# Mechanical Properties of Photoaged In Situ Polymerized PS/EPDM Blends

#### Emerson Lourenço, Maria Isabel Felisberti

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-862 Campinas, Sao Paulo, Brazil

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**ABSTRACT:** In this study, the mechanical properties of in situ polymerized PS/EPDM blends with different composition were evaluated before and after accelerated photoaging and compared with the properties of commercial HIPS submitted to similar aging conditions (ASTM G53). The mechanical properties of the PS/EPDM blends as well as their photochemical stability are influenced by the polymerization temperature and blend composition. Although the initial mechanical properties of HIPS are superior in comparison with the *in situ* polymerized PS/EPDM blends, a pronounced drop of them was observed already for short time exposure. For example, after the aging period, all PS/EPDM blends showed higher strain at break than HIPS. Because PS/EPDM blends present higher resistance to photoaging stability than HIPS, the mechanical properties of the HIPS become worse than the other blends as the aging time increases. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3617–3623, 2007

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

# **INTRODUCTION**

Rubber toughening is one of the key inventions of plastics industry. The incorporation of dispersed elastomeric particles in a rigid polymer matrix has attracted significant attention because of its industrial importance.<sup>1-3</sup> High impact polystyrene (HIPS) is one of the most important toughened commercial systems in which the brittle polystyrene (PS) becomes more ductile.<sup>4,5</sup> However, aging is a serious problem for HIPS and for other rubber-toughened plastics, especially those based on polybutadiene (PB). The major contribution to photodegradation of HIPS is usually attributed to the PB phase, which is constituted of different isomers that present different stabilities to degradation, although the degradation also affects the PS matrix.6 Exposure to sunlight causes a drastic drop in impact resistance attributed to the photooxidation of the unsaturated rubber phase induced by UV radiation, limiting the lifetime of molded parts in outdoor applications.<sup>4,7</sup> To overcome this problem, it has been suggested that PB be replaced in the polymer composition by a saturated rubber such as poly(ethylene-co-propylene-co-2-ethylidene-5-norbornene), EPDM.<sup>8</sup>

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Aging of polymeric materials may be defined as a progressive deterioration of the physical properties because of the action of heat, oxygen, UV radiation, or mechanical work, either separately or in combination. Degradation of polymers includes all changes in chemical structure and physical properties of polymers because of external chemical or physical stresses leading to materials with characteristics different from those of the starting material. Usually, degradation means worsened properties. Degradation because of mechanically induced thermal processes takes place during melt processing of polymers at high temperatures in an oxygen deficient atmosphere and accounts for chemical changes in the polymer structure. Consequently, it modifies mechanical properties and weathering resistance of the final material.<sup>9</sup>

After the polymerization step of styrene-based polymers the temperature is increased to between 200 and 250°C for short times, to remove residual monomers and any low molar mass compounds. Problems with vacuum conditions during this step may lead to oxidation of the polymer.<sup>10</sup> The thermal and photodegradation of PS in the presence of oxygen occurs through a typical radical chain mechanism and is well described in the literature. The hydrogen bonded to the same carbon as the phenyl group is labile and its loss occurs by the absorption of energy producing a radical group that undergoes subsequent reactions such as depolymerization and oxidation, resulting in low molar mass compounds.<sup>6,11,12</sup>

Differences in sensitivity to individual degradation processes arise from the effects of low amounts of structural polymeric inhomogeneities (e.g., unsatura-

*Correspondence to:* M. I. Felisberti (misabel@iqm. unicamp.br).

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$\overline{Mw}/\overline{Mn}^{b)}$
2.4
2.1
2.1
2.1
2.1
2.5
2.1
1.7
1.2
1.5
1.2
1.5
2.5
2.6
2.2

TABLE I PS/EPDM Blends Composition

<sup>a</sup> EPDM content in the blends obtained gravimetrically,

<sup>b</sup> From GPC analyses.

tion, oxygenated structures) and nonpolymeric impurities such as metallic contaminants or photoactive pigments. The knowledge of degradation mechanisms of homopolymers and copolymers is helpful only to some extent in elucidation of degradation of polymer blends. However, the individual components of a blend may behave rather differently from their behavior as isolated polymers. Consequently, the degradation behavior of blends is hardly predictable without experiments, because of the coreaction phenomena on interfaces of blended polymers controlled by the morphology of the blend.<sup>9</sup>

Several chemical reactions take place in polymer blend systems with possible interactions between the macromolecular components themselves, or with their degradation products. If neither interactions between polymers nor between degradation products occur, the degradation of a blend is additive with respect to that of the pure components, as occurs in poly(methyl methacrylate)/PS (PMMA/ PS) blends.9 In some cases, destabilizing effects take place leading to the acceleration of degradation rates, whereas in others the resulting effect is a stabilizing one. For example, in blends of PS with poly (vinylidene chloride) (PVDC), polyacrylonitrile (PAN), PB, poly(phenylene oxide) (PPO), and polyacrylonitrile-g-styrene-g-(ethylene-co--propylene-co-2-ethylidene-5-norbornene)] (AES), the decomposition of the PS component occurs at higher temperatures than that of pure PS.<sup>9</sup> This is due to the stabilization of PS caused by the deactivation of PSmacroradicals by intermolecular reactions with structural units of the second component. On the other hand, in blends of PS with poly(ethylene glycol) (PEG), PS degradation is accelerated by reaction of PS chains with the small radicals produced from PEG decomposition.<sup>9</sup>

This work has studied the influence of accelerated photochemical aging on the mechanical properties of *in situ* polymerized PS/EPDM blends. The goal of the present study is the preparation of a material with a higher photochemical stability than HIPS.

### **EXPERIMENTAL**

# Materials

Rhodia Brazil (Paulínia, Brazil) supplied the styrene. DSM Elastomers (Triunfo, Brazil) supplied EPDM (Keltan<sup>®</sup> 5508) with 2-ethylidene-5-norbornene (ENB) as diene. EPDM contains 69.0 wt % of ethylene, 26.2 wt % of propylene and 4.8 wt % of ENB. EPDM presents a Mooney viscosity (ML, 1 + 4, 125°C) of 55.3 (ISO 289). BASF S/A (São José dos Campos, Brazil) supplied HIPS (HIPS/Polystyrol 495  $F^{\infty}$ ). HIPS contains 10 wt % of PB and flow index of 8 g/ 10 min (ASTM D1238–200 $^{\circ}$ C/5 kg). The PS/EPDM blends were prepared by dissolving EPDM in styrene monomer, followed by bulk polymerization of the monomer at 60 and 80°C for 168 h.13 PS homopolymer was also prepared at 60 and 80°C. Table I shows the composition of the PS/EPDM blends expressed in terms of "wt % EPDM in the blends" and the molar mass of the PS phase of the blends. The nomenclature used to describe the blends is based on the EPDM content and on the temperature of polymerization. For example, the blend containing 5 wt % of EPDM polymerized at 60°C is named 5E60, where E represents EPDM.

# Photochemical aging

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). No additives were used to process the PS/EPDM blends. HIPS contains additives normally used to prevent thermal degradation during the mechanical processing and a combination of stabilizers and antioxidants. The following temperature profile was kept along the barrel zones: 200/210/220/230/ 240°C. The mold temperatures were kept at 40°C. 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 an emission range from 315 to 400 nm.<sup>14</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 and 720 h.

#### Fourier transformed infrared spectroscopy

The reflectance infrared analyses of the aged homopolymers and PS/EPDM blends were performed in a FTIR Nicolet 520 spectrophotometer (Waltham, MA), using 256 scans and  $4 \text{ cm}^{-1}$  resolution.

#### Tensile and impact resistance tests

The aged and nonaged injection-molded specimens (at least five specimens) were submitted to impact resistance and tensile tests in an EMIC AIC 1 apparatus (São José dos Pinhais, Brazil) and in an EMIC DL 200 apparatus (5000N load cell, 5 mm min<sup>-1</sup> speed) (São José dos Pinhais, Brazil), respectively.

#### **RESULTS AND DISCUSSION**

The aim of this study was to evaluate the influence of photochemical aging on the mechanical properties of *in situ* polymerized PS/EPDM. Thus, the PS/ EPDM blends were submitted to photochemical aging in an apparatus developed by our research group, following the procedures in ASTM G53 standard. As previously reported,<sup>13</sup> *in situ* polymerized PS/EPDM blends present EPDM dispersed in the PS matrix. The phase behavior of these blends as well as their thermal and mechanical properties are strongly affected by the polymerization temperature.

Even though some mechanical properties of *in situ* polymerized PS/EPDM blends do not reach the exceptional properties of HIPS, the mechanical performances of the former are quite superior to those shown by blends prepared by mechanical mixing. As discussed previously the extent of phase segregation, the morphology and the intrinsic properties of



**Figure 1** Fourier transformed infrared spectra of PS, HIPS and PS/EPDM blends; (a) nonaged specimens and (b) specimens photoaged for 720 h. Blends prepared at: (I)  $60^{\circ}$ C and (II)  $80^{\circ}$ C.

the elastomer are responsible for the main differences between the properties of *in situ* polymerized PS/EPDM blends and HIPS.<sup>13</sup>

#### Fourier transformed infrared spectroscopy

Figure 1 shows the infrared spectra of nonaged [Fig. 1(a)] and aged [Fig. 1(b)] PS, HIPS and PS/EPDM blends with different compositions. The presence of characteristic bands of oxidized products around 1700 and 3500  $\text{cm}^{-1}$ , observed in Figure 1(b), indicates that chemical modifications occurred on the exposed surfaces of the blends. The yellowing observed in the exposed specimens is caused by the presence of chromophores and their interaction with the aromatic ring of the PS matrix.<sup>15</sup> Surface embrittlement was also observed for the exposed specimens.<sup>16</sup> For HIPS, the presence of intense bands corresponding to chemical bonds that indicate a high degree of oxidation of the HIPS surface is due to the higher amount of labile sites of polybutadienic phase. For example, the bands corresponding to the C=O bond at 1700 cm<sup>-1</sup> and O-H bond at 6.5E60

8E60

11E60

14E60

TABLE II Carbonyl Index Obtained from Infrared Spectra for PS and PS/EPDM Blends Photoaged for 720 h							
Matariala	Carbonyl	Matoriala	Carbony				
	index	Iviaterials	index				
3E60	0.76	3E80	0.68				

0.42

0.92

0.68

0.60

and	<b>PS/EPDM Blends</b>	S Photoaged for	d for 720 h			
	Carbonyl		Carbony			
Matoriale	indov	Matoriale	indov			

6.5E80

11E80

0.39

0.46

	0.00		
17E60	0.56	17E80	0.46
PS60	0.64	PS80	0.64
HIPS	5.10	-	—
$3500 \text{ cm}^{-1}$	could be attrib	uted to a wide r	ange of ox-
ygen-contai	ning groups s	uch as aldehyd	es, ketones,
peroxides,	carboxylic acid	s, etc., resulting	from auto-

oxidation of the polymer components of HIPS.<sup>15</sup> Natural and accelerated degradations of HIPS have been described in the literature as a process of two-phase oxidation, where air oxygen preferentially attacks the PB component, the oxidation rate being a function of the PB content. In the early stage of aging, the PS matrix remains almost intact, whereas crosslinking reactions take place in the PB phase. The PB phase, as the component more sensitive toward oxidation because of the unsaturated double bonds in its structure, first undergoes degradation followed by degradation of the PS matrix.<sup>6,15</sup>

The carbonyl index (CI) was calculated as the ratio of the areas of bands centered in 1708  $cm^{-1}$  (C=O bond) and 2922  $\text{cm}^{-1}$  (C–H bond) for samples photoaged for 720 h and the results are presented in Table II. In spite of the CI of PS60 and PS80 is close, the blends with EPDM obtained at 60°C present higher CI than the corresponding blends obtained at 80°C. Moreover, the CI of the blends shows the tendency of decreasing with the increase of the EPDM content, assuming in some compositions values lower than those observed for PS60 and PS80. This is due to the stabilization caused by EPDM deactivating the formed PS macroradicals through intermolecular reactions.9,13 Although commercial HIPS contains additives against degradation, it presented the highest CI, proving that it is more susceptible to photodegradation than PS/EPDM blends.

# **Tensile test (ASTM D638)**

Figure 2 shows representative stress versus strain curves obtained from tensile tests for PS60, PS80, and PS/EPDM blends. The PS/EPDM blends showed stress whitening during the tensile tests indicating that dilatational processes occur during the loading, such as crazing and cavitation.<sup>17</sup> The stress-strain profiles of PS and PS/EPDM blends undergo modifications after photochemical aging, as

can be seen in Figure 2(b,c), for blends photoaged for 168 and 720 h, respectively.

The mechanical properties of aged and nonaged samples are summarized in Table III.

Figure 3 shows the Young's modulus as a function of EPDM content for aged and nonaged PS and PS/ EPDM blends. For nonaged samples, the Young's modulus of PS decreases about 20% with the addition of 11 wt % of EPDM. For the blends prepared at 60°C, the increase in the EPDM content leads to a drop of 60% in comparison with the value of the PS. Whereas, for the blend with 17 wt % of EPDM, the drop in the modulus is of 32%. In general, the Young's modulus behaves in a similar way with the blend composition, except for blends containing 17 wt % of EPDM, whose behavior is hard to explain. The decrease of the Young's modulus of PS/EPDM is higher in comparison with PS/AES blends with comparable content of elastomer obtained by *in situ* polymerization, because of the stiffening of PS promoted by the SAN phase of AES.<sup>18</sup> The decrease in modulus with increasing the elastomer content is expected and well reported for rubber toughening of rigid polymers.<sup>8</sup>

The Young's modulus is higher for photoaged samples, but the dependence of this property on the blend composition (up to 11 wt % of EPDM) is not affected by aging. The Young's modulus of the nonaged PS/EPDM blends (between 973 and 1363 MPa), except for 14E60 and 17E60 (591 and 554 MPa, respectively), are higher than the Young's modulus of the 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% except for 14E60 and 17E60 that presented an average increase of 85%. The blends became stiffer than nonaged blends probably due to crosslinking reactions of the rubber phase.19,20

Figure 4 shows the strain at break as a function of EPDM content for aged and nonaged PS and PS/ EPDM blends. For both groups of blends the increase of EPDM content leads to an increase of the strain at break, being higher this effect for blends obtained at 80°C. The blend 17E80 shows a strain at break of 20.3%, an enhancement of 480% in comparison with the value of PS.

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 47%  $\pm$  4% to 2.2%  $\pm$  0.1% after 720 h of photoaging attributed to the rubber phase crosslinking and also the degradation of the matrix. The most of PS/EPDM blends prepared in this work shows strain at break at least comparable to the commercial HIPS after aging. Table III shows that the strain at break of nonaged PS/EPDM blends (the



Figure 2 Representative stress versus strain curves for PS60, PS80, and PS/EPDM blends; (a) nonaged, (b) aged for 168 h, and (c) aged for 720 h. Blends prepared at: (I)  $60^{\circ}$ C and (II)  $80^{\circ}$ C.

highest one 20.3% for 17E80) is not comparable to the strain at break of nonaged HIPS (47.3%). But, after 168 or 720 h of aging, the PS/EPDM blends showed a higher strain at break (the strain at break of most blends are higher than 3.0%) than HIPS (around 2.0% after 168 and 720 h of aging). It is important to note that the PS/EPDM blends do not contain any stabilizers, what is not the case for the commercial HIPS used in this work. Thus, the goal of this work, to prepare a material with higher pho-

TABLE III Mechanical Properties of Aged and Nonaged Samples

Mechanical Properties of Agea and Monagea Sumpres											
n	Young's modulus (MPa)		Strain at break (%)		Impact strength (J/m)		Tensile strength (MPa)				
0 h	168 h	720 h	0 h	168 h	720 h	0 h	168 h	720 h	0 h	168 h	720 h
1302 ± 26	1363 ± 4	1379 ± 1	6.1 ± 0.1	3.8 ± 0.7	3.5 ± 0.2	41 ± 5	25 ± 4	19 ± 4	44 ± 1	42 ± 7	39 ± 1
$1272 \pm 4$	$1308 \pm 6$	$1331 \pm 10$	$6.3 \pm 0.3$	$5.0 \pm 0.4$	$3.7 \pm 0.2$	$37 \pm 5$	$24 \pm 4$	$20 \pm 4$	$50 \pm 1$	$46 \pm 1$	38 ± 2
$1202~\pm~10$	$1279 \pm 17$	$1271 \pm 12$	$6.7 \pm 0.7$	$2.6 \pm 0.2$	$3.9 \pm 0.3$	$38 \pm 3$	$25 \pm 2$	$17 \pm 2$	$41 \pm 1$	29 ± 2	$41 \pm 1$
$1139 \pm 13$	$1216 \pm 11$	$1198\pm4$	$7.4 \pm 0.8$	$3.8 \pm 0.4$	$3.4 \pm 0.1$	$37 \pm 4$	$27 \pm 5$	26 ± 6	$40 \pm 1$	$41 \pm 2$	$34 \pm 2$
$591 \pm 4$	$1141~\pm~7$	$1101 \pm 22$	$7.9\pm0.9$	$6.7\pm0.3$	$2.6\pm0.2$	$34 \pm 2$	$33 \pm 1$	$25 \pm 3$	$20 \pm 1$	$41~\pm~1$	$24 \pm 2$
$554 \pm 8$	$1075 \pm 3$	$986 \pm 52$	$10 \pm 1$	$7.9 \pm 0.9$	$4.6 \pm 0.4$	$37 \pm 3$	$33 \pm 5$	$30 \pm 5$	19 ± 1	$38 \pm 1$	$21 \pm 5$
$1260\pm18$	$1157~\pm~42$	$1307\pm19$	$6.0\pm0.2$	$2.1\pm0.2$	$3.2 \pm 0.2$	$20 \pm 2$	$11 \pm 2$	$11 \pm 1$	$35 \pm 1$	19 ± 3	$31 \pm 3$
$1192 \pm 13$	$1071 \pm 113$	$1257 \pm 12$	$6.7 \pm 0.4$	$2.2 \pm 0.5$	$3.2 \pm 0.1$	$25 \pm 1$	$14 \pm 4$	$12 \pm 1$	$34 \pm 1$	$17 \pm 3$	$30 \pm 1$
$1083\pm11$	$1102~\pm~41$	937 ± 29	$14 \pm 2$	$3.1\pm0.1$	$1.6\pm0.1$	$31 \pm 4$	$27 \pm 7$	$18 \pm 3$	$32 \pm 1$	$18 \pm 2$	11 ± 11
973 ± 9	$1028 \pm 12$	$871 \pm 34$	$20 \pm 0.7$	$3.9 \pm 0.1$	$1.9 \pm 0.1$	$48\pm10$	$57 \pm 8$	$44~\pm~10$	$30 \pm 1$	$24 \pm 3$	$12 \pm 1$
$1394~\pm~14$	$1484 \pm 31$	$1438\pm24$	$3.7 \pm 0.3$	$4.4 \pm 0.6$	$3.2 \pm 0.1$	$23 \pm 5$	$17 \pm 2$	$14 \pm 1$	$43 \pm 1$	$48 \pm 3$	$38 \pm 1$
$1432 \pm 16$	$1505 \pm 4$	$1360 \pm 34$	$3.5 \pm 0.2$	$3.0 \pm 0.2$	$2.2 \pm 0.3$	$20 \pm 3$	$16 \pm 1$	$14 \pm 2$	$42 \pm 1$	$38 \pm 2$	$25 \pm 4$
$786~\pm~20$	$816~\pm~48$	$822\pm18$	$47~\pm~4$	$2.2\pm0.1$	$2.1\pm0.1$	$88~\pm~5$	$74~\pm~2$	$64~\pm~4$	$16~{\pm}~1$	$14~\pm~1$	$14~\pm~1$
	$\begin{array}{c} & \\ & \\ \hline 0 \text{ h} \\ \hline \\ 1302 \pm 26 \\ 1272 \pm 4 \\ 1202 \pm 10 \\ 1139 \pm 13 \\ 591 \pm 4 \\ 554 \pm 8 \\ 1260 \pm 18 \\ 1192 \pm 13 \\ 1083 \pm 11 \\ 973 \pm 9 \\ 1394 \pm 14 \\ 1432 \pm 16 \\ 786 \pm 20 \\ \end{array}$	$\begin{tabular}{ c c c c c } & Young's \\ \hline modulus (MP) \\\hline 0 h & 168 h \\\hline \\ \hline 1302 \pm 26 & 1363 \pm 4 \\ 1272 \pm 4 & 1308 \pm 6 \\ 1202 \pm 10 & 1279 \pm 17 \\ 1139 \pm 13 & 1216 \pm 11 \\ 591 \pm 4 & 1141 \pm 7 \\ 554 \pm 8 & 1075 \pm 3 \\ 1260 \pm 18 & 1157 \pm 42 \\ 1192 \pm 13 & 1071 \pm 113 \\ 1083 \pm 11 & 1102 \pm 41 \\ 973 \pm 9 & 1028 \pm 12 \\ 1394 \pm 14 & 1484 \pm 31 \\ 1432 \pm 16 & 1505 \pm 4 \\ 786 \pm 20 & 816 \pm 48 \\\hline \end{tabular}$	Young's modulus (MPa) $0$ h $168$ h $720$ h $1302 \pm 26$ $1363 \pm 4$ $1379 \pm 1$ $1272 \pm 4$ $1308 \pm 6$ $1331 \pm 10$ $1202 \pm 10$ $1279 \pm 17$ $1271 \pm 12$ $1139 \pm 13$ $1216 \pm 11$ $1198 \pm 4$ $591 \pm 4$ $1141 \pm 7$ $1101 \pm 22$ $554 \pm 8$ $1075 \pm 3$ $986 \pm 52$ $1260 \pm 18$ $1157 \pm 42$ $1307 \pm 19$ $1192 \pm 13$ $1071 \pm 113$ $1257 \pm 12$ $1083 \pm 11$ $1102 \pm 41$ $937 \pm 29$ $973 \pm 9$ $1028 \pm 12$ $871 \pm 34$ $1394 \pm 14$ $1484 \pm 31$ $1438 \pm 24$ $1432 \pm 16$ $1505 \pm 4$ $1360 \pm 34$ $786 \pm 20$ $816 \pm 48$ $822 \pm 18$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Young's modulus (MPa)Strain at break $1302 \pm 26$ $1363 \pm 4$ $1379 \pm 1$ $6.1 \pm 0.1$ $3.8 \pm 0.7$ $1272 \pm 4$ $1308 \pm 6$ $1331 \pm 10$ $6.3 \pm 0.3$ $5.0 \pm 0.4$ $1202 \pm 10$ $1279 \pm 17$ $1271 \pm 12$ $6.7 \pm 0.7$ $2.6 \pm 0.2$ $1139 \pm 13$ $1216 \pm 11$ $1198 \pm 4$ $7.4 \pm 0.8$ $3.8 \pm 0.4$ $591 \pm 4$ $1141 \pm 7$ $1101 \pm 22$ $7.9 \pm 0.9$ $6.7 \pm 0.3$ $554 \pm 8$ $1075 \pm 3$ $986 \pm 52$ $10 \pm 1$ $7.9 \pm 0.9$ $1260 \pm 18$ $1157 \pm 42$ $1307 \pm 19$ $6.0 \pm 0.2$ $2.1 \pm 0.2$ $1192 \pm 13$ $1071 \pm 113$ $1257 \pm 12$ $6.7 \pm 0.4$ $2.2 \pm 0.5$ $1083 \pm 11$ $1102 \pm 41$ $937 \pm 29$ $14 \pm 2$ $3.1 \pm 0.1$ $973 \pm 9$ $1028 \pm 12$ $871 \pm 34$ $20 \pm 0.7$ $3.9 \pm 0.1$ $1394 \pm 14$ $1484 \pm 31$ $1438 \pm 24$ $3.7 \pm 0.3$ $4.4 \pm 0.6$ $1432 \pm 16$ $1505 \pm 4$ $1360 \pm 34$ $3.5 \pm 0.2$ $3.0 \pm 0.2$ $786 \pm 20$ $816 \pm 48$ $822 \pm 18$ $47 \pm 4$ $2.2 \pm 0.1$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Young's modulus (MPa)Strain at break (%)str $0$ h $168$ h $720$ h $0$ h $168$ h $720$ h $0$ h $168$ h $720$ h $0$ h $1302 \pm 26$ $1363 \pm 4$ $1379 \pm 1$ $6.1 \pm 0.1$ $3.8 \pm 0.7$ $3.5 \pm 0.2$ $41 \pm 5$ $1272 \pm 4$ $1308 \pm 6$ $1331 \pm 10$ $6.3 \pm 0.3$ $5.0 \pm 0.4$ $3.7 \pm 0.2$ $37 \pm 5$ $1202 \pm 10$ $1279 \pm 17$ $1271 \pm 12$ $6.7 \pm 0.7$ $2.6 \pm 0.2$ $3.9 \pm 0.3$ $38 \pm 3$ $1139 \pm 13$ $1216 \pm 11$ $1198 \pm 4$ $7.4 \pm 0.8$ $3.8 \pm 0.4$ $3.4 \pm 0.1$ $37 \pm 4$ $591 \pm 4$ $1141 \pm 7$ $1101 \pm 22$ $7.9 \pm 0.9$ $6.7 \pm 0.3$ $2.6 \pm 0.2$ $34 \pm 2$ $554 \pm 8$ $1075 \pm 3$ $986 \pm 52$ $10 \pm 1$ $7.9 \pm 0.9$ $4.6 \pm 0.4$ $37 \pm 3$ $1260 \pm 18$ $1157 \pm 42$ $1307 \pm 19$ $6.0 \pm 0.2$ $2.1 \pm 0.2$ $3.2 \pm 0.2$ $20 \pm 2$ $1192 \pm 13$ $1071 \pm 113$ $1257 \pm 12$ $6.7 \pm 0.4$ $2.2 \pm 0.5$ $3.2 \pm 0.1$ $25 \pm 1$ $1083 \pm 11$ $1102 \pm 41$ $937 \pm 29$ $14 \pm 2$ $3.1 \pm 0.1$ $1.6 \pm 0.1$ $31 \pm 4$ $973 \pm 9$ $1028 \pm 12$ $871 \pm 34$ $20 \pm 0.7$ $3.9 \pm 0.1$ $1.9 \pm 0.1$ $48 \pm 10$ $1394 \pm 14$ $1484 \pm 31$ $1438 \pm 24$ $3.7 \pm 0.3$ $4.4 \pm 0.6$ $3.2 \pm 0.1$ $23 \pm 5$ $1432 \pm 16$ $1505 \pm 4$ $1360 \pm 34$ $3.5 \pm 0.2$ $3.0 \pm 0.2$ $2.2 \pm 0.3$ $20 \pm 3$ $786 \pm 20$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

1600 1600 1500 (1) (11) 1500 1400 1400 Young's modulus (MPa 1300 1300 1200 1200 1100 1100 1000 1000 900 900 800 800 700 700 non-aged aged for 168h 600 600 aged for 720h 500 500 2 6 10 12 14 16 18 20 ó ż 4 10 12 20 EPDM content (wt%)

Figure 3 Young's modulus as a function of EPDM content for PS60, PS80, and PS/EPDM blends. Blends prepared at: (I) 60°C and (II) 80°C.

tochemical stability than HIPS, was achieved, because, 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. This was also observed for PS/AES blends prepared by *in situ* polymerization.<sup>21</sup>

In general, the drop of the strain at break after photochemical aging increases as EPDM content in the blends increases. Thus, PS60 and PS80 show lower drop in this property than their blends, as can be concluded from data in Table III.

The tensile stress of the nonaged blends prepared at 60°C shows a slight increase up to 6.5 wt % of EPDM, and subsequent increases of EPDM content leads to a decrease in the tensile stress. For the blends prepared at 80°C, the tensile stress shows a steady decrease with the increase of EPDM content. All PS/EPDM blends present higher tensile stress than the value for HIPS. After 720 h of photoaging the tensile stress has the tendency of decreasing (Table III), being this effect more pronounced for blends

(I)

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22

20

18

16 14

12

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(11)

12 14 16 18 20

richer in EPDM and obtained at 80°C. This behavior could be attributed to the embrittlement of the sample as a consequence of crosslinking. The tensile stress of nonaged PS/EPDM blends (between 19 and 50 MPa) is higher than that of nonaged HIPS (16 MPa). After 168 and 720 h of aging, the tensile stress of the blends is still higher than for HIPS (15 MPa, after 168 h of aging).

The tensile properties are very sensitive to any defect or imperfection on the surface. It is known that the degradation starts on the surface resulting in a brightness of the superficial layer. Because of the difference of properties of the material in the surface and in the bulk, the surface can present cracks that act as defects and as the starting point of the rupture of the material. The loss of the tensile properties of PS/EPDM blends and HIPS is a consequence of the superficial chemical modifications, which are more intense for HIPS, as demonstrated by FTIR. Because of this, the drop of the tensile properties of HIPS is higher in comparison to the values of PS/EPDM blends.

#### Impact resistance test (ASTM D256)

The polymerization temperature also influences the Izod impact resistance (Fig. 5). For the blends polymerized at 60°C, the addition of 5 wt % EPDM leads to an enhancement of the impact resistance from  $(23 \pm 5)$  J/m for PS60 to  $(41 \pm 5)$  J/m, and subsequent increases in the EPDM content do not change the value of impact resistance. For the blends obtained at 80°C, the increase at EPDM content up to 17 wt % leads to a increase in the impact resistance from 20  $\pm$ 3 J/m for PS80 to  $48 \pm 10 \text{ J/m}$  at 17 wt %.

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. For both series of blends, the increase of EPDM delays

Figure 4 Strain at break as a function of EPDM content

EPDM content (wt%)

16 18 20 ó 2 4 6 8 10





Figure 5 Impact resistance as a function of EPDM content for PS60, PS80, and PS/EPDM blends. Blends prepared at: (I) 60°C and (II) 80°C.

24

22

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ó 2

Strain at break (%)

non-aged

aged for 168h

aged for 720h

10 12 the drops of the impact resistance with the aging time.

The impact resistance of nonaged PS/EPDM blends (the highest was  $48 \pm 10$  J/m for 17E80) is not comparable to that of nonaged HIPS ( $88 \pm 5 \text{ J/m}$ ). However, after 168 h of aging, the blends 14E60, 17E60, 11E80, and 17E80 showed a higher retention of impact resistance (0.97, 0.89, 0.87, and 1.19, 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 the time  $t_i$  and the value of this property for the nonaged sample  $(t_0)$  (Impact Resistance<sub>t<sub>1</sub></sub>/Impact Resistance<sub>t<sub>0</sub></sub>). This indicates that these compositions are more photochemically stable than HIPS. Another interesting result is that the blends 14E60, 17E60, and 17E80 also presented higher retention of impact resistance (0.74, 0.81, and 0.92, respectively) than that of HIPS (0.73) after 720 h of aging. Even though the impact resistance of aged HIPS is higher than the impact resistances of aged 14E60, 17E60, 11E80, and 17E80 blends, the PS/ EPDM blends presented a higher stability to photochemical aging than HIPS. The impact resistance is more dependent on the mechanical properties of the bulk of the material than on those of the surface. As a consequence of this changes of the impact properties of the PS/EPDM blends and HIPS with aging time are very similar.

#### CONCLUSIONS

The results showed in this work clearly make evident the higher photostability of *in situ* polymerized PS/ EPDM blends in comparison with commercial HIPS. Although this conclusion is really not a surprise, one important feature of PS/EPDM blends is that their properties after aging are in most cases superior than photoaged HIPS properties. Besides EPDM, a saturated elastomer, be more stable than PB phase of HIPS, it plays a decisive role in the degradation process of PS phase deactivating macroradicals.

Tensile properties are very sensitive to the aging of the surface of the material. The loss of the tensile properties of PS/EPDM blends and HIPS are a consequence of superficial chemical modifications, which are more intense for HIPS. Because of this, the PS/EPDM blends presented higher tensile properties than HIPS. The impact resistance of nonaged PS/EPDM blends is not comparable to that of nonaged HIPS. However, after 168 h of aging, the blends 14E60, 17E60, 11E80, and 17E80 showed a higher retention of impact resistance than that of HIPS. This indicates that these compositions are more photochemically stable than HIPS. Another interesting result is that the blends 14E60, 17E60, and 17E80 also presented higher retention of impact resistance than that of HIPS after 720 h of aging. Even though the impact resistance of aged HIPS is higher than the impact resistances of aged 14E60, 17E60, 11E80, and 17E80 blends, the PS/EPDM blends presented a higher stability to photochemical aging than HIPS. Because the impact resistance is more dependent on the mechanical properties of the bulk of the material than on those of the surface, changes of the impact properties of the PS/EPDM blends and HIPS with aging time are very similar.

The polymerization temperature affects the photostability of *in situ* polymerized PS/EPDM blends, probably due to the presence of higher concentration of oxidizing species and other defects into the chain in the materials polymerized at higher temperature.

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