

# PS/EPDM Blends Prepared by *In Situ* Polymerization of Styrene

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**ABSTRACT:** PS/EPDM blends formed by *in situ* polymerization of styrene in the presence of EPDM were prepared. EPDM has excellent resistance to factors such as weather, ozone and oxidation and it could be a good alternative for substituting polybutadiene-based rubbers in PS toughening. The PS/EPDM blends present two phases, an EPDM elastomeric phase dispersed into a rigid matrix. The blends show higher thermal stability than polystyrene homopolymer due to the stabilizing effect of EPDM incorporation. The mechanical properties of *in situ* polymerized PS/EPDM blends with different compositions were evaluated before and after accelerated

photoaging and compared with the properties of HIPS submitted to the same aging conditions. The blend containing 17 wt % of EPDM presents an increase in the impact resistance of 210% in comparison with the value of PS. Although the initial mechanical properties of HIPS are superior, a pronounced drop was observed after an exposure time. For example, after the aging period, all PS/EPDM blends showed higher strain at break than HIPS. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1804–1813, 2008

**Key words:** blends; mechanical properties; polystyrene

## INTRODUCTION

A group of important polymers, such as polystyrene, presents poor impact resistance.<sup>1</sup> Polymer blending is a simple and efficient method for designing and controlling the performance of polymeric materials using available polymers.<sup>2</sup> The incorporation of dispersed elastomeric particles into a rigid polymer matrix has attracted considerable attention because of the industrial importance of the resulting materials among other types of polymer blends.<sup>3–6</sup> The essential characteristic of rubber toughening is that the impact resistance of the rigid polymer is substantially increased, in return for a limited reduction in stiffness.<sup>7–9</sup> Most polymer pairs in blends are thermodynamically immiscible and also incompatible. These incompatible blends often give poor mechanical properties due to poor interfacial adhesion and the lack of physical and chemical interactions between different phases. Thus, the compatibilization of such blends has been studied for decades.<sup>10,11</sup> The great deal of rubber toughening is to improve interfacial adhesion, rubber particle dispersion and

stress transfer between the phases to provide a good balance of properties.

High impact polystyrene (HIPS) is one of the most important toughened commercial systems in which brittle polystyrene becomes more ductile.<sup>12,13</sup> This elastomer-modified thermoplastic provides a good balance between rigidity and elasticity.<sup>14</sup> HIPS is produced by polymerization of styrene in the presence of polybutadiene and is widely applied in the automotive industry and in home appliances.<sup>15–17</sup>

Another example of a successful blend obtained by *in situ* polymerization is SBS-toughened polystyrene with 6.5 wt % of SBS with a molar mass of 22,000 g mol<sup>-1</sup>, reported by Sardelis et al.<sup>18</sup> For this material an increase of three-fold in the impact resistance was observed, in comparison with PS.

Aging is a great problem in HIPS and other rubber-toughened plastics, especially those based on polybutadiene. The major contribution to photodegradation of HIPS is usually attributed to the polybutadiene phase, which is constituted by different isomers that present different stabilities against degradation.<sup>16,19</sup> Exposure to sunlight causes a drastic drop in impact resistance attributed to photooxidation of the rubber phase induced by UV radiation, limiting the lifetime of molded parts in outdoor applications.<sup>12,15,20</sup> To overcome this problem, polybutadiene has been replaced in the polymer composition by a saturated rubber, such as poly(ethylene-co-vinyl acetate) (EVA), poly(butyl acrylate) or ethylene-propylene-diene terpolymer (EPDM).<sup>7,12</sup>

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Cheng et al.<sup>21</sup> prepared EVA-toughened polystyrene by *in situ* polymerization using benzoyl peroxide as initiator and *tert*-butyl peroctoate as chain transfer agent. The addition of 10 wt % EVA in PS increased the impact resistance and strain at break of PS by a factor of five but reduced the modulus by the same factor.

EPDM is widely used in outdoor applications, because it is more stable than the other conventional elastomers, such as butadiene and isoprene rubbers.<sup>22</sup> In EPDM, ethylene and propylene monomers provide a saturated backbone interrupted by the incorporation of nonconjugated diene monomers, such as ENB, which provide unsaturated groups in EPDM that can be easily crosslinked.<sup>22</sup> Shaw and Singh<sup>23–25</sup> utilized graft copolymers of EPDM with polystyrene (EPDM-*g*-PS), poly(styrene-*co*-methyl methacrylate) [EPDM-*g*-(PS-*co*-MMA)], and poly(styrene-*co*-maleic anhydride) (EPDM-*g*-(PS-*co*-MAH)) to prepare blends with PS/graft copolymers by mechanical mixing. They obtained blends with an enhancement in impact resistance of 400% for the PS/(EPDM-*g*-(PS-*co*-MMA)) (96/4) blend and for the PS/(EPDM-*g*-(PS-*co*-MAH)) (94/6) blend, and of 500% for the PS/(EPDM-*g*-PS) (90/10) blend. They attributed these improvements in impact resistance to the compatibilization of the graft copolymers of EPDM with the polystyrene matrix, resulting in good interfacial adhesion.

In this context, the aim of this work was to prepare and thermally and mechanically characterize *in situ* polymerized PS/EPDM blends as well as the study of the influence of accelerated photoaging on the mechanical properties.

In a previous work,<sup>26</sup> PS/EPDM blends were prepared by *in situ* polymerization using EPDM (Keltan<sup>®</sup> 5508) containing 69.0 wt % of ethylene, 26.2 wt % of propylene, and 4.8 wt % of ENB with  $\overline{Mn}$  133 g mol<sup>-1</sup> (polydispersity 1.9). In this work, EPDM richer in propylene and diene and with  $\overline{Mn}$  80 g mol<sup>-1</sup> (polydispersity 1.9) was used and the properties of the new blends are compared with earlier ones.

## EXPERIMENTAL

### Materials

Rhodia Brazil (Paulínia, Brazil) supplied styrene. DSM Elastomers (Triunfo, Brazil) supplied EPDM (Keltan<sup>®</sup> 1446A) with 2-ethylidene-5-norbornene (ENB) as diene. This EPDM contains 59.0 wt % of ethylene, 34.0 wt % of propylene and 7.0 wt % of ENB.

### Styrene monomer purification

Styrene monomer was submitted to extraction of polymerization inhibitors with a 5% NaOH solution.

After this, the organic layer was washed with distilled water. The water residue was extracted with dry Na<sub>2</sub>SO<sub>4</sub> and the styrene was then distilled at 50°C under vacuum.

### PS/EPDM blends prepared by *in situ* polymerization of styrene

EPDM was dissolved in styrene monomer under stirring, then benzoyl peroxide (0.1 wt %) was added to the viscous and homogeneous solution and the polymerization was carried out at 60°C. Each polymerization reaction produced ~ 600 g of material. After this, the styrene monomer residue (~ 5 wt %) was removed at 50°C in a vacuum oven during 48 h. Polystyrene homopolymer was also prepared at 60°C. The concentration of the EPDM in the blends was varied from 8 wt % to 17 wt %, the same concentration range of polybutadiene in commercial HIPS.

### Gel permeation chromatography

The homopolymer polystyrene was extracted from the blends using a Soxhlet apparatus with dichloromethane for 72 h. The extracted polystyrene corresponds to 97 wt % of the synthesized polystyrene. The average molar mass ( $\overline{Mw}$ ), number average molar mass ( $\overline{Mn}$ ) and polydispersity ( $\overline{Mw}/\overline{Mn}$ ) of the polystyrene matrix were measured by gel permeation chromatography in a Waters 510 Gel Permeation Chromatograph (Milford, MA) with a Waters 410 Differential Refractometer Detector. Separation was performed on polystyrene-divinylbenzene Tosoh-Haas columns (Montgomeryville, PA) with 10 μm particles. High performance liquid chromatography grade-THF was used as mobile phase at a flow rate of 1 mL min<sup>-1</sup>. Standard molar mass polystyrene in the molar range between 9,100 g mol<sup>-1</sup> and 2,890,000 g mol<sup>-1</sup> was used for calibration.

### Tensile and impact resistance tests

The crushed materials were dried in a vacuum oven for 48 h at 50°C and injection molded into Izod bars (ASTM D256) and dog-bone shaped tensile specimens (ASTM D638) using an Arburg Allrounder molding machine model 221M 250-55 (Lossburg, Germany). The following injection conditions were used for all blends: (1) temperatures along the barrel zones: 200, 210, 220, 230, and 240°C; (2) screw speed of 100 rpm; (3) mold temperature of 40°C; (4) injection time of 20 s; (5) holding pressure time of 6 s; (6) cooling time of 25 s; injection flow of 19 cm<sup>3</sup> s<sup>-1</sup>; (7) automatic mode. At least five injection-molded specimens of each sample were submitted to impact resistance and tensile tests in an EMIC AIC 1 apparatus

TABLE I  
PS/EPDM Blends Prepared in This Work

Name	Wt % EPDM in styrene solution	$\overline{Mw}$ of PS ( $\times 10^3$ g mol $^{-1}$ )	$\overline{Mn}$ of PS ( $\times 10^3$ g mol $^{-1}$ )	$\overline{Mw}/\overline{Mn}$ PS
PS	–	367	140	2.6
8%	8.0	471	308	1.5
11%	11.0	570	409	1.4
14%	14.0	487	296	1.7
17%	17.0	459	243	1.9
EPDM	–	156	80	1.9

(São José dos Pinhais, Brazil) and in an EMIC DL 200 apparatus (São José dos Pinhais, Brazil) (5000 N load cell, 5 mm min $^{-1}$  speed), respectively.

### Dynamic mechanical analysis

The injection-molded blend specimens (9.0 mm  $\times$  6.0 mm  $\times$  1.0 mm) were submitted to sinusoidal deformation in tension mode analysis at a frequency of 1.0 Hz, strain amplitude of 0.01% and temperature rate of 2°C min $^{-1}$  in the temperature range from  $-100$  to 180°C in a Rheometric Scientific DMTA V Analyzer (Piscataway, NJ).

### Thermogravimetric analysis

The thermogravimetric analyses of the injection-molded specimens were performed using a TA Instruments 2950 Thermogravimetric Analyzer (New Castle, DE) in the temperature range of 40–600°C, at a heating rate of 10°C min $^{-1}$  under air or argon flows (100 dm $^3$  min $^{-1}$ ).

### Scanning electron microscopy

The fracture surfaces obtained during Izod impact resistance tests were covered by a carbon layer and observed by using a JEOL JSM-6360 LV scanning electron microscope (SEM) (Middleton, WI) at an acceleration rate of 20 kV.

### Photochemical aging

The injection-molded specimens were submitted to accelerated photochemical aging (only one side of the specimens was exposed) according to the procedures described in ASTM G53. The photochemical aging was carried out in a special apparatus composed of PHILIPS model CLEO performance 80 WR Mercury Lamps (Eindhoven, The Netherlands), with emission ranges from 315 to 400 nm.<sup>27</sup> The aging program consisted of cycles of 24 h irradiation at room temperature followed by water condensation at 40°C for 2 h. The samples were exposed for 168 or 720 h.

## RESULTS AND DISCUSSION

In the present work, PS/EPDM blends were prepared by *in situ* polymerization of styrene at 60°C with the aim of obtaining rubber toughened polystyrene with higher photochemical resistance than PS and HIPS. The initial styrene solutions were transparent and show high-viscosity. The *in situ* polymerized blends are opaque to white, like commercial HIPS, showing that phase separation took place during the polymerization. The styrene polymerization yielded at least 94% of conversion for all compositions.

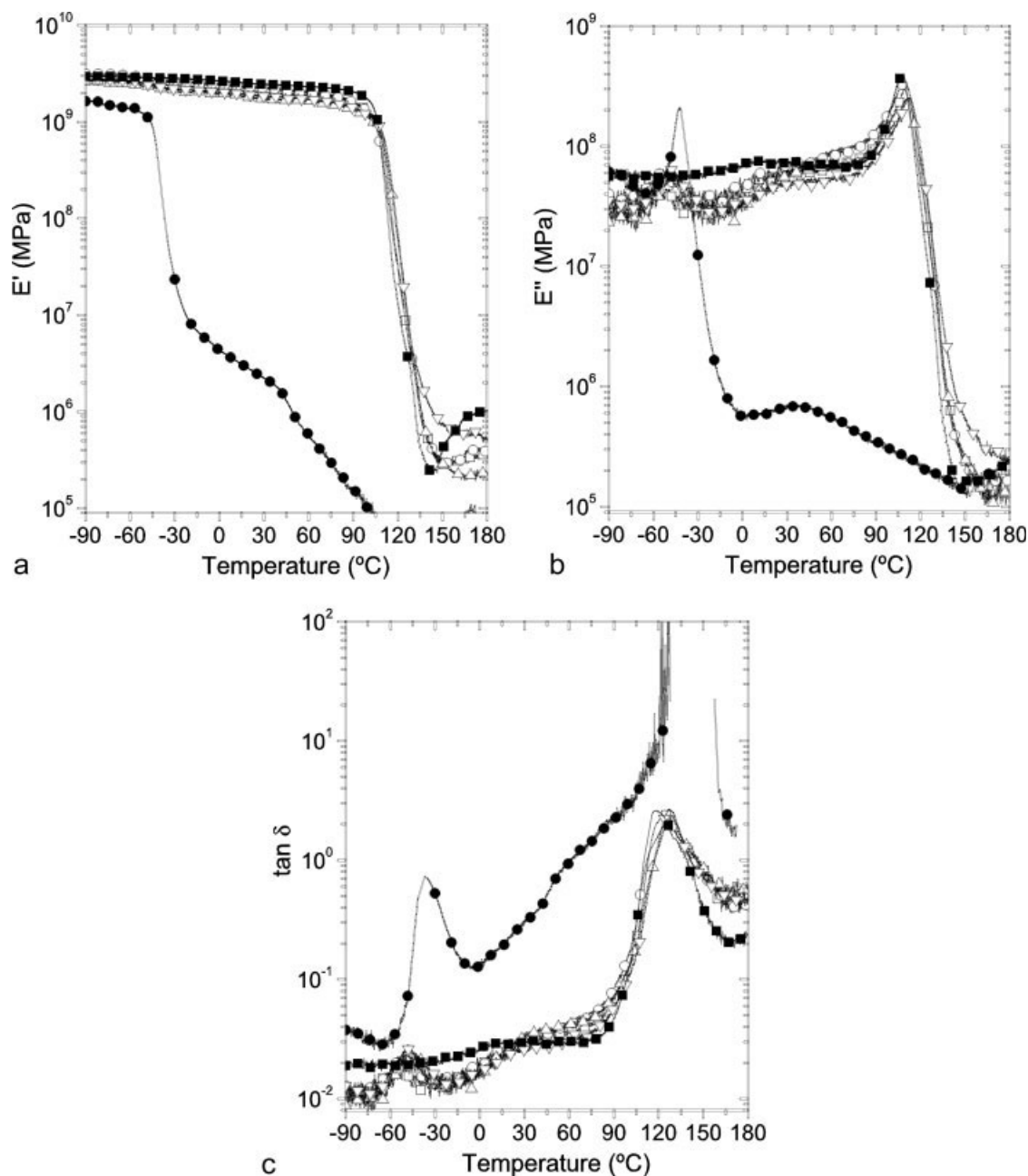
Table I shows the composition of the EPDM solution in styrene, the average molar mass ( $\overline{Mw}$ ), number average molar mass ( $\overline{Mn}$ ) and polydispersity ( $\overline{Mw}/\overline{Mn}$ ) of the polystyrene matrix.

The average molar mass and molar mass distributions of PS polymerized in the presence of EPDM at 60°C do not differ significantly, except for the blend containing 11 wt % of EPDM, for which  $\overline{Mw}$  = 570,000 g mol $^{-1}$  and polydispersity is around 1.7, whereas polystyrene obtained at 60°C presents  $\overline{Mw}$  of 367,000 g mol $^{-1}$ .

The  $\overline{Mw}$  and polydispersity of the blends prepared in the previous work<sup>26</sup> using EPDM (Keltan<sup>®</sup> 5508) containing 69.0 wt % of ethylene, 26.2 wt % of propylene, and 4.8 wt % of 2-ethylidene-5-norbornene (ENB) are higher than the properties of these blends but they also do not vary significantly with the increase in the EPDM content. For instance, the molar mass and molar mass distributions of PS polymerized in the presence of EPDM - Keltan 5508 at 60°C was between 518,000 and 591,000 g mol $^{-1}$  and polydispersity around 2, respectively.

### Dynamic mechanical analysis

Figure 1 shows the dynamic mechanical behavior of PS, EPDM and the PS/EPDM blends. The glass transition temperatures are obtained from the maximum of loss modulus peaks in the  $E'' \times T$  curves and damping peaks in the  $\tan \delta \times T$  curves. The storage modulus curves for PS [Fig. 1(a)] show a drastic drop around 95°C, corresponding to the glass transition of polystyrene. The EPDM curve shows a drop



**Figure 1** Dynamic mechanical behavior of (■) PS, (●) EPDM and PS/EPDM blends containing (□) 8, (○) 11, (△) 14 and (▽) 17 wt % of EPDM: (a) Storage modulus ( $E'$ ), (b) Loss modulus ( $E''$ ) and (c) damping ( $\tan \delta$ ).

of a decade around  $-45^{\circ}\text{C}$  corresponding to the glass transition of EPDM.<sup>20</sup> The storage moduli of all PS/EPDM blends show small change in the region of EPDM glass transition (approximately  $-40^{\circ}\text{C}$ ) and a drop of three decades at the region of the PS glass transition ( $\sim 120^{\circ}\text{C}$ ). This behavior indicates that the morphology of the PS/EPDM blends is of dispersed elastomeric domains (EPDM) in the glassy matrix of PS.

The damping curve for EPDM shows a broad peak at  $\sim 60^{\circ}\text{C}$  that is attributed to a secondary transition of the EPDM phase. Sheng et al.<sup>28</sup> also observed a liquid-liquid transition ( $T_{ll}$ ) for EPDM by

thermally stimulated current (TSC) at  $\sim 100^{\circ}\text{C}$ . Keinath et al.<sup>29</sup> described the liquid-liquid transition as relaxation above the glass transition temperature where the material experiences increased fluidity.

The EPDM phase of all blends presents a glass transition temperature at lower temperature than neat EPDM (Table II). This behavior was also observed in earlier works of our research group for PMMA/AES blends,<sup>30</sup> PS/EPDM (Keltan 5508),<sup>26</sup> and PS/AES blends.<sup>31</sup> However, for the blends prepared with Keltan 5508 the shift in the glass transition of the EPDM phase to lower temperatures is smaller than for the blends prepared in this work.



TABLE II  
Glass Transition Temperatures Obtained from  $E'' \times T$  and  $\tan \delta \times T$  Curves

Materials	Glass transition temperature ( $^{\circ}\text{C}$ )			
	EPDM Phase		PS Phase	
	From $E'' \times T$ curves	From $\tan \delta \times T$ curves	From $E'' \times T$ curves	From $\tan \delta \times T$ curves
8%	-55	-52	111	125
11%	-52	-52	108	126
14%	-52	-49	111	129
17%	-49	-48	112	127
PS60	-	-	108	119
EPDM	-42	-37	-	-

This shift to lower temperatures is attributed to hydrostatic dilatational thermal stresses generated within the rubber particles due to the differences in thermal expansion coefficient between the rubber and the glassy matrix. This dilatational stress promotes an increase in the rubbery phase free volume, which allows reduction of the relaxation time of the rubbery chains and therefore, reduces the glass transition temperature of the corresponding phase.<sup>20,32</sup>

### Thermogravimetric analysis

Figure 2 presents the thermogravimetric curves for PS, EPDM and PS/EPDM blends in air and under an argon atmosphere. Under an inert atmosphere, EPDM presents only one mass loss process and, in air, presents several processes beginning at lower temperatures. At the beginning of degradation, the EPDM chains react with oxygen yielding hydroperoxides that decompose to hydroxyl and carbonyl

groups. This reaction occurs by a typical mechanism of hydrocarbon oxidation, involving secondary and tertiary carbons of propylene. The decomposition of hydroperoxides may lead to crosslinking of either reactive olefine sites or repeating ethylene units, stiffening the material, or may lead to chain-scission resulting from hydrogen abstraction from tertiary carbons.<sup>33</sup>

The PS/EPDM blends and neat polystyrene show a small weight loss process ( $\sim 2-3\%$ ) at  $\sim 180^{\circ}\text{C}$  probably due to the presence of volatile PS oligomers. Under an inert atmosphere, the significant weight loss process begins at  $\sim 350^{\circ}\text{C}$ , whereas it begins at  $\sim 260^{\circ}\text{C}$  in air. The PS/EPDM blends show higher thermal and thermo-oxidative stability than neat PS due to the stabilization caused by EPDM deactivating PS macroradicals through intermolecular reactions.<sup>34</sup> This stabilization is observed in Figure 3 where the temperature of a 5 wt % loss is plotted as a function of EPDM content. A positive

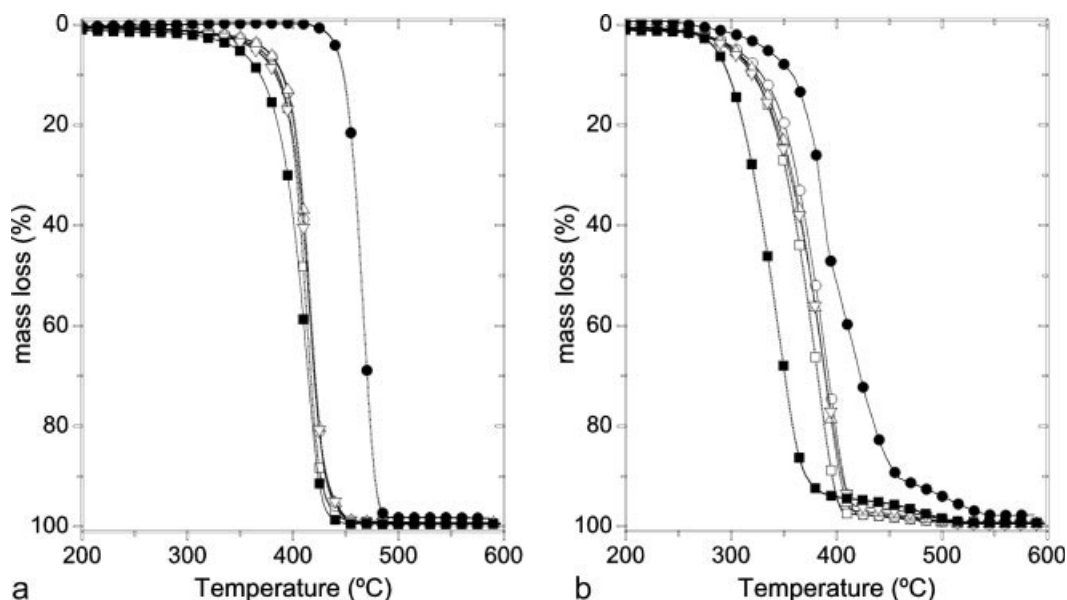
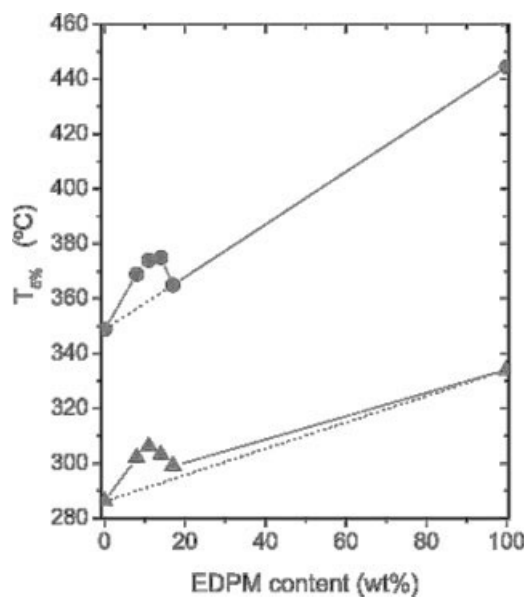


Figure 2 Thermogravimetric curves (a) under an argon atmosphere and (b) in air of (■) PS, (●) EPDM and PS/EPDM blends containing (□) 8, (○) 11, (△) 14 and (▽) 17 wt % of EPDM.



**Figure 3** Temperature for a 5 wt % loss as a function of the composition of the PS/EPDM blends: (○) inert atmosphere and (△) in air.

deviation from the additive rule (dashed lines) is observed for all blends, indicating that the addition of EPDM into a PS matrix stabilizes the blends.

Similar results were observed for PS/EPDM (Keltan 5508)<sup>26</sup> and PS/AES<sup>31</sup> blends prepared in other work by *in situ* polymerization. For the blends prepared with Keltan 5508 the temperatures of a 5 wt % loss under an inert atmosphere is 10°C higher than the temperatures observed for the blends prepared in this work.

The data from thermogravimetric analysis allowed the conclusion that *in situ* polymerized blends can be processed at the temperatures used in this work in the molding injection process without pronounced composition modification and oxidation.

### Tensile test (ASTM D638)

The influence of photochemical aging on the mechanical properties of PS/EPDM blends prepared by *in situ* polymerization of styrene was evaluated. The PS/EPDM blends were submitted to photochemical aging in an apparatus developed by our research group,<sup>27</sup> following the procedures in ASTM G53 standard.

Figure 4 shows the representative tensile versus strain curves obtained from tensile tests for PS and PS/EPDM blends. The mechanical properties, such as Young's modulus and strain at break, obtained from these curves, are shown in Table III. The PS/EPDM blends showed stress whitening during the tensile tests indicating that dilatational processes, such as crazing and cavitation, occur during the loading.<sup>20</sup> The stress-strain profiles of PS and PS/

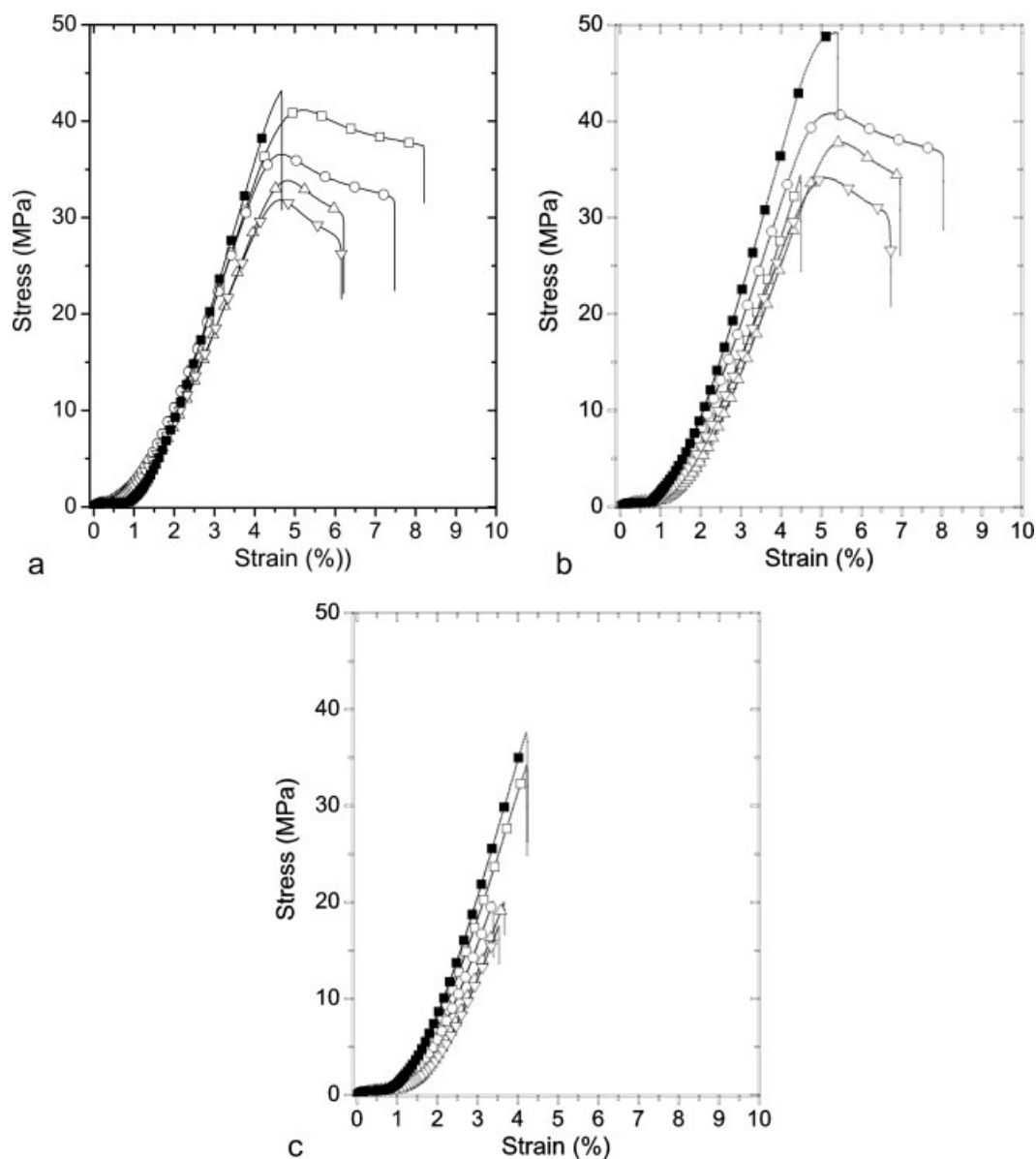
EPDM blends undergo modifications after photochemical aging, as can be seen in Figure 5(b,c) for blends photoaged for 168 and 720 h, respectively.

The mechanical properties of the materials are summarized in Table III. The Young's modulus of PS/EPDM blends decreases about 25% with the addition of 17 wt % of EPDM in comparison with the value of polystyrene. The decrease in modulus with increasing elastomer content is expected and well reported for rubber toughening of rigid polymers.<sup>7</sup> Furthermore, the decrease of the Young's modulus of PS/EPDM is similar to the decrease of Young's modulus of PS/AES blends<sup>31</sup> and is lower than the decrease observed for PS/EPDM blends (Keltan 5508)<sup>26</sup> with comparable elastomer content, for which a decrease of 60% of the Young's modulus was observed. Cheng et al.<sup>21</sup> prepared EVA-toughened polystyrene by *in situ* polymerization using benzoyl peroxide as initiator and *tert*-butyl peroxoate as chain transfer reagent. The addition of 10 wt % of EVA decreased the Young's modulus by 20%, a result comparable with those obtained in the present work for blends with higher elastomer content.

The Young's modulus is higher for photoaged samples, but the dependence of this property on the blend composition is not affected by aging. The Young's modulus of the nonaged PS/EPDM blends (between 1023 and 1263 MPa) are higher than the Young's modulus of nonaged HIPS (786 MPa). After photochemical aging for 168 or 720 h, the Young's modulus of most PS/EPDM blends and HIPS presented the same behavior, an average increase of 5%. The blends became stiffer than nonaged blends due to crosslinking reactions of the rubber phase.<sup>35,36</sup>

In comparison with the blends of the earlier articles<sup>26,38</sup> with Keltan 5508, the blends of this work present Young's modulus higher than those blends mainly for higher EPDM contents. The Young's modulus of the aged blends is slightly higher than the former blends. Both groups of blends present the same behavior of increasing of the Young's modulus after the period of aging. One possible explanation for the enhancement of the Young's Modulus of the photoaging blends is the crosslinking.

The strain at break increases with the initial addition of EPDM and remains almost constant with subsequent enhancements in EPDM content [Fig. 5(b)]. The blend containing 11 wt % of EPDM shows a strain at break of 8.2%, an enhancement of 120% in comparison with the value of neat PS. Sardelis et al.<sup>18</sup> produced SBS-toughened polystyrene by *in situ* polymerization with 6.5 wt % of SBS, increasing the strain at break only by 10%. The strain at break is a mechanical property of commercial HIPS, which is more sensitive to photochemical aging and shows a pronounced drop of this property from



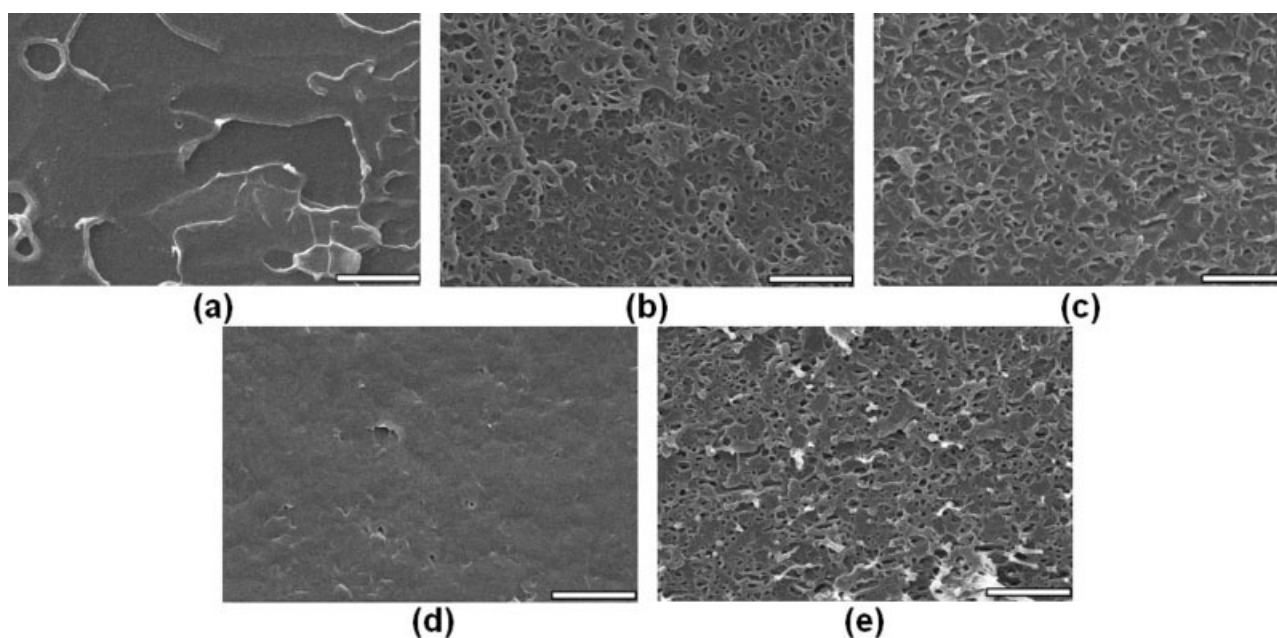
**Figure 4** Representative stress versus strain curves for (■) PS, (●) EPDM and PS/EPDM blends containing (□) 8, (○) 11, (△) 14 and (▽) 17 wt % of EPDM: (a) nonaged, (b) aged for 168 h and (c) aged for 720 h.

$47 \pm 4\%$  to  $2.2 \pm 0.1\%$  after 720 h of photoaging attributed to rubber phase crosslinking. After aging, the PS/EPDM blends prepared in this work show

strain at break higher than commercial HIPS. This was also observed for PS/AES<sup>37</sup> and PS/EPDM (Keltan 5508)<sup>38</sup> blends prepared by *in situ* polymerization.

**TABLE III**  
Mechanical Properties of Aged and NonAged Samples

Materials	Young's modulus (MPa)			Strain at break (%)			Impact resistance ( $\text{J m}^{-1}$ )		
	0 h	168 h	720 h	0 h	168 h	720 h	0 h	168 h	720 h
8%	$1263 \pm 13$	$1333 \pm 22$	$1327 \pm 10$	$8.2 \pm 0.5$	$4.4 \pm 0.2$	$4.2 \pm 0.3$	$28 \pm 3$	$27 \pm 3$	$21 \pm 3$
11%	$1167 \pm 13$	$1260 \pm 4$	$1169 \pm 31$	$7.2 \pm 1.0$	$8.3 \pm 1$	$3.4 \pm 0.1$	$27 \pm 4$	$22 \pm 4$	$18 \pm 4$
14%	$1081 \pm 10$	$1162 \pm 8$	$1130 \pm 24$	$5.9 \pm 0.8$	$6.9 \pm 0.9$	$3.7 \pm 0.3$	$29 \pm 5$	$27 \pm 5$	$19 \pm 5$
17%	$1023 \pm 18$	$1090 \pm 12$	$1061 \pm 28$	$7.2 \pm 1$	$7.3 \pm 2$	$3.5 \pm 0.3$	$71 \pm 6$	$63 \pm 6$	$34 \pm 6$
PS60	$1394 \pm 14$	$1484 \pm 31$	$1438 \pm 24$	$3.7 \pm 0.3$	$4.4 \pm 0.6$	$3.2 \pm 0.1$	$23 \pm 5$	$17 \pm 2$	$14 \pm 1$
HIPS	$786 \pm 20$	$816 \pm 48$	$822 \pm 18$	$47 \pm 4$	$2.2 \pm 0.1$	$2.1 \pm 0.1$	$88 \pm 5$	$74 \pm 2$	$64 \pm 4$



**Figure 5** SEM photographs of fracture surfaces resulting from impact resistance tests. Scale bars correspond to 10  $\mu\text{m}$ . (a) PS, (b) 8 wt %, (c) 11 wt %, (d) 14 wt % and (e) 17 wt %.

Table III shows that the strain at break of nonaged PS/EPDM blends (the highest 8.2% for the blend containing 8 wt % EPDM) is not comparable to the strain at break of nonaged HIPS (47.3%). But, after aging, the PS/EPDM blends showed a higher strain at break (higher than 3.0%) than HIPS (2.2%). It is important to note that the PS/EPDM blends do not contain any stabilizers, which is not the case for commercial HIPS used in this work. Although the PS/EPDM blends do not present a comparable initial strain at break to HIPS, after a period of use (or in this case a period of aging), their final mechanical performance is better.

#### Impact resistance test (ASTM D256)

For the blends polymerized at 60°C, the addition of 8 wt % of EPDM leads to a slight enhancement in the impact resistance (Table III) from  $23 \pm 5 \text{ J m}^{-1}$  for PS to  $28 \pm 3 \text{ J m}^{-1}$ . Subsequent increases in the EPDM content, up to 14 wt %, do not change the value of impact resistance. But the blend with 17 wt % of EPDM presents an increase in the impact resistance to  $71 \pm 6 \text{ J m}^{-1}$  (increase of 210%). The impact resistance of PS/EPDM blends prepared using poly(styrene/ethylene-propylene) (SEP) as compatibilizer has been reported.<sup>39</sup> The authors reported that both non compatibilized and compatibilized blends present higher impact resistance than PS. Moreover, the crosslinking of the elastomer phase in the blends contributes positively for the enhancement of the impact resistance of the blends. The results obtained by Crevecouer et al.<sup>39</sup> for PS/EPDM and PS/

EPDM/SEP blends are very interesting and the comparison with the results obtained in the present work leads to the conclusion that the polymerization of styrene in the presence of EPDM did not result in a sufficient quantity of grafting copolymer (PS-*g*-EPDM) to promote *in situ* compatibilization. In the work of Crevecouer et al., when SEP was added, an improvement in the impact resistance of 350% against 80% of the blend without SEP was observed. Another important consideration is the characteristics of the elastomer. The crosslinking of EPDM improved the impact resistance about 800%. On the other hand, the PS/EPDM blend with 17 wt % of EPDM polymerized at 60°C showed an increase in impact resistance of 210% against 100% of the mechanical PS/EPDM blend (84/16).<sup>23,24,25</sup> These results suggest that there are some differences between these blends, but also reinforce the idea that the extent of grafting copolymerization is low.

A decrease of the impact resistance of PS/EPDM blends was observed after photoaging, but the dependence of this property on the blend composition is almost the same for nonaged and aged blends. The impact resistance of nonaged PS/EPDM blends (the highest was  $71 \pm 6 \text{ J m}^{-1}$  for 17 wt % of EPDM) is not comparable to that of nonaged HIPS ( $88 \pm 5 \text{ J m}^{-1}$ ). However, after 168 h of aging, the blends with 8, 14, and 17 wt % of EPDM showed a higher retention of impact resistance (0.96, 0.93, and 0.88, respectively) than that of HIPS (0.84). The retention of impact resistance was defined as the ratio between the value of the impact resistance for the aged sample at time  $t_i$  and the value of this property for the



TABLE IV  
Impact Resistance and Strain at Break of *In Situ* Polymerized Blends

Reference/Type	Blends	Impact resistance	Strain at break (%)
Present work <i>in situ</i> polymerization	PS polymerized at 60°C	23 ± 5 J m <sup>-1</sup>	3.7 ± 0.3
	PS/EPDM (83/17)	71 ± 6 (+210%)	7.2 ± 1 (+95%)
<i>In situ</i> polymerization[26]	PS polymerized at 80°C	20 ± 3 J m <sup>-1</sup>	3.5 ± 0.2
	PS/EPDM (83/17) polymerized at 80°C	48 ± 10 (+140%)	20.3 ± 1 (+480%)
<i>In situ</i> polymerization[31]	PS polymerized at 80°C	20 ± 3 J m <sup>-1</sup>	3.5 ± 0.2
	PS/AES (83/17) polymerized at 80°C (EPDM content: 8.5 wt %)	32 ± 6 J m <sup>-1</sup> (+60%)	6.3 ± 0.4 (+80%)

nonaged sample ( $t_0$ ) (Impact Resistance,  $t_i$ /Impact Resistance,  $t_0$ ). This indicates that these compositions are more photochemically stable than HIPS.

In comparison with the blends prepared with Keltan 5508 in the previous papers,<sup>26,38</sup> the blends prepared here show slightly lower impact resistance than the former blends for the nonaged specimens containing up to 14 wt % of EPDM. For blends with Keltan 5508 the impact resistance of the blends is around 37 J m<sup>-1</sup> independent of the composition. However, the blend from this work with 17 wt % of EPDM presented the highest impact resistance (71 ± 6) J m<sup>-1</sup> for all PS/EPDM blends prepared by *in situ* polymerization.<sup>26,31</sup> Both blends presented a decrease in impact resistance after photochemical aging.

### Scanning electron microscopy

Figure 5 shows micrographs of fracture surface resulting from the impact resistance tests for PS and PS/EPDM blends. Figure 5(a) shows the bands of brittle fracture for PS, resulting from the repeated arrest and re-initiation of the fracture.<sup>40</sup> In addition, the toughened fracture surfaces [Fig. 5(b–e)] are rougher than that of PS, and the roughness seems to be maximal for the blend containing 17 wt % of EPDM [Fig. 5(e)], in agreement with the higher impact resistance. The roughness of the fracture surface indicates that PS/EPDM blends absorb more energy than polystyrene during impact resistance tests. The fracture surfaces of the blends prepared with Keltan 5508 presented the same behavior as the blends of this work.

Table IV shows the impact resistance and strain at break for PS/EPDM blends prepared in this work and other *in situ* polymerized blends.<sup>26,31</sup> In comparison with our recent work, the blend prepared in this work containing 17 wt % of EPDM at 60°C presents higher enhancement in the impact resistance (210%) than the blends polymerized at 80°C containing 17 wt % of EPDM (140%)<sup>26</sup> and 17 wt % of AES (60%).<sup>31</sup> But the blends prepared with Keltan 5508 containing 17 wt % showed the highest strain at break for the three systems.

### CONCLUSIONS

The PS/EPDM (Keltan 1446A) blends are immiscible and present a dispersed EPDM phase in a rigid matrix. The PS/EPDM blends are thermally and thermo-oxidatively more stable than neat PS. Moreover, the blend containing 17 wt % of EPDM presents an increase in the impact resistance of 210% in comparison with the value of PS. Although the initial mechanical properties of HIPS are superior in comparison with PS/EPDM blends, a pronounced drop of these properties was observed after photoaging. For example, after the aging period, all PS/EPDM blends showed higher strain at break than HIPS. Thus, we concluded that the mechanical performance of PS/EPDM blends become better in comparison with HIPS after a period of use.

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