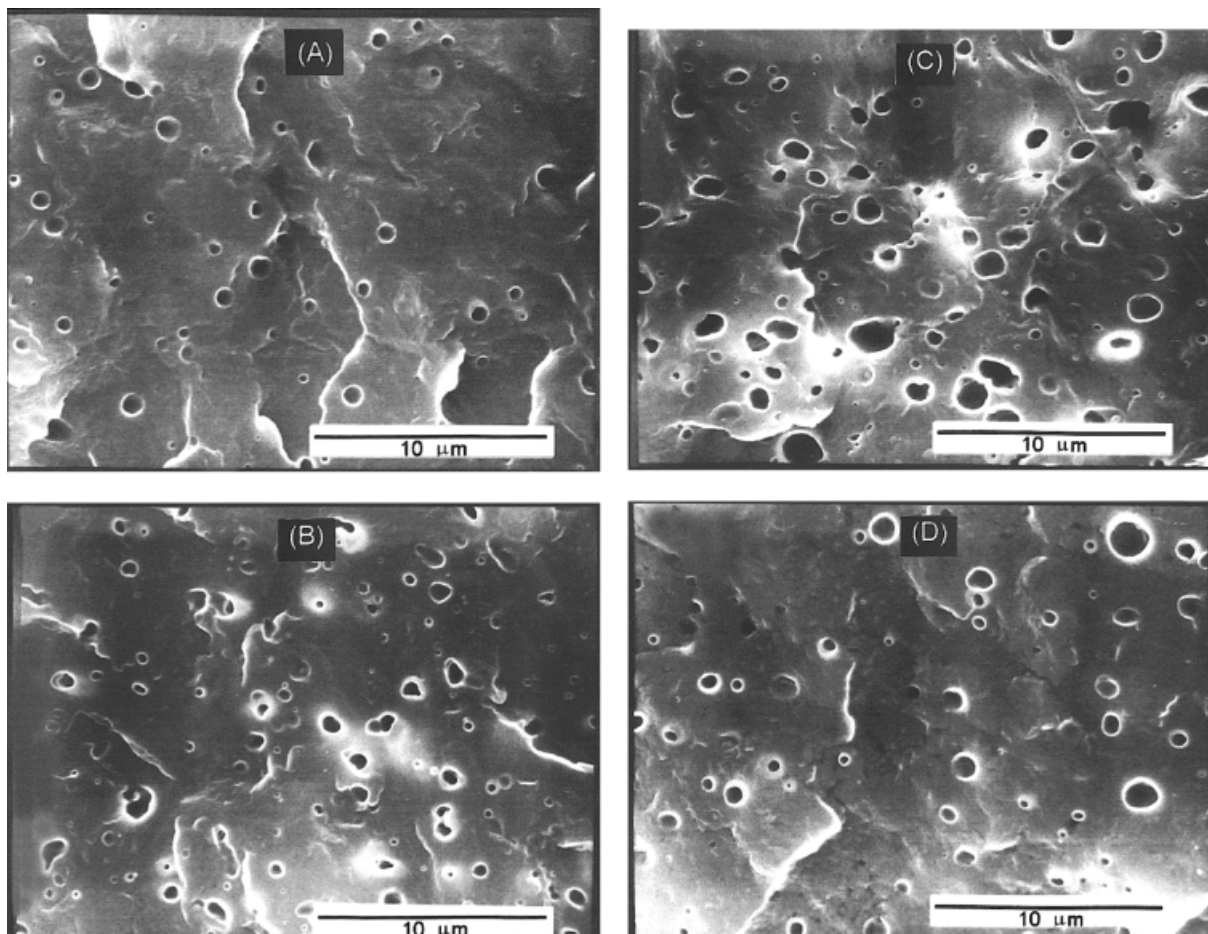


Figure 7 SEM photomicrographs of ternary reactive I blends i-PP/PP-MAH/SBS-MAH at different compositions after SBS-MAH extraction with cold toluene: (A) 70/25/5, (B) 70/15/15, (C) 70/10/20, and (D) 70/5/25.

and 5 show the photomicrographs of the i-PP/SBS and nonreactive i-PP/PP-MAH/SBS blends, respectively. The dark regions correspond to the extracted elastomeric phase. For these blends, a homogeneous dispersion of SBS is observed in the continuous i-PP matrix.

The weight-average particle diameter as a function of the SBS contents in the i-PP/SBS and i-PP/PP-MAH/SBS blends is shown in Figure 6(a). The average size of the dispersed SBS phase increases as the elastomer content in the blends increases. This behavior is attributed to the coalescence of the disperse elastomer particles. The occurrence of coalescence at higher concentrations of one the components was reported by other authors.^{25,38} The domain size is similar for binary and ternary nonreactive blends.

The size of the particles of the disperse phase depends on the viscosity of the matrix, the viscos-

ity ratio of the blends components, and the interfacial tension. Figure 6(b) shows the torque ratio of disperse SBS phase and matrix. The matrix for binary blends is i-PP, whereas for ternary blends the matrix is i-PP/PP-MAH. The torque ratio was calculated from the data for SBS, I-PP, and i-PP/PP-MAH mixtures at different compositions.³⁹ The torque ratio is independent of the SBS content in the binary blends, but decreases with increased SBS concentration in the ternary nonreactive blends, reflecting the viscosity drop of the matrix when PP-MAH is added. Despite the different rheological behaviors, both blends, i-PP/PP-MAH/SBS and i-PP/SBS, present similar domains size, suggesting that the interfacial tension is the primary factor determining the morphology.

The photomicrographs of the ternary reactive I, II, and III blends are shown in Figures 7, 8, and

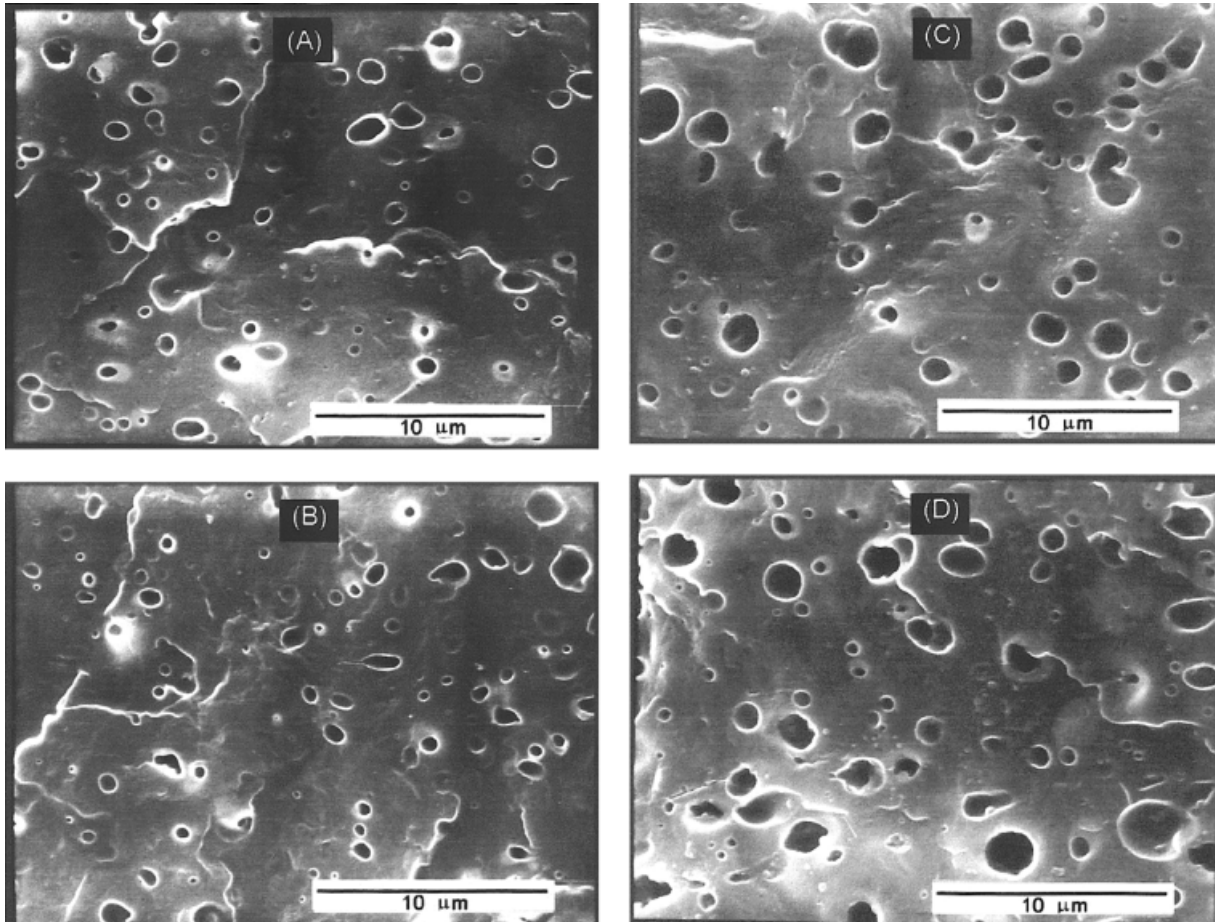


Figure 8 SEM photomicrographs of ternary reactive II blends i-PP/PP-MAH/SBS-MAH at different compositions after SBS-MAH extraction with cold toluene: (A) 70/25/5, (B) 70/15/15, (C) 70/10/20, and (D) 70/5/25.

9, respectively. The average domain size and the polydispersity d_w/d_n of the ternary blends were analyzed as a function of elastomer fractions (Ta-

ble I). The average domain size for the ternary reactive I blends is independent of the elastomer fraction, indicating a low tendency of the disperse

Table I Average Domains, Size, and Polydispersity for Ternary Nonreactive, Reactive I, II, and III Blends

Elastomer (wt %)	Average Domain Size (μm)									
	PP/SBS		Nonreactive		Ternary Blends					
	d_w	d_w/d_n	d_w	d_w/d_n	Reactive I		Reactive II		Reactive III	
	d_w	d_w/d_n	d_w	d_w/d_n	d_w	d_w/d_n	d_w	d_w/d_n	d_w	d_w/d_n
5	0.25	1.2	0.25	1.2	0.40	1.3	0.45	1.4	—	—
10	0.40	1.3	0.35	1.3	0.40	1.4	0.60	1.5	—	—
15	0.45	1.4	0.60	1.4	0.40	1.4	0.40	1.4	0.70	1.3
20	0.65	1.3	0.70	1.5	0.50	1.6	0.70	1.4	0.70	1.3
25	0.70	1.4	0.85	1.4	0.45	1.4	0.60	1.7	0.65	1.3

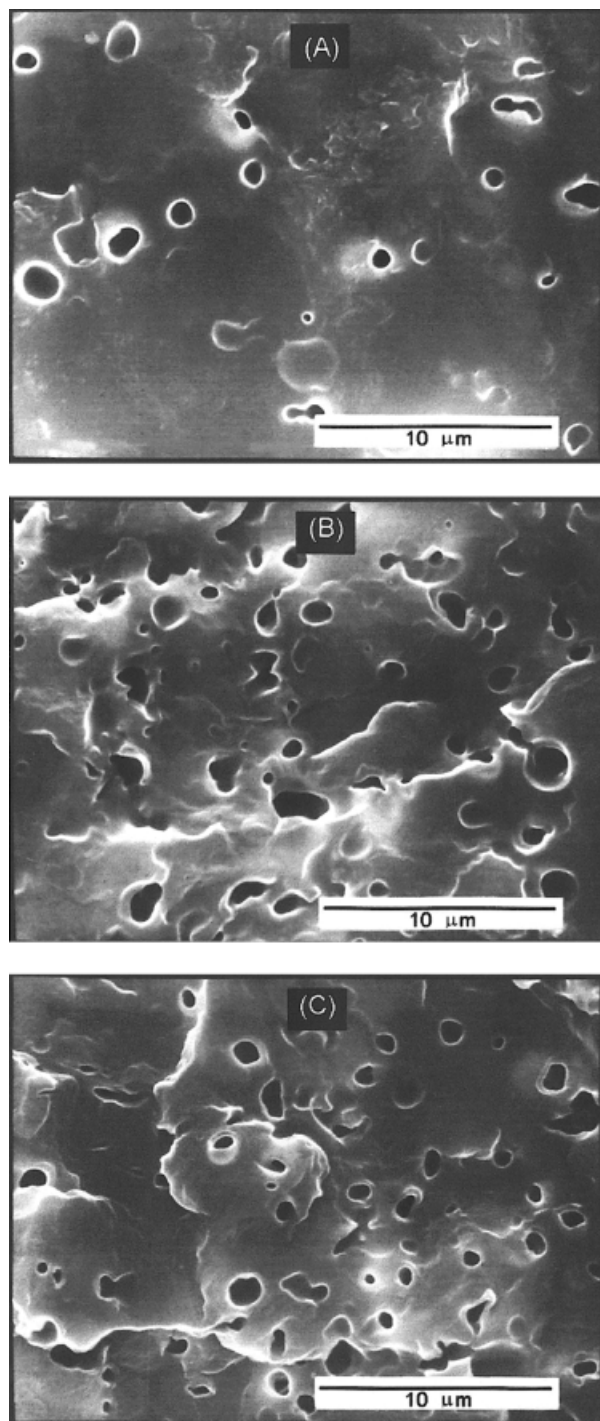


Figure 9 SEM photomicrographs of ternary reactive III blends i-PP/PP-MAH/SBS-MAH at different compositions after SBS-MAH extraction with cold toluene: (A) 70/25/5, (B) 70/15/15, (C) 70/10/20, and (D) 70/5/25.

phase to coalescence. This fact is attributed to the formation of the graft copolymer between SBS-MAH and PP-MAH through the coupling agent

(4,4'-diaminediphenylmethane) that stabilizes the morphology against coalescence. Among the ternary blends, there are no significant differences in the domain size, indicating that the morphology is governed by the extension of grafting and crosslinking. Those remain practically constant as the diamine and anhydride molar ratio increases, as suggested from torque data.

The ternary reactive III blends 70/10/20 and 70/5/25 are characterized by the nonspherical domains (Fig. 9). The average domain size for these blends is practically independent of the elastomer fraction (Table I).

CONCLUSION

The morphology of the binary and ternary nonreactive blends do not differ significantly, exhibiting a disperse elastomer phase in the thermoplastic matrix. The domain size increases with increased elastomer concentration as a consequence of the coalescence. The viscosity of the ternary reactive blends increases with increased elastomer contents, but does not vary for blends containing the same elastomer concentration and variable diamine and anhydride molar ratio. This result suggests that the grafting degree is not dependent on the diamine and anhydride molar ratio. The morphology of the ternary reactive blends does not vary with elastomer concentration as well as with the diamine and anhydride molar ratio. The domain size is determined by the viscosity of the disperse phase and of the matrix and also by the interfacial tension. Both parameters must vary in inverse proportion to explain the fact that the domain size does not change with the elastomer concentration. The presence of the grafting copolymer stabilizes the generated morphology against coalescence.

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