

Morphology and Mechanical Properties of Polypropylene/Maleated Styrene–Butadiene–Styrene Triblock Copolymer Blends

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ABSTRACT: The morphology and mechanical properties of blends of isotactic polypropylene (i-PP) and a maleated butadiene–styrene–butadiene triblock copolymer with maleic anhydride (SBS–MAH), i-PP/SBS–MAH, were investigated and compared with those of corresponding blends of i-PP and a styrene–butadiene–styrene triblock copolymer (SBS), i-PP/SBS. The blends were prepared in a mixer at 190°C with 5–25 wt % elastomer compositions. The blends exhibited a two-phase morphology with a dispersed elastomer phase in the continuous i-PP matrix. The size and shape of the elastomer particles and the mechanical proper-

ties of the blends depended on the nature and concentration of the elastomer. The i-PP/SBS–MAH blends showed an impact strength superior to that of the corresponding i-PP/SBS blends. These results were attributed to the formation of the graft copolymer during the melt blending, which was verified by Fourier transform infrared. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 359–365, 2002

Key words: blends; elastomers; poly(propylene) (PP); reactive processing

INTRODUCTION

Despite some excellent properties, isotactic polypropylene (i-PP) presents a low impact strength, especially at low temperatures. For improved impact strength of i-PP, various elastomers have been incorporated under melt-blending conditions. This is the simplest technique offering custom-tailored materials for varied requirements at comparatively low cost. Ethylene–propylene–diene terpolymers,^{1–6} ethylene–propylene copolymers,^{7–13} polybutadiene,¹⁴ nitrile rubber,^{15,16} styrene–ethylene–butylene–styrene triblock copolymer (SEBS),^{17–20} and styrene–butadiene–styrene triblock copolymer (SBS)²¹ have been used as elastomeric components. Generally, the incorporation of an elastomer improves the impact strength, but it also results in the deterioration of tensile properties.

Although the structures of i-PP and elastomers are similar, i-PP/elastomer blends are immiscible, with poor interfacial adhesion between the elastomer and i-PP phases. For improved mechanical properties of the final blends, attempts have been made to enhance the miscibility or promote polymer/elastomer interfa-

cial interaction. The latter gives rise to a more appropriate method for achieving desired material properties, such as the impact strength. The interfacial interaction can be improved by the addition of a compatibilizer, normally a graft or block copolymer, and by reactive blending. During reactive blending, the reaction between the polymers results in a graft copolymer.

Numerous factors affect the morphology of thermo-plastic/elastomer blends obtained by melt blending, such as interfacial tension, relative viscosities between the two components, mixing intensity, and other processing parameters. Morphology is an important factor determining the mechanical properties of blends.

For i-PP/SEBS, it has been demonstrated that the elastomer particle size must be below a critical particle size for toughness to be achieved. For blends containing 10, 15, and 20 wt % SEBS, it corresponds to 0.4, 0.5, and 0.7 μm , respectively.²⁰ There is a critical lower limit on elastomer particle size (0.27 μm) above which toughness is not achieved for i-PP/SEBS blends.²⁰ However, it has been argued that the true critical dimension determining the mechanical properties is the interparticle distance rather than the particle size.²²

The purpose of this article is the further exploration of the differences in the morphology and mechanical properties of i-PP blends with SBS and a maleated styrene–butadiene–styrene triblock copolymer with maleic anhydride (SBS–MAH). Maleic anhydride

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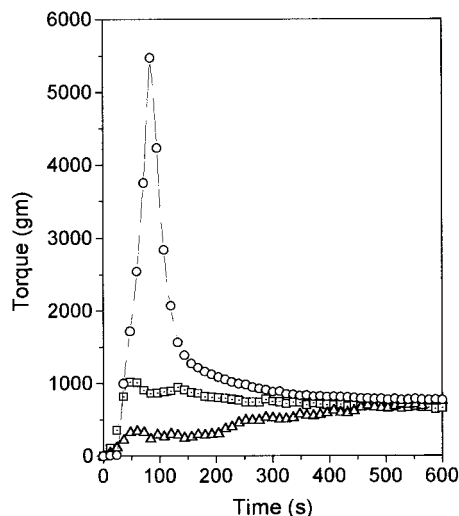


Figure 1 Torque of i-PP, SBS, and SBS-MAH at 400 s of mixing measured at 170°C and 55 rpm: (○) i-PP; (□) SBS, and (△) SBS-MAH.

(MAH) was first grafted onto the elastomer as described in a previous work.²³

EXPERIMENTAL

Materials

i-PP (3.5 g/10 min) was obtained from OPP SA (Triunfo, Brazil). SBS (33 wt % styrene; weight-average molecular weight = 105,000 g/mol; weight-average molecular weight/number-average molecular weight = 1.1) was supplied by Coperbo Petroflex Co. SA (Rio de Janeiro, Brazil). SBS-MAH containing 0.33 wt % MAH was obtained as described in ref. 23. SBS rubber

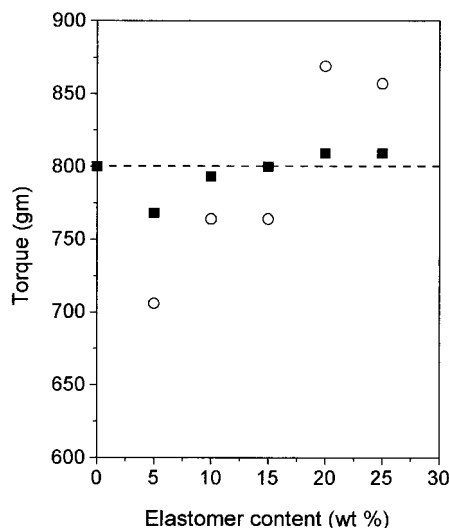


Figure 2 Torque at 400 s of mixing, 170°C, and 55 rpm as a function of the elastomer concentration: (■) i-PP/SBS and (○) i-PP/SBS-MAH.

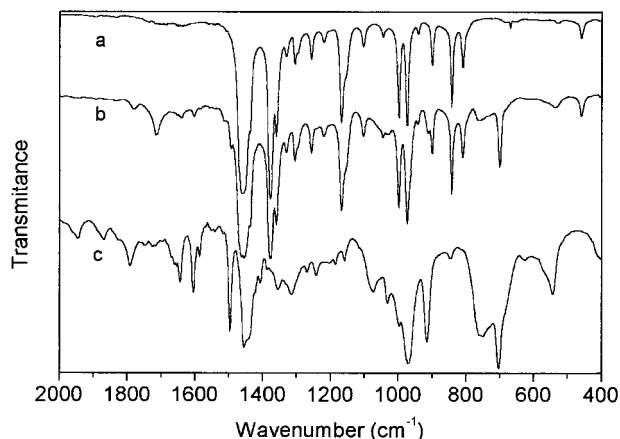


Figure 3 FTIR spectra of (a) i-PP, (b) chloroform-insoluble fractions of i-PP/SBS-MAH blends containing 10 wt % elastomer, and (c) SBS-MAH.

was mixed with an appropriate molar ratio of MAH, benzoyl peroxide, and 4,4'-diaminodiphenylmethane in a Haake Rheomixer (Karlsruhe, Germany) at 150°C and 55 rpm for 20 min. The obtained SBS-MAH was used without further purification; therefore, it must have contained free residual MAH and diamine.

Preparation of the blends

The i-PP/SBS-MAH and i-PP/SBS blends containing 5, 10, 15, 20, and 25 wt % elastomers were prepared by melt mixing at 190°C and 55 rpm for 10 min in a Haake Rheomixer 600. During the melt mixing, a 0.3 wt % stabilizer (Irganox 1010, Ciba Geigy, São Paulo, Brazil) was added to all the blends.

The blends were further powdered in a Croton mill (Marconi MA 580, São Paulo, Brazil) and then molded by compression in plane sheets 1.10 mm thick in a laboratory press at 190°C and 2 MPa with an appropriate metal mold that was immediately cooled in water after molding. The specimens for the tensile test were obtained from these sheets with an appropriate knife according to ASTM Standard D 1708. The specimens for impact testing were injection-molded in an LMM-2017 Mini Max Molder, from Custom Scientific Instruments, Inc. (Whippany, NJ).

The insoluble fraction of the i-PP/SBS-MAH blends was determined by the extraction of powdered samples in xylene under reflux for 1 h. The isolated soluble and insoluble fractions were analyzed by infrared spectroscopy with Bomem, Hartman & Braun-Michelson MB series equipment (Quebec, Canada). The transmittance spectra were obtained of films compression-molded from 400 to 4000 cm^{-1} with 20 scans and 2 cm^{-1} resolution.

Compression-molded blends were fractured in liquid nitrogen. The fractured samples were kept im-

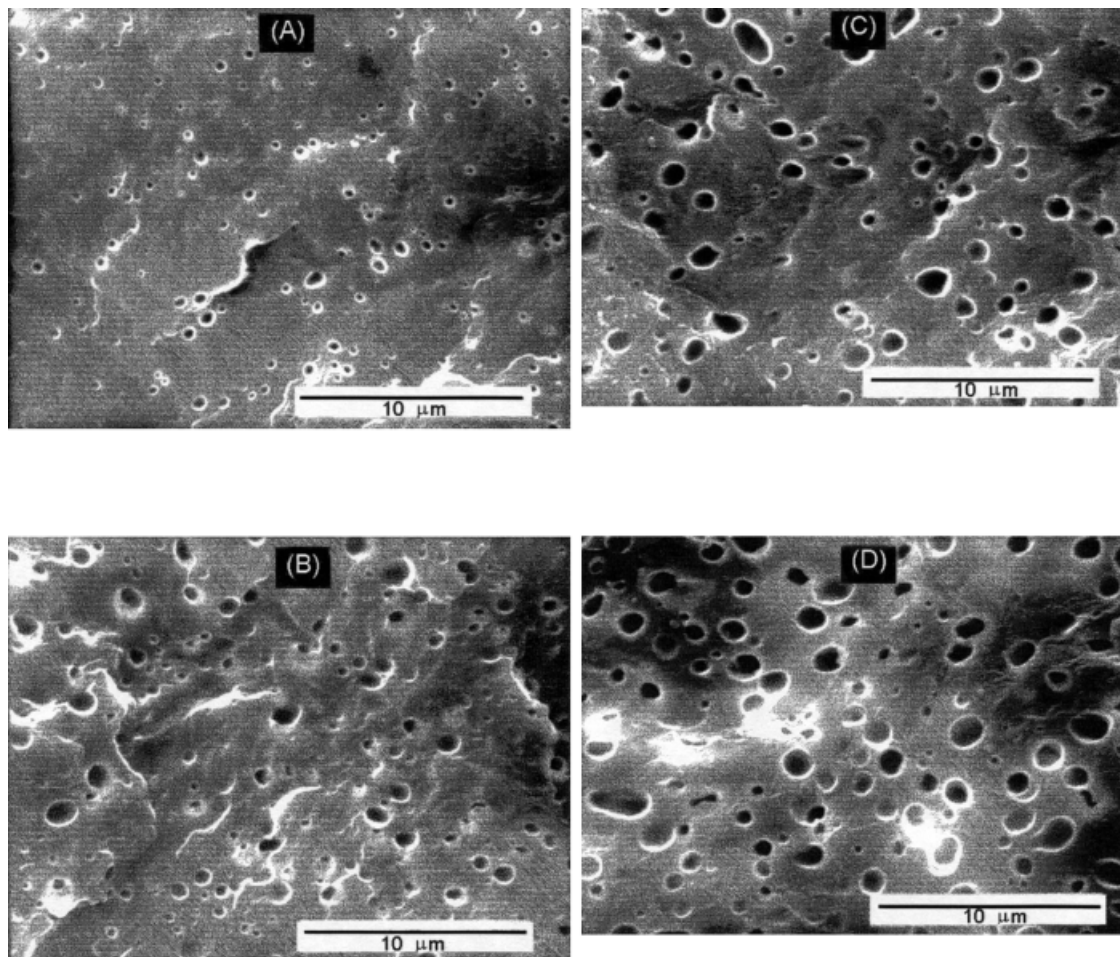


Figure 4 SEM photomicrographs of i-PP/SBS blends of different compositions after SBS extraction with toluene: (A) 95/05, (B) 85/15, (C) 80/20, and (D) 75/25.

mersed in toluene at room temperature for 3 weeks for the removal of only the elastomer phase. The samples were then dried in vacuo. For morphological studies, the samples were sputter-coated with gold, and photomicrographs were taken with a JEOL T-300 scanning electron microscope (Middleton, WI). The domain size was determined from the photomicrographs with the Image Pro Plus software from Media Cybernetics (Silver Spring, MD). Several micrographs were taken for each blend, and about 100 domains were analyzed.

Tensile testing of the blend samples was carried out at $25 \pm 2^\circ\text{C}$ on an EMIC MEM 500 instrument (São José dos Pinhais, Brazil) at a 10 mm/min strain rate with an initial gauge length of 22.9 mm according to ASTM Standard D 638.

The Izod impact strength was measured on notched specimens with an EMIC impact AIC-1 tester (São José dos Pinhais, Brazil) according to ASTM Standard D 256 at 25°C . Rectangular specimens ($37.5 \text{ mm} \times 3.0 \text{ mm} \times 0.3 \text{ mm}$) with 2-mm-deep triangular notches of 45° were used.

The crystallinity degree of i-PP in the blends was determined from differential scanning calorimetry (DSC) curves obtained with a TA Instruments DSC 2910 (New Castle, DE) at a heating rate of $10^\circ\text{C}/\text{min}$ and within a temperature range of $50\text{--}200^\circ\text{C}$. The crystallinity degree of the i-PP phase in the blends was calculated on the basis of its fraction in the mixture and the melting enthalpy of the 100% crystalline i-PP (138 J/g).¹⁵

RESULTS AND DISCUSSION

The torque of the polymers and their blends was monitored as a function of the mixture time (Fig. 1). After an initial transient period, all polymers reached an approximately constant torque value. The torque values for the pure SBS, SBS-MAH, and i-PP after 400 s were very close; this indicated that the components of the blend had similar viscosities. This fact allows a direct comparison of the torque for i-PP/SBS and i-PP/SBS-MAH blends.

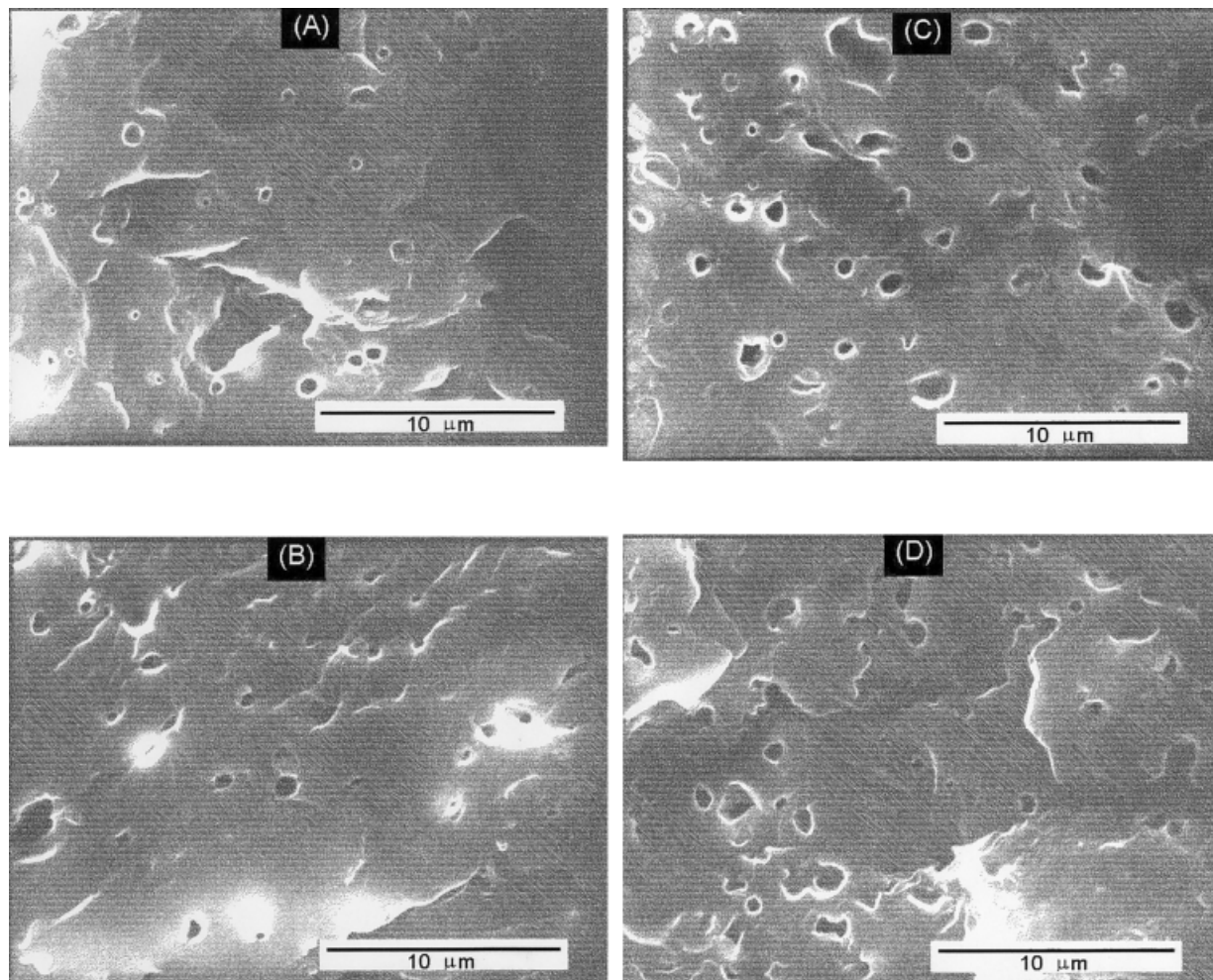


Figure 5 SEM photomicrographs of i-PP/SBS-MAH blends of different compositions after SBS-MAH extraction with toluene: (A) 95/05, (B) 85/15, (C) 80/20, and (D) 75/25.

The torque as a function of the elastomer content in the i-PP/SBS and i-PP/SBS-MAH blends at 400 s of mixing is shown in Figure 2. The addition of SBS to i-PP did not practically affect the viscosity of the mixtures because the polymers presented similar viscosities. Despite the pure SBS, the torque was similar to the pure SBS-MAH torque (Fig. 1); the torque values of the i-PP/SBS and i-PP/SBS-MAH blends at the same composition were different. Blends containing up to 15 wt % SBS-MAH presented lower torque than the corresponding i-PP/SBS blends. This behavior suggests a decrease in the i-PP molecular weight due to degradation or plasticization, both induced by the free residual 4,4'-diaminodiphenylmethane used to prepare SBS-MAH.²³ For SBS-MAH concentrations higher than 15 wt %, the torque was superior to that of the i-PP/SBS blends, probably because of SBS-MAH crosslinking or a grafting reaction between i-PP and SBS-MAH. Solubility tests were performed for the evaluation of these possibilities.

The i-PP/SBS-MAH blends containing 10 and 25 wt % elastomers were submitted to extraction with xylene at 120°C for 1 h. The blend containing 10 wt % SBS-MAH dissolved completely in xylene. However, for the blend containing 25 wt % SBS-MAH, a 15 wt % fraction did not dissolve. An analysis of this xylene-insoluble fraction showed a composition of 3.6 wt % i-PP and 96.4 wt % SBS-MAH. Chloroform was added to the xylene-soluble fraction of the blends, resulting in soluble and insoluble fractions. The chloroform-soluble fraction must have contained predominantly elastomer, whereas the precipitate must have been richer in i-PP. Fourier transform infrared (FTIR) spectra in the wave-number range of 400–2000 cm^{-1} for the chloroform-insoluble fraction corresponding to the blend containing 10 wt % SBS-MAH, pure i-PP, and pure SBS-MAH are shown in Figure 3. The FTIR spectrum of the precipitate presents characteristics bands of i-PP and SBS-MAH that suggest the graft copolymer formation (Fig. 3). This graft copolymer

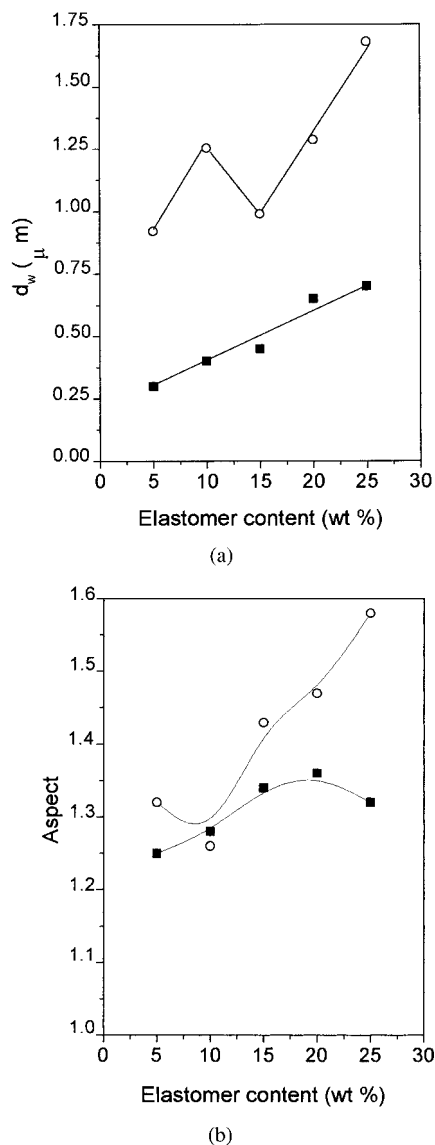


Figure 6 (a) d_w values of the elastomer phase and (b) aspect ratios for i-PP/SBS and i-PP/SBS-MAH blends: (■) i-PP/SBS and (○) i-PP/SBS-MAH.

was observed only in SBS-MAH blends; this implies that the anhydride groups participated in the reaction.

Scanning electron microscopy (SEM) images of i-PP/SBS and i-PP/SBS-MAH polymer blends are provided in Figures 4 and 5, respectively. The dark areas correspond to the place at which the elastomer domains were located before extraction with toluene. The dispersion of SBS in the i-PP matrix was homogeneous, and the SBS particles were almost spherical.

In contrast, the dispersion of SBS-MAH in the i-PP matrix was not homogeneous; the number of domains was lower than that for the i-PP/SBS blends, and the domains shapes were irregular. The irregular particle shape could be attributed to the elastic properties of SBS-MAH, crosslinked SBS-MAH, and i-PP-g-SBS-

MAH graft copolymer. It is also possible that only a fraction of the SBS-MAH could be extracted because of crosslinking and grafting to i-PP.

Figure 6(a) shows the average domain diameter (d_w) as a function of the elastomer concentration in the blends. The increase in the elastomer concentration resulted in a larger domain diameter, as expected.^{24,25} However, the diameter of the SBS-MAH domain was larger than that of the SBS domains at the same concentration.

The domain diameter reflects the rates of droplet breakup and coalescence. The model proposed by Tokita²⁴ quantifies these mechanisms. The particles of SBS-MAH in the i-PP matrix were at least 4 orders of magnitude larger than the SBS particles. This suggests that the dominant reason for the larger particles in i-PP/SBS-MAH blends is the difficulty in breaking up these particles, which is primarily due to the crosslinking. The crosslinking of SBS-MAH is also possibly responsible for the deflection of the particle aspect ratio from unity [Fig. 6(b)]. The aspect ratio is the medium ratio of the largest axis to the smallest axis of the particle. The more the aspect ratio approaches unity, the more the shape of the particle approaches a spherical form.

Young's modulus and the elongation at break as a function of blend composition are shown in Figures 7 and 8, respectively. The SBS elastomers caused a decrease in the modulus in relation to i-PP, with no significant difference between the two blends.

The crystallinity degree, as determined from DSC measurements, is shown in the Table I. The results expressed in relation to the weight percentage of i-PP in the blends did not change with the blend composition, indicating that neither SBS nor SBS-MAH affected the i-PP crystallinity and the crystal morphol-

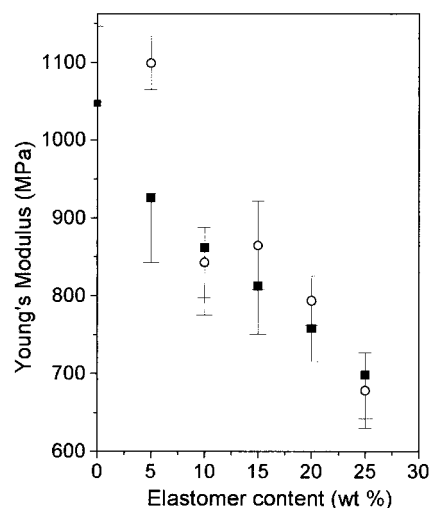


Figure 7 Young's modulus as a function of (■) i-PP/SBS and (○) i-PP/SBS-MAH composition.

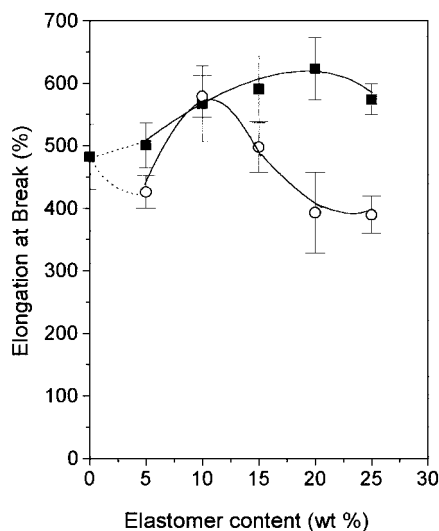


Figure 8 Elongation at break as a function of (■) i-PP/SBS and (○) i-PP/SBS-MAH composition.

ogy.²⁶ Therefore, the drop in Young's modulus with the increase in the elastomer concentration was due to the elastomer phase rather than matrix changes.

Figure 8 shows the effect of the nature and concentration of the elastomers on the elongation at break. The i-PP/SBS blends exhibited higher elongation at break than pure i-PP, and this property increased with the elastomer concentration. However, the i-PP/SBS-MAH blends presented an elongation at break lower than that of pure i-PP, except for the blend containing 10 wt % SBS-MAH, which presented the highest value of the elongation of break for the i-PP/SBS-MAH blends.

The Izod impact strength of notched samples of i-PP/SBS and i-PP/SBS-MAH blends are shown in Figure 9. The incorporation of SBS or SBS-MAH elastomers into i-PP resulted in a significant improvement in the impact strength of the binary blends. The impact strength increased gradually with increasing elastomer content, and this effect was more pronounced for the i-PP/SBS-MAH blends. The overall higher impact strength of i-PP/SBS-MAH blends can be explained by their higher interfacial adhesion. The graft copolymer formed during the melt blending was lo-

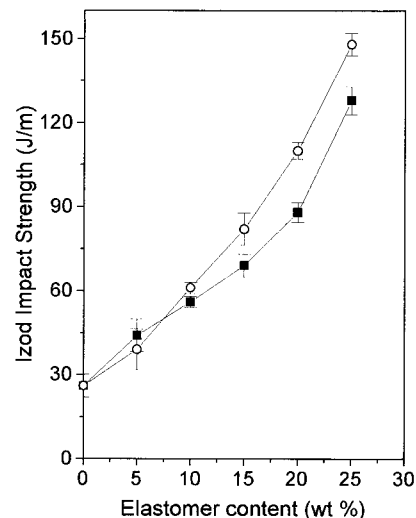


Figure 9 Impact strength as a function of (■) i-PP/SBS and (○) i-PP/SBS-MAH composition.

cated at the interface between i-PP and the elastomer particle, increasing the interfacial adhesion. The better interfacial adhesion allowed the transference of the stress from the matrix to the elastomer particles, which increased the amount of energy that could be dissipated before the catastrophic break.

The better impact strength of the i-PP/SBS-MAH blends in comparison with the corresponding i-PP/SBS blends could also be attributed to the higher gel fraction of SBS-MAH, as determined by solubility testing. The addition of 25 wt % SBS-MAH elastomer to i-PP resulted in a sixfold increase in impact strength with respect to i-PP.

CONCLUSIONS

The addition of SBS and SBS-MAH to i-PP resulted in two-phase mixtures exhibiting the morphology of elastomer domains dispersed in a thermoplastic matrix. The morphology and mechanical properties of the blends were very influenced by the nature of the elastomer. The size of the elastomer domains and the impact strength of i-PP/SBS-MAH were larger than those of the corresponding i-PP/SBS blends. These results were attributed to the crosslinking of SBS-MAH and to the formation of a graft copolymer between i-PP and SBS-MAH.

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TABLE I
Crystallinity Degree for i-PP Phase in the i-PP/SBS and i-PP/SBS-MAH Blends

Elastomer (wt %)	i-PP/SBS (%)	i-PP/SBS-MAH (%)
5	61	61
10	63	57
15	61	58
20	61	62
25	61	63

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