

Toughened Polystyrene with Improved Photoresistance: Effects of the Compatibilizers

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ABSTRACT: The dispersion of ethylene–propylene–diene terpolymer (EPDM) rubber in a polystyrene (PS) matrix is an alternative for improving the weathering resistance of high-impact polystyrene (HIPS), which commonly contains polybutadiene as an impact modifier. However, EPDM and PS are immiscible, and compatibilizers are required to improve the final properties. In this study, EPDM–PS blends were prepared by melt mixing, and the compatibilizing effects of two block copolymers on these blends was studied. The materials were analyzed by scanning electron microscopy, tensile and impact tests, and exposure to UV light for 20 days. The addition of styrene–butadiene–styrene block copolymer (SBS) and styrene–ethylene–*co*-butylene–styrene block copolymer (SEBS) improved the dispersion of

EPDM in the PS matrix. The compatibilized blends showed lower tensile properties, but an important increase in the impact strength was observed compared to the noncompatibilized blend. With regard to the impact strength, SBS was more effective than SEBS as a compatibilizer. All of the blends showed higher UV resistances than the commercial HIPS, and the best performance was observed in the blends compatibilized with SEBS. These results are discussed and explained in terms of the blends' morphologies and chemical compositions. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: block copolymers; compatibilization; polystyrene; structure–property relations; toughness

INTRODUCTION

Polystyrene (PS) is a versatile thermoplastic that is easily synthesized and processed, showing only slight degradation by extrusion or injection-molding techniques.¹ However, PS is a very brittle polymer, and this limits its use in some fields. This drawback has been overcome with the development of high-impact polystyrene (HIPS). The dispersion of rubber particles in the rigid PS matrix has proven to improve the toughness and help PS meet specifications for new useful applications. HIPS is one of the most important toughened polymers and is usually produced by radical polymerization of styrene in the presence of polybutadiene (PB).² This methodology allows for the formation of PS-*graft*-PB copolymers during PS polymerization, which behave as *in situ* generated compatibilizers. The toughening mechanism is quite complex, and a minimum rubber volume fraction with adequate particle sizes are required for efficient toughening.³ However, the use of PB in HIPS imparts some limitations to outdoor appli-

cations because this rubber presents a relatively low stability to photodegradation.⁴ To overcome this problem, PB can be replaced by saturated or at least less unsaturated rubbers, such as ethylene–propylene–diene terpolymer (EPDM). EPDM elastomers are produced with variable amounts and types of diene monomers and usually show relatively high resistance to ozone and oxidation.⁵

In comparison to *in situ* polymerization, polymer blending is an easy way to obtain HIPS because it can be performed with processing equipment that is commonly available in industry. Blends can also be prepared with postconsumer PS. However, PS and EPDM form thermodynamically incompatible blends because of the differences in their chemical natures and polarities. The lack of physical or chemical interactions between the phases may lead to poor mechanical properties.⁶

In a series of articles, Singh and Shaw^{7–9} described the preparation of PS with increased impact strength through the bulk polymerization of styrene in the presence of EPDM. The authors found that this process improved the properties compared to those of mechanically prepared PS–EPDM blends. More recently, Felisberti and coworkers^{4,10–13} studied the properties of PS–EPDM compositions prepared by the same process. The authors found that blends containing 17 wt % EPDM presented the highest

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impact resistance. Although the mechanical properties of PB-based HIPS were found to be higher than those of EPDM-based HIPS, the studies revealed that after photoaging, a more pronounced drop in the properties was observed for HIPS.¹²

With the objective of improving the properties of mechanically prepared PS–EPDM blends, some different methodologies have been described in the literature. PS-grafted EPDM,¹⁴ silane-modified EPDM,¹⁵ interlinking agents,¹⁶ styrene–ethylene–propylene block copolymers,¹⁷ and Lewis acids¹⁸ have been used to increase the compatibility of PS–EPDM blends. Ultrasound treatment during processing was also studied by Guo et al.¹⁹

Block copolymers have been used efficiently in immiscible polymer blends to improve the compatibility between polymer phases.²⁰ The effectiveness of these interfacial agents stems from their capacity to reduce the interfacial tension, which prevents the coalescence of the second-phase particles and improves adhesion. Fang et al.²¹ used a 10 wt % styrene–butadiene–styrene block copolymer (SBS) to compatibilize PS blends with different concentrations of EPDM. The blends were prepared by processing in a torque rheometer for 15 min. The authors observed that the composition containing 21 wt % EPDM attained the highest impact strength, which was about 20-fold compared to that of pure PS. However, the tensile strength of the system decreased approximately 50%.

The main goal of this study was to prepare HIPS based on PS–EPDM blends with better UV resistance than commercial HIPS. Aiming to improve the mechanical properties, we added different concentrations of SBS and styrene–ethylene-*co*-butylene–styrene block copolymer (SEBS) block copolymers with similar styrene contents. The impact strength, tensile properties, and UV resistance of the materials were compared. The properties of the blends are discussed in terms of their morphological and chemical properties.

EXPERIMENTAL

Materials

The polymers used in this study were amorphous PS N1841 from Innova S. A. [Triunfo, Brazil; weight-average molecular weight (M_w) = 225,000 g/mol], amorphous EPDM Keltan 4703 from DSM Elastomers (Triunfo, Brazil; containing 48% ethylene and 9% 2-ethylidene-5-norbornene), linear SEBS CH6110 from Dynasol Elastomers (Altamira, Mexico; containing 30% styrene, M_w = 74,700 g/mol), linear Kraton D1101 BT from Kraton Polymers (Paulínia, Brazil; containing 31% styrene, M_w = 77,400 g/mol), and HIPS R870E from Innova S. A. (M_w = 185,000

TABLE I
Composition and Properties of the PS–EPDM Blends

| Sample | EPDM (wt %) | Impact strength (kJ/m ²) | Tensile strength (MPa) |
|--------|-------------|--------------------------------------|------------------------|
| 1 | 0 | 1.2 ± 0.2 | 42.6 ± 2.1 |
| 2 | 12 | 1.6 ± 0.3 | 32.7 ± 3.8 |
| 3 | 15 | 1.5 ± 0.3 | 31.0 ± 1.6 |
| 4 | 17 | 1.6 ± 0.3 | 26.0 ± 4.0 |
| 5 | 20 | 1.9 ± 0.5 | 28.3 ± 2.0 |
| 6 | 25 | 1.2 ± 0.2 | 25.3 ± 1.0 |

g/mol, 6% PB). All of the polymers were used as received.

Methods

The blends were prepared by melt mixing with a Haake internal mixer (Offenburg, Germany), equipped with contrarotatory rotors, at a speed of 60 rpm at 180°C for 6 min. PS was first processed for 2 min; then, the other polymer was added and processed for more 4 min. After mixing, the products were ground with a Barth knife mill and injected with a Haake Minijet II at 230°C. Izod impact tests were performed according to ASTM 256 with a Ceast Resil impactor. Tensile tests were done according to ISO 527 with an EMIC DL universal testing machine with a cell load of 5000 kN at 5 mm/min. Electron micrographs [scanning electron microscopy (SEM)] were obtained from impact-fractured surfaces with a JEOL JSM-6060 microscope. Artificial aging experiments were performed with a Xenotest Atlas SUNTEST CPS/CPS+ instrument with a window glass filter by exposure of the samples to UV light from a xenon arc (irradiation = 765 W/m², black standard temperature = 55°C) according to ASTM D 4459 (indoor) and ASTM G 155. The yellowness index values of the samples were measured according to ASTM E 313. The measurements were done at intervals of 24 h.

RESULTS AND DISCUSSION

PS–EPDM blends

A first set of PS–EPDM binary blends was prepared to analyze the impact and tensile properties of the noncompatibilized systems. The compositions of the blends and the impact and tensile properties are shown in Table I.

It was observed that the addition of 5–20 wt % EPDM produced a discrete increase in the PS impact strength. Compared with a commercial sample of HIPS (impact strength = 7.4 ± 0.5 kJ/m²), the impact strength of the blends was considered to be very low. The blend with the highest EPDM level (25 wt %) presented an impact strength identical to

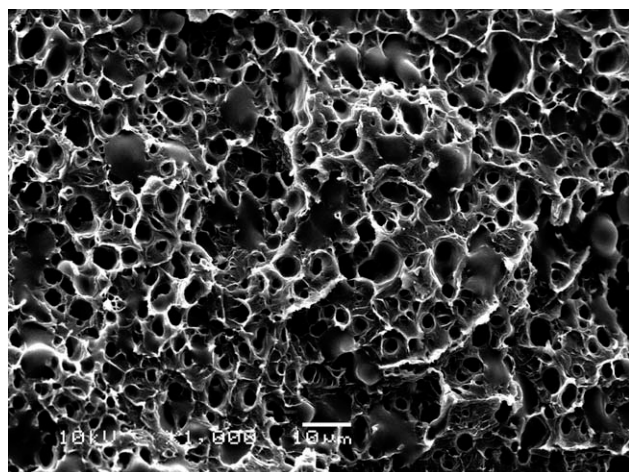


Figure 1 SEM micrograph of the PS-EPDM blend (80/20; bar = 10 μm).

that of the PS homopolymer. These results indicate that the elastomer alone did not efficiently improve the impact properties of PS.

According to Akkapeddi,²² the effect of EPDM particles on the impact strength of a thermoplastic matrix depends on the particle size and the interfacial bonding. The dominant mechanism for deformation in PS is craze formation. It is multiple craze formation that leads to a toughness enhancement,⁹ and also, an optimum rubber particle size is a determinant for toughening. The literature presents different values for the optimum size of the dispersed rubber particles in HIPS: 2.5 μm for diameter from Akkapeddi²² and 1–2 μm from Robeson.²³ In our study, the particles were very heterogeneous in size, with some featuring diameters around 10 μm , as shown in Figure 1. This morphology in the PS-EPDM blends explained the observed poor impact properties. Most EPDM particles were observed to be pulled out from the surface during the impact test; this indicated poor interfacial bonding, which was deleterious to the impact strength.

As shown in Figure 2, the incorporation of the EPDM toughening component in the rigid PS matrix decreased its brittleness and, as a consequence, its modulus. In all of the blends, the elongation at break was improved by the addition of the ductile rubber component in the brittle PS.

On the basis of our results and literature descriptions,²¹ PS-EPDM blends containing 20 wt % EPDM were chosen for subsequent experiments in our study.

PS-SBS and PS-SEBS blends

Two kinds of block copolymers were used as compatibilizers. One of them was a linear SBS, contain-

ing 31% styrene and with a molecular weight of 77,400 g/mol, and the second one was a linear SEBS containing 30% styrene and with a molecular weight of 74,700 g/mol. To investigate the effect of the compatibilizers on the properties of the PS matrix, some binary blends with no EPDM were prepared. Table II shows the compositions and properties of these blends.

Low impact strengths were found for the PS-SBS and PS-SEBS binary blends. It is well known that the morphology of polymer blends determine their mechanical properties, such as the impact strength and tensile strength.²⁰ It was verified that the elastomeric domains in the PS-SBS and PS-SEBS blends were very small (Fig. 3), and this behavior probably resulted from the good affinity between the PS matrix and the PS blocks of SBS and SEBS. However, very small rubber particles were not adequate for conferring toughness to PS.²² Figure 3 illustrates this finding: the blends containing 10 wt % SBS or SEBS showed well dispersed but very small particles embedded in the PS matrix.

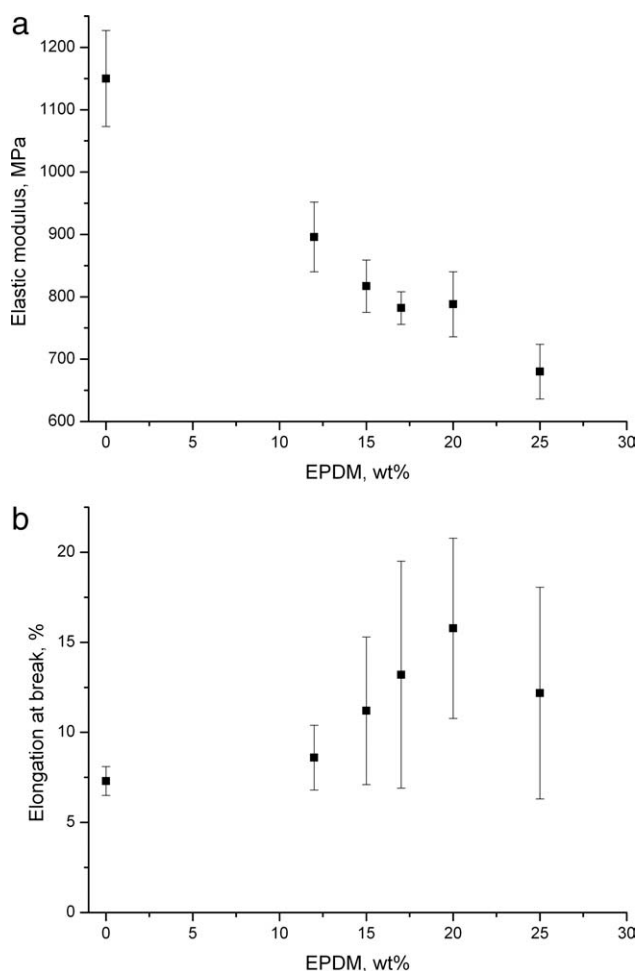


Figure 2 (a) Elastic modulus and (b) elongation at break of the PS-EPDM blends.

TABLE II
Composition and Properties of the PS–SBS and PS–SEBS Blends

| Sample | SBS (wt %) | SEBS (wt %) | Impact strength (kJ/m ²) | Tensile strength (MPa) | Elastic modulus (MPa) | Elongation at break (%) |
|--------|------------|-------------|--------------------------------------|------------------------|-----------------------|-------------------------|
| 7 | 2.5 | 0 | 1.0 ± 0.1 | 23.6 ± 1.9 | 788 ± 86 | 4.1 ± 0.5 |
| 8 | 5.0 | 0 | 1.1 ± 0.4 | 31.9 ± 2.6 | 813 ± 67 | 12.9 ± 2.9 |
| 9 | 7.5 | 0 | 1.2 ± 0.1 | 31.7 ± 1.3 | 784 ± 30 | 17.2 ± 8.0 |
| 10 | 10.0 | 0 | 1.3 ± 0.4 | 27.8 ± 2.4 | 782 ± 29 | 27.6 ± 2.4 |
| 11 | 0 | 2.5 | 1.3 ± 0.1 | 32.9 ± 1.8 | 810 ± 33 | 6.7 ± 1.7 |
| 12 | 0 | 5.0 | 1.4 ± 0.3 | 31.4 ± 1.8 | 786 ± 71 | 14.0 ± 4.2 |
| 13 | 0 | 7.5 | 1.6 ± 0.3 | 31.8 ± 2.5 | 629 ± 81 | 20.1 ± 3.2 |
| 14 | 0 | 10.0 | 1.7 ± 0.4 | 29.8 ± 3.9 | 629 ± 74 | 16.1 ± 3.5 |

As with EPDM, the addition of SBS and SEBS diminished the tensile strength of PS. This could be explained by the low tensile strength of the elastomer compared to that of the rigid PS matrix. The elastic modulus did not show significant variation up to 10 wt % SBS. However, the compositions with 7.5 and 10% SEBS showed a decrease in the elastic modulus, probably due to the lower brittleness of this component. SBS increased the elongation at break; however, SEBS did not produce any significant variation.

PS–EPDM–SBS and PS–EPDM–SEBS blends

To compare the compatibilizing effect of SBS and SEBS with similar PS contents and molecular weights, ternary blends were prepared and characterized. The level of EPDM was kept constant at 20 wt %. The compositions of these blends are shown in Table III.

Impact strength

As shown in Figure 4, the addition of SBS or SEBS to PS–EPDM blends containing 20 wt % EPDM substantially increased the impact properties. The impact strengths of these compositions varied from 1.8 kJ/m² (noncompatibilized blend) up to 14 kJ/m² (blend containing 10 wt % SBS); this represented an increase of more than 600%. Considering that the compatibilizers alone did not improve the impact resistance of PS, a significant interfacial action could be attributed to these block copolymers. The impact strength determined for the commercial HIPS used as reference (7.4 kJ/m²) was higher than those of the blends compatibilized with SEBS. However, all of the blends compatibilized with 5% or more SBS showed higher impact strengths than commercial HIPS. This could be an intriguing result because blocks of hydrogenated butadiene from SEBS were expected to have more affinity with the EPDM

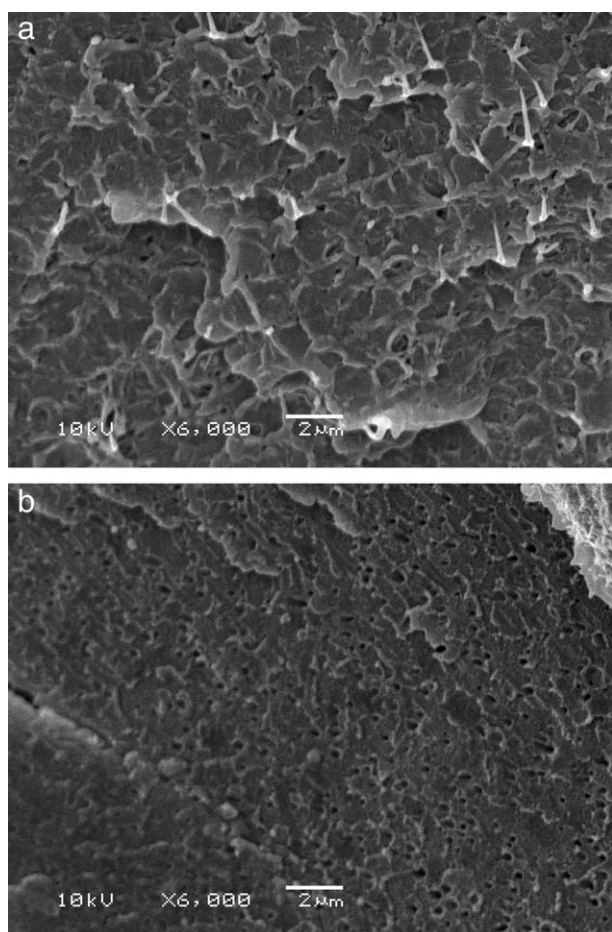


Figure 3 SEM micrograph of the 90/10 blends: (a) PS–SBS and (b) PS–SEBS (bar = 2 μm).

TABLE III
Composition of the PS–EPDM–SBS and PS–EPDM–SEBS Blends

| Sample | PS (wt %) | EPDM (wt %) | SBS (wt %) | SEBS (wt %) |
|--------|-----------|-------------|------------|-------------|
| 15 | 77.5 | 20 | 2.5 | 0 |
| 16 | 75.0 | 20 | 5.0 | 0 |
| 17 | 72.5 | 20 | 7.5 | 0 |
| 18 | 70.0 | 20 | 10.0 | 0 |
| 19 | 77.5 | 20 | 0 | 2.5 |
| 20 | 75.0 | 20 | 0 | 5.0 |
| 21 | 72.5 | 20 | 0 | 7.5 |
| 22 | 70.0 | 20 | 0 | 10.0 |

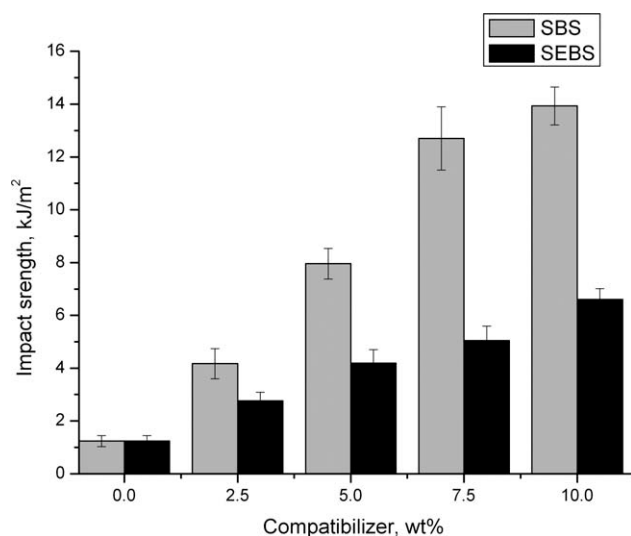


Figure 4 Impact strength of the 70/20/10 PS-EPDM-SBS and PS-EPDM-SEBS blends.

component than butadiene blocks from SBS. SEM micrographs helped to explain these impact results, as is shown in the next section.

Morphology

Figure 5 shows the images of the impact-fractured surfaces of the ternary blends compatibilized with 10 wt % SBS and 10 wt % SEBS. Figure 5(a,b) clearly demonstrates that the addition of SBS diminished the size of the dispersed EPDM particles, and this effect was probably responsible for increasing the impact properties of this material. According to Cigana et al.,²⁰ as in classical emulsions, a rapid drop in the particle size characterizes polymer blends at low concentrations of interfacial agent. This is followed by a leveling off to a constant value at a certain concentration of interfacial agent, known as the *critical concentration for emulsification*. They found that 20 wt % of a diblock PS-hydrogenated PB copolymer was the critical concentration for emulsification in PS/ethylene-propylene rubber blends (80/20). In our case, the size of dispersed particles was not measured. However, we observed that the impact strength was greatly increased at the beginning and slowed down at higher concentrations of interfacial agent (7.5 and 10%). This behavior matched the findings of Cigana et al. because the stabilization of the particle sizes stabilized the impact strength.

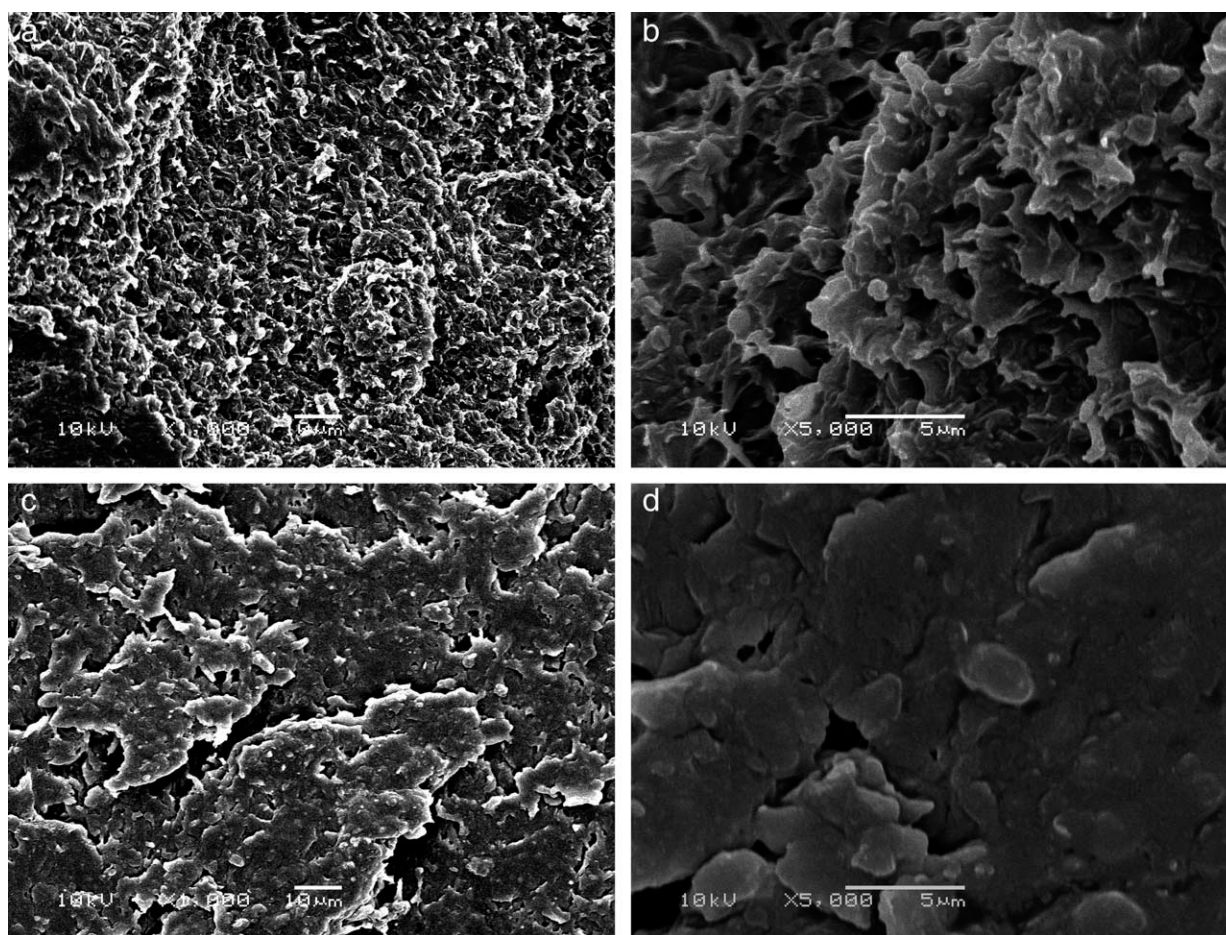


Figure 5 SEM micrographs of the 70/20/10 blends: (a) PS-EPDM-SBS at 1000 \times , (b) PS-EPDM-SBS at 5000 \times , (c) PS-EPDM-SEBS at 1000 \times , and (d) PS-EPDM-SEBS at 5000 \times (bars = 10 and 5 μ m).

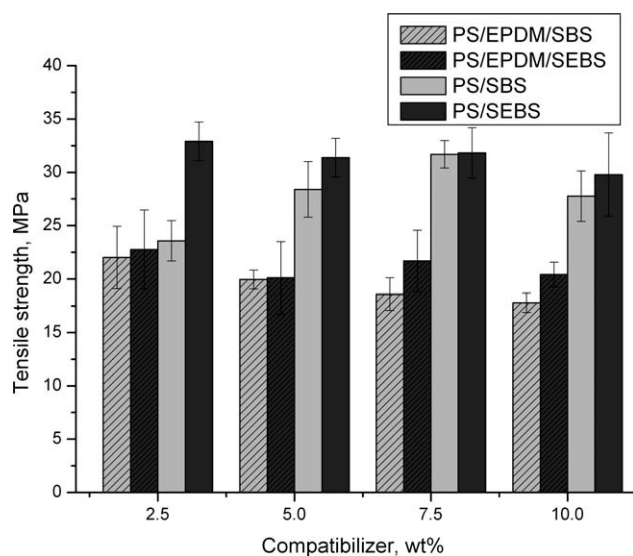


Figure 6 Tensile strength of the blends (20 wt % EPDM).

On the other hand, the addition of SEBS [Figs. 5(c,d)] turned the blend so homogeneous that the toughness did not show any similar improvement.

Tensile strength

Block copolymers with chemically identical or similar sequences to blend components are usually added as compatibilizers in incompatible polymer blends. In most cases, compatibilizers act to reduce the interfacial tension; this results in a fine dispersion of one phase in the other. Usually, better dispersion allows a better impact strength; however, improvements in the mechanical properties are not achieved.²⁴ To analyze the effect of the presence of SBS and SEBS on the tensile properties of the blends, it was important to know the values of the properties of the individual systems. Pure PS showed a very good tensile strength, around 43 MPa, whereas the PS–EPDM (80/20) blend had a decreased tensile strength of about 29 MPa. The commercial HIPS showed a tensile strength of 22.5 ± 0.7 MPa. In Figure 6, it is possible to observe that the block copolymers decreased the tensile strength of PS, with most values varying from 28 to 33 MPa. However, the combination of the three polymers resulted in even lower tensile strength (ca. 20 MPa in all cases), with little difference among the SBS- and SEBS-coupled systems, even after their concentrations were varied.

Artificial aging

PS–EPDM blends were exposed to UV light to evaluate their resistance to artificial aging and to compare them with commercial HIPS. Surface embrittlement is a common effect observed in exposed specimens.²⁵ Furthermore, yellowing can be caused by the pres-

ence of chromophores, which suffer chemical modification through the action of UV light. Natural and accelerated degradations of HIPS have been described in the literature as oxidation processes, where the PB phase is the component more sensitive because of the unsaturated double bonds in its structure.¹¹ In this study, the presence of diene monomers in EPDM, SBS, and SEBS could have led to different degradation behaviors in the face of UV light. The yellowness index of the blends was measured according to ASTM E 313, and the results are plotted in Figure 7.

We observed that all of the PS–EPDM blends showed lower yellowness indices than commercial HIPS when exposed to UV light, even when we considered that that blends had higher rubber contents (≥ 20 wt %) than commercial HIPS (only 6 wt %). Such behavior was considered the consequence of the low double-bond level in the PS–EPDM blends and proved that they could be good substitutes for butadiene-based HIPS.

The SBS block copolymer, apart from increasing interaction between the different components of the blends, could have participated in the initiation of the degradation reactions because of the presence of the unsaturated C=C bonds in the butadiene units.²⁶ In fact, blends compatibilized with SBS were more sensitive to UV light than the binary PS–EPDM blend, as shown in Figure 7. On the other hand, blends compatibilized with SEBS presented yellowness index values that were even lower than those of the noncompatibilized blend. This means that the hydrogenated elastomeric component in SEBS, in fact, presented lower sensitiveness to UV light.

Considering the overall properties, we concluded that PS–EPDM blends compatibilized with SBS

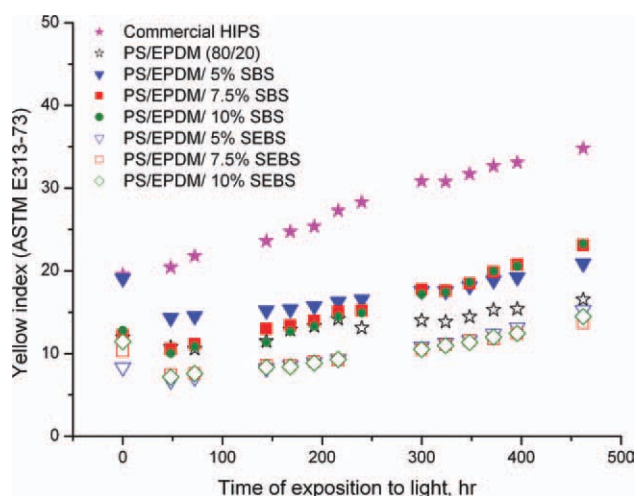


Figure 7 Yellow index of the blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

showed the best balance of properties and are a very interesting alternative for obtaining UV-resistant HIPS.

CONCLUSIONS

PS-EPDM blends were prepared to obtain toughened PS with a higher stability to UV light degradation than commercial PB-based HIPS. The influence of SBS and SEBS linear block copolymers of similar molecular weights and styrene contents on the properties of the blends was studied. The PS-EPDM, PS-SBS, and PS-SEBS binary blends did not present high impact strength. However, the combination of PS, EPDM, and both block copolymers significantly improved this property. The addition of SBS showed the best effect and led to blends with higher impact strengths than that of the commercial HIPS used as a reference. The morphological analysis showed that SEBS decreased the size of rubber domains too much; this was probably due to the higher affinity of this elastomer with EPDM.

As expected, all of the formulations showed lower tensile strengths than the pure PS matrix. However, the tensile strength was always higher than that of commercial HIPS.

A very important result was the observed behavior in the face UV light exposure. All of the PS-EPDM blends showed lower yellow indices than HIPS after UV exposure, even the noncompatibilized blend. With regard to the UV resistance of the compatibilized blends, SEBS was the most efficient, probably because of its lower unsaturation compared to SBS.

These results show that PB can be efficiently replaced by EPDM in HIPS. Blends of PS and EPDM prepared by melt mixing showed better UV resistance values and a good balance of impact and tensile properties when compatibilized with SBS or SEBS.

Considering these results as a whole, we concluded that the use of SBS as a compatibilizer produced the best final properties.

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