

Blends of i-PP and SBS. II. Influence of *In Situ* Compatibilization on the Mechanical Properties

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ABSTRACT: This article concerns the *in situ* compatibilization of immiscible isotactic polypropylene/styrene-butadiene-styrene triblock copolymer blends (i-PP/SBS) by use of a reactive mixture. For this purpose, maleated PP (PP-MAH) and SBS (SBS-MAH) were used as functionalized polymers and 4,4'-diaminodiphenylmethane was used as a coupling agent between maleated polymers, resulting in a graft copolymer. Binary blends of i-PP/SBS, nonreactive ternary blends of i-PP/PP-MAH/SBS, and reactive ternary blends of i-PP/PP-MAH/SBS-MAH with varying diamine/

anhydride molar ratios were prepared. The mechanical properties of the blends were determined by tensile and impact-resistance tests. The optimum improvement in the mechanical properties was found when the diamine/anhydride molar ratio in the ternary reactive blends was 0.5/1. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 516–522, 2003

Key words: compatibilization; poly(propylene) (PP); mechanical properties

INTRODUCTION

The combination of elastomers with rigid polymers is one of the methods to improve toughness. Isotactic polypropylene (i-PP) is one of the widely used thermoplastics showing very interesting mechanical and thermal properties. However, for many applications as engineering plastic, its toughness and, in particular, its notched toughness are deficient. Studies on the blends of i-PP with various elastomers have generated considerable interest owing to desirable improvement in certain properties useful for various specific applications. Elastomers such as the ethylene-propylene copolymer (EPR),^{1–7} ethylene-propylene-diene terpolymer (EPDM),^{8–13} and styrene-butadiene block copolymer^{14–18} have been extensively used for this purpose. The morphology of the blend or, more specifically, the rubber particle size has a strong influence on the toughening, but its influence may vary widely from one system to another. The optimal domain size depends on the deformation and fracture mechanisms involved, among other factors. Jang et al.¹⁹ found, for PP/EPDM blends, that particles with a size below 0.5 μm initiate yielding, while particles with a size above 0.5 μm initiate crazes. The modulus as well as the yield stress of PP-rubber blends decreases with the

rubber content. However, the particle size has no or only a slight effect on these properties.²

Wu²⁰ proposed that the distance between particles, rather than their size, is the most fundamental parameter controlling the toughening of polyamide blends. Similar conclusions were pointed out for PP/SEBS blends. The PP/SEBS blends are ductile when the interparticle distance is less than 0.27 μm and brittle above this value.¹⁷

It is also recognized that some degree of adhesion or coupling of the rubber and matrix phases is necessary for effective rubber toughening. Generally, PP/elastomer blends are immiscible and incompatible, exhibiting poor mechanical properties, such as low impact resistance and low tensile elongation. The incorporation of functional groups into polymer chains is one of the efficient ways to improve adhesion or to make PP reactive with other polymers. A copolymer compatibilizer can be generated *in situ* by chemical reaction among the functional groups of the components of the blends.^{21–26} Such grafting reactions provide the necessary adhesion between the phases and promote a better dispersion of the elastomer. The smaller phase size plus the increased phase adhesion results in improved physical properties such as impact strength^{20,27,28} and tensile strength.²⁹ An example of this is the compatibilization of blends of maleated PP and maleated EPR blends by addition of a third reactive phase, a polyetheramine, which can react with both polymers, building an imide linkage. The mechanical properties of the compatibilized blends are better than those of the noncompatibilized blends and are influenced by the compatibilizer contents. A mixture containing 3 wt

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TABLE I
Mechanical Properties for the Different Blends

Blends	Elastomer (wt %)	Young's modulus (MPa)	Elongation at break (%)	Izod impact strength (J/m)
PP/SBS	5	926 ± 83	501 ± 36	44 ± 6
	10	861 ± 86	567 ± 61	56 ± 2
	15	812 ± 62	590 ± 53	69 ± 4
	20	758 ± 42	623 ± 50	88 ± 4
	25	698 ± 56	574 ± 25	128 ± 13
PP/SBS-MAH	5	1099 ± 34	426 ± 26	39 ± 7
	10	843 ± 45	579 ± 33	61 ± 2
	15	865 ± 56	498 ± 40	82 ± 6
	20	794 ± 31	393 ± 64	110 ± 3
	25	678 ± 48	390 ± 30	148 ± 4
Ternary nonreactive	5	1056 ± 89	13 ± 4	38 ± 1
	10	935 ± 42	36 ± 7	50 ± 5
	15	884 ± 58	306 ± 74	61 ± 4
	20	716 ± 48	438 ± 65	79 ± 4
	25	673 ± 67	326 ± 50	137 ± 6
Ternary reactive I	5	1015 ± 84	16 ± 6	26 ± 3
	10	986 ± 72	21 ± 4	43 ± 4
	15	880 ± 54	25 ± 9	53 ± 7
	20	795 ± 51	51 ± 28	76 ± 9
	25	787 ± 43	368 ± 34	101 ± 7
Ternary reactive II	5	1018 ± 71	20 ± 5	30 ± 3
	10	984 ± 60	78 ± 12	48 ± 4
	15	889 ± 40	281 ± 70	66 ± 4
	20	831 ± 43	261 ± 60	70 ± 5
	25	744 ± 58	234 ± 109	163 ± 6
Ternary reactive III	15	765 ± 34	607 ± 47	85 ± 5
	20	609 ± 33	460 ± 14	111 ± 3
	25	553 ± 44	394 ± 19	170 ± 7

% of the compatibilizer, which corresponds to a diamine/anhydride molar ratio equal to 0.5/1, presents the best interfacial adhesion and, consequently, the best mechanical properties.²¹

In the previous work,³⁰ we reported on the preparation and the morphology of the binary blends of the i-PP/ styrene-butadiene-styrene triblock copolymer (SBS) and of the nonreactive and reactive ternary blends. The ternary reactive blends were prepared from i-PP and maleated PP and SBS (PP-MAH and SBS-MAH), using 4,4'-diaminediphenylmethane as a coupling agent, while for nonreactive ternary blends, SBS was used instead of SBS-MAH. A graft copolymer is formed during the mechanical mixture of the reactive ternary blends and the reaction extension is not dependent on the diamine/anhydride molar ratio above 0.5. The morphology of the binary and ternary nonreactive blends with the same elastomer concentration do not differ significantly, exhibiting a disperse elastomer phase in the thermoplastic matrix. The domain size increases with increased elastomer concentration. However, the morphology of the ternary reac-

tive blends does not vary with the elastomer concentration or with the diamine/anhydride molar ratio. This behavior was explained based on the hypothesis that the ratio of the viscosity of the dispersed phase and of the matrix and the interfacial tension vary in inverse proportion. In this article, the mechanical properties of the blends were studied.

EXPERIMENTAL

Materials

i-PP (IF = 3.5 g/10 min) was obtained from OPP SA (Triunfo, Brazil). SBS (33% styrene content, IF = 4.4 g/10 min) was supplied by COPERBO Petroflex Ind. Com. SA. (Rio de Janeiro, Brazil). A maleated SBS (SBS-MAH) containing 0.33 wt % of maleic anhydride was obtained as described in ref. 31 and a maleated PP (PP-MAH, Polybond 3200, IF = 100 g/10 min) containing 0.56 wt % of maleic anhydride was supplied by UNIROYAL Chemical (Rio Claro, Brazil).

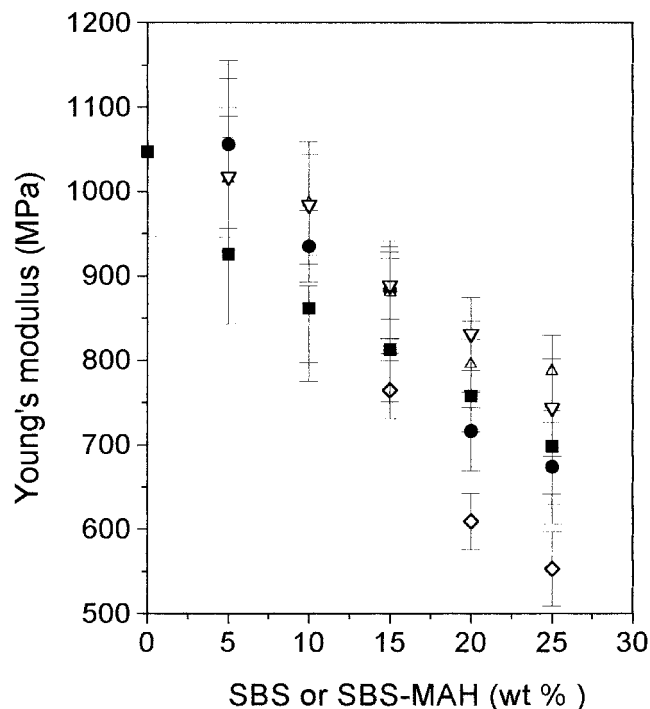


Figure 1 Young's modulus: (■) i-PP/SBS; (●) i-PP/PP-MAH/SBS; (△) reactive I, (▽) reactive II, and (◇) reactive III ternary i-PP/PP-MAH/SBS-MAH blends.

Preparation of blends

The i-PP/SBS binary blends containing 5, 10, 15, 20, and 25 wt % of the elastomers were prepared by melt mixing at 190°C for 10 min and 55 rpm, in a HAAKE Rheomix 600. Ternary nonreactive blends of 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 ratio was varied to a total of 30 wt %.

Ternary reactive blends were obtained in the same compositions and conditions as those of the ternary nonreactive blends. However, in these blends, SBS was replaced by SBS-MAH. SBS-MAH contains residual free maleic anhydride and 4,4'-diaminediphenylmethane, used for the grafting reactions.³¹ Three groups of ternary reactive blends were prepared: The first one, denominated ternary reactive I blends, was

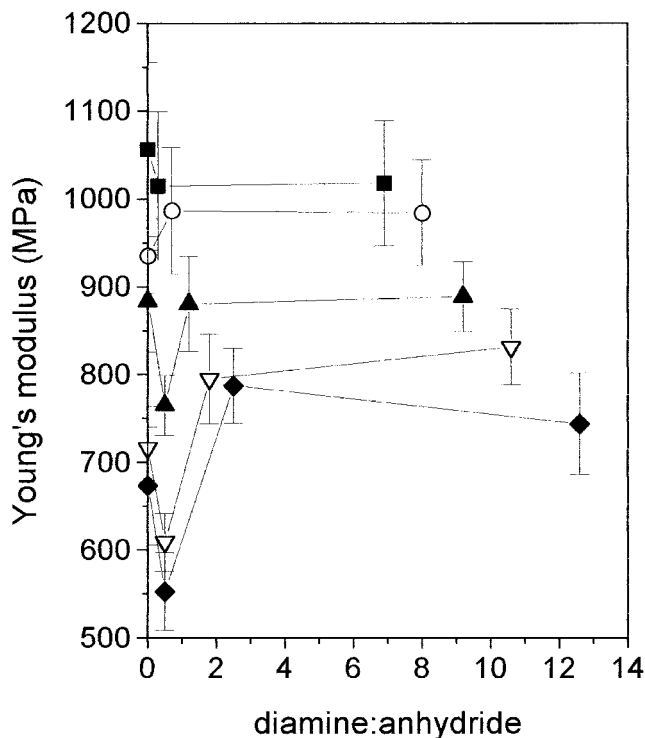


Figure 2 Young's modulus as a function of the diamine/anhydride molar ratio for the nonreactive and reactive I, reactive II, and reactive III ternary i-PP/PP-MAH/SBS-MAH blends: (■) 70/25/5; (○) 70/20/10; (▲) 70/15/15; (▽) 70/10/20; (◆) 70/5/25.

obtained without addition of diamine; the second one, denominated ternary reactive II blends, was obtained with the addition of 2 wt % of diamine after 5 min at the beginning of the processing in the mixer; and the third group, denominated ternary reactive III blends, was prepared by using the SBS-MAH previously purified, free from diamine and maleic anhydride, with 15, 20, and 25 wt % of the elastomer. For ternary reactive III blends, after 5 min of the beginning of the processing of these mixtures, diamine was added in an amount to maintain a diamine/anhydride molar ratio equal to 0.5/1. The stabilizer, Irganox 1010 (Ciba Geiger, São Paulo, Brazil) was added to the blends at a concentration of 0.3 wt %.

TABLE II
Crystallinity Degree (X_c) for Binary and Ternary Blends

Elastomer (wt %)	X_c (%)				
	i-PP/SBS	Ternary non-reactive	Ternary reactive I	Ternary reactive II	Ternary reactive III
5	61	64	61	60	
10	63	65	62	62	
15	61	62	64	61	63
20	61	59	65	62	64
25	61	61	64	63	65

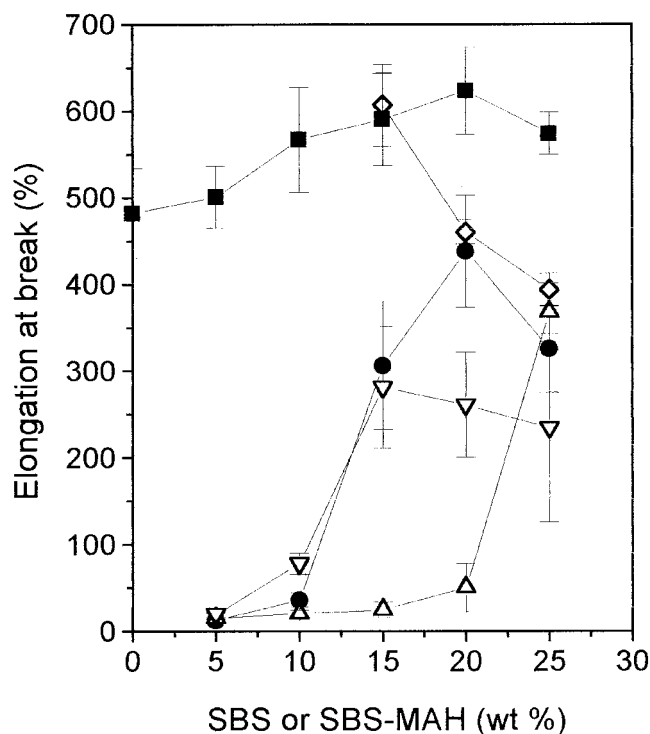


Figure 3 Elongation at break: (■) i-PP/SBS; (●) i-PP/PP-MAH/SBS; (△) reactive I, (▽) reactive II, and (▽) reactive III ternary i-PP/PP-MAH/-SBS-MAH blends.

The blends were milled in a Croton-type mill (Marconi) at room temperature, 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.

The specimens for tensile testing were obtained from sheets using an appropriate knife according to ASTM-D1708. The samples for the impact test were injected into a mini Max Molder (Model LMM – 2017) at 190°C in an appropriate mold according to ASTM D-256 at room temperature. Tensile testing of the blends was carried out at $25 \pm 2^\circ\text{C}$ on an EMIC MEM 500 equipment at a 10-mm/min strain rate with an initial gauge length of 22.9 mm according to ASTM D-1708.

The Izod impact strength was measured on notched specimens with an EMIC impact tester Model AIC-1 at 25°C according to ASTM D-256. Rectangular specimens of $37.5 \times 3.0 \times 0.3$ -mm dimensions with 2-mm-deep triangular notches of 45° were used.

The crystallinity of the i-PP phase in the blends was determined from DSC curves obtained using a DSC 2910 (TA Instruments) at a heating rate of 10°C/min in the temperature range from 50 to 200°C. The degree of crystallinity for the blend was calculated as the ratio of the heat of fusion of the i-PP in the

blend and that corresponding to the 100% crystalline i-PP: 138 J/g.²⁴

RESULTS AND DISCUSSION

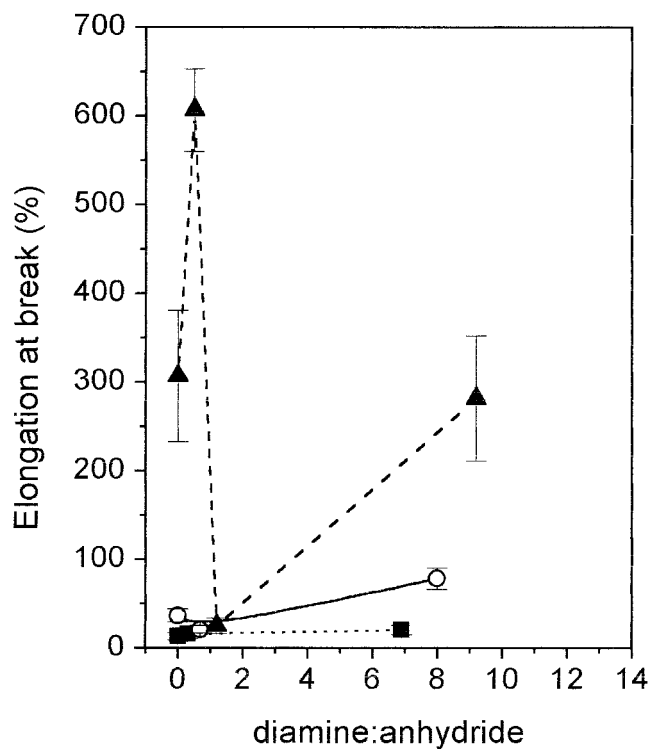
The tensile properties of the blends are shown in Table I. The Young's modulus as a function of the blend composition is shown in Figure 1. The increase of the SBS or SBS-MAH concentration in the blends causes a decrease of the Young's modulus. This behavior can be attributed to the presence of the soft elastomer phase and to the decrease of i-PP crystallinity. However, the incorporation of the elastomer and the PP-MAH to i-PP does not affect the degree of crystallinity of i-PP (Table II) or the crystal morphology, as observed from DSC and X-ray diffraction,³² respectively.

The Young's modulus is minimum for the reactive ternary blends with a diamine/anhydride molar ratio equal to 0.5/1, independently of the elastomer content (Fig. 2). The elongation at break of the i-PP/SBS blends is higher than for the pure i-PP (Fig. 3) and increases with the SBS content. However, nonreactive and reactive I and II ternary blends present lower elongation at break in comparison with pure i-PP. The mechanical behavior of the blends is attributed to the presence of PP-MAH, which exhibits low viscosity.³⁰ On the other hand, the decrease of the elongation at break for the ternary reactive blends in relation to the nonreactive ones is attributed to the plasticization and degradation effect of the diamine excess.

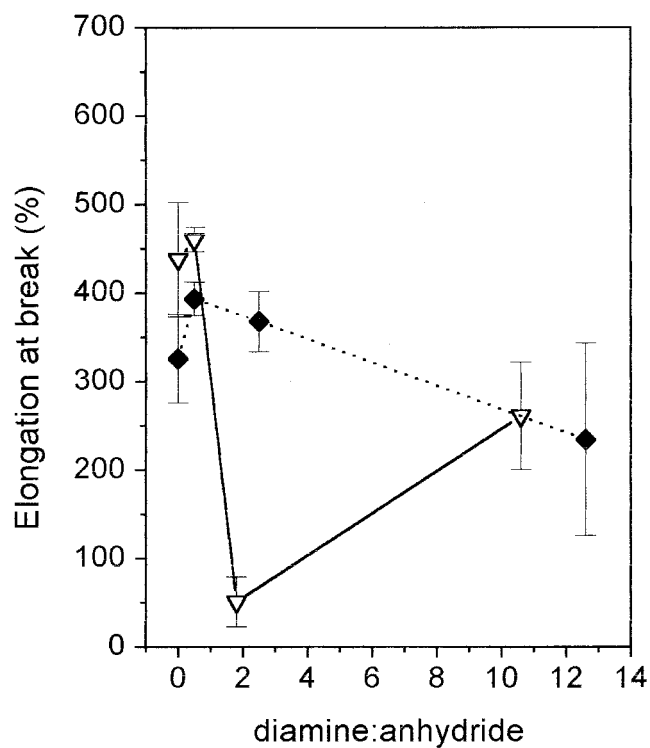
This last hypothesis was tested using mechanical tests performed on the reactive I and II ternary blends at a composition of i-PP/PP-MAH/SBS-MAH equal to 70/15/15, submitted to extraction with acetone, a nonsolvent for the blends' components. This procedure should eliminate all low molecular weight molecules present in the blends as free diamine, maleic anhydride, and also the antioxidant. The blends were carefully dried after the extraction and the films were compression-molded as described in the Experimental section without addition of antioxidants. The temperature and time of the molding could cause degrada-

TABLE III
Tensile Properties of the i-PP/PP-MAH/SBS 70/15/15 Blend Before and After Acetone Extraction

	Elongation at break (%)	Young's modulus (MPa)
Ternary blends 70/15/15		
Reactive I before extraction	25 ± 9	880 ± 54
Reactive I after extraction	380 ± 14	820 ± 64
Reactive II before extraction	281 ± 70	889 ± 40
Reactive II after extraction	392 ± 43	824 ± 59
Reactive III	607 ± 47	765 ± 34
Nonreactive	306 ± 74	88 ± 58



(a)



(b)

Figure 4 Elongation at break as a function of the diamine/anhydride molar ratio for the nonreactive and reactive I, reactive II, and reactive III ternary i-PP/PP-MAH/SBS-MAH blends with (a) (■) 70/25/5, (○) 70/20/10, and (▲) 70/15/15 and (b) (▽) 70/10/20 and (◆) 70/5/25.

tion of the blends. However, there is no evidence of significant degradation because the mechanical properties of these blends are better than those of the other blends. The tension properties for these extracted blends are shown in the Table III. A significant improvement in the elongation at break was observed for extracted reactive ternary I and II blends, while the Young's modulus remained constant. The elongation at break of the extracted reactive I blends is about 1520% higher than the value obtained for the corresponding nonextracted blends, indicating a strong influence of the free diamine and anhydride on the mechanical properties. On the other hand, comparison of the elongation at break results for the nonreactive and reactive I and II ternary blends after the extraction allows one to conclude that the grafting copolymer formed in the reactive ternary blends promotes a better elastomer-matrix adhesion. Ternary reactive III blends exhibit the highest elongation at break, suggesting a better adhesion between the phases, since the morphology of the ternary blends was not affected by the diamine/anhydride molar ratio.³⁰

The elongation at break exhibits a maximum value for the blends containing 15, 20, and 25 wt % of the elastomer when the diamine/anhydride molar ratio is equal to 0.5/1, a stoichiometric condition [Fig. 4(a,b)]. On the other hand, for blends containing 5 and 10 wt % of the elastomer, the dependence of the elongation

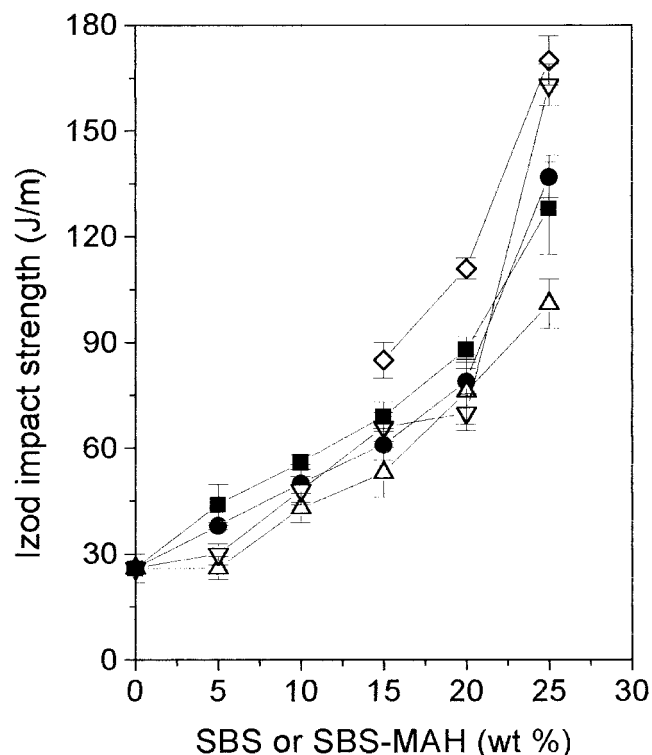


Figure 5 Impact strength: (■) i-PP/SBS; (●) i-PP/PP-MAH/SBS; (△) reactive I, (▽) reactive II, and (◇) reactive III ternary i-PP/PP-MAH/SBS-MAH blends.

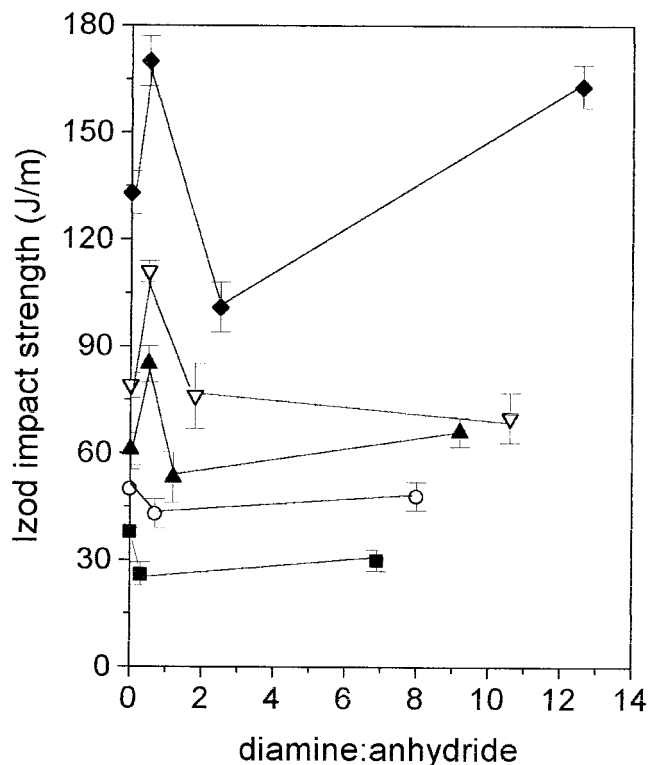


Figure 6 Izod impact strength as a function of the diamine/anhydride molar ratio for the nonreactive and reactive I, reactive II, and reactive III ternary i-PP/PP-MAH/SBS-MAH blends: (■) 70/25/5; (○) 70/20/10; (▲) 70/15/15; (▽) 70/10/20; (◆) 70/5/25.

at break on the diamine/anhydride molar ratio was not observed.

The variation of the notched Izod impact strength with the elastomer fraction in the blends is shown in Figure 5. The i-PP used in this study has a notched Izod impact strength of 26 J m^{-1} . After processing in the Haake mixer at 190°C , 55 rpm, and 10 min, the resistance to impact remains practically unaffected. The addition of SBS to i-PP promotes increase of the impact resistance as the SBS concentration increases (Fig. 5). When PP-AM is added to the i-PP/SBS to form i-PP/PP-MAH/SBS blends, a slight loss in the impact resistance occurs. There was no improvement in the impact strength of the reactive I and II ternary blends over the nonreactive blends (Fig. 5). However, the reactive III ternary blends present an improvement in the impact resistance in comparison with the corresponding reactive I and II and nonreactive blends. The impact resistance for the ternary reactive III blend containing 25 wt % of the elastomer is 6.5 times greater than for i-PP.

Figure 6 shows the impact resistance as a function of the diamine/anhydride molar ratio. A maximum in the notched Izod impact strength occurs at a 0.5/1 diamine/anhydride molar ratio. At greater ratios, the

impact resistance decreases and then it remains constant.

Torque measurements and morphological analysis suggest that the extension of graft copolymerization involving diamine and anhydride groups is more efficient at the molar ratio of diamine/anhydride of 0.5/1, the stoichiometric ratio.³⁰ Therefore, the observed mechanical behavior should be related to the graft copolymer concentration, which is responsible for phase adhesion and for the morphology.

CONCLUSIONS

The graft copolymer generated *in situ* during the mechanical mixture in the melt state of I-PP/SBS blends affects the processing properties and, consequently, the mechanical properties of the blends. The addition of the SBS elastomer provides an improvement in the tensile properties as well as in the resistance to the impact comparatively to pure i-PP. However, this effect is more pronounced for blends *in situ* compatibilized, when the molar ratio of diamine and anhydride groups is equal to 0.5.

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