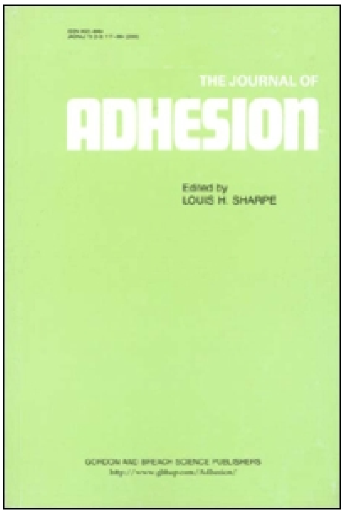

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Influence of Additives in Adhesion of UV Radiation Surface-Treated SBS Rubber

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In this study, the effect of additives (oils, lubricants) included in the formulations of different block styrene–butadiene–styrene (SBS) rubbers on the effectiveness of the ultraviolet (UV) radiation treatment to improve adhesion to polyurethane adhesive was analyzed. The modifications on the UV-treated rubber surfaces for different lengths of treatment have been characterized by contact-angle measurements (ethylene glycol, 25°C), Attenuated Total Reflectance-Infrared (ATR-IR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Scanning Electron Microscopy (SEM). The adhesion properties have been evaluated from T-peel strengths of treated rubber/polyurethane adhesive/leather joints. The UV-radiation treatment on all rubber surfaces produced an increase in wettability, carbon–oxygen polar moieties, and ablation. The oxidation degree produced on the rubber surface treated with UV radiation was less when oils and lubricants were included in the formulation, likely due to competition of the oxidation process with the migration of low-molecular-weight additives to the rubber surface. On the SBS2 rubber surface (rubber containing carbon black and calcium carbonate fillers), the migration of oils and lubricants was also produced during the UV-radiation treatment, but a decrease in adhesion occured likely due to the lower tensile strength and higher extent of oxidation produced by the UV radiation treatment.

Keywords: Contact-angle measurements; Infrared spectra; Peel strength; SBS rubber; SEM; UV radiation; XPS

1. INTRODUCTION

Additives (processing oils, plasticizers, fillers) are usually added to improve the mechanical, rheological, and other properties of block styrene–butadiene–styrene rubbers (SBS) [1]. To enhance the abrasion

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resistance of SBS rubber, the addition of carbon black is very common. Plasticizers (*i.e*, aromatic or paraffinic/naphthenic oils) modify the flow properties of the SBS rubber to facilitate processing, but hardness and mechanical resistance can be reduced. On the other hand, addition of lubricants and oils allows easy rubber processing. Generally, plasticizers, lubricants, and oils are low-molecular-weight compounds, which are not compatible with the base rubber polymer in which they are incorporated. Thus, they can migrate with time to the SBS rubber surface, giving antiadhesion properties [2].

On the other hand, SBS rubbers are nonpolar, and they show poor adhesion mainly to polar adhesives, such as polyurethanes. Thus, to allow adequate adhesive joints, a surface treatment is necessary to improve wettability and polarity and, thus, to enhance adhesion of SBS rubbers. Previous studies [3,4] have shown the effectiveness of different treatments (*i.e.*, halogenation, corona discharge, low-pressure plasma) to modify the SBS rubber surface and to improve its adhesion to polyurethane adhesives. Recently, UV treatment has been shown [5] to be very effective for increasing the adhesion of SBS rubber. Because the formulations of SBS rubbers contain several ingredients, the performance of UV surface treatment cannot be anticipated, because several processes are taking place at the same time [6,7].

The extent of the modifications produced by UV treatment on polymers and rubber surfaces (*i.e.*, roughness creation, formation of polar moieties, wettability improvement, and adhesion) may differ depending on their composition [8–12]. More precisely, it has been established [6,13] that the modifications produced by surface treatment of rubbers are very sensitive to the presence of additives and fillers in their formulation.

Additives may facilitate or inhibit the degree of cross-linking of polymer chains on the treated rubber surface (*i.e.*, additional cross-links can be produced between the additives and the rubber) [14]. Furthermore, low molecular weight surface fragments may react with the rubber or migrate to the rubber surface, reducing the effectiveness of the UV radiation treatment and also adhesion of the rubber likely due to the competence of the surface oxidation process with respect to additive migration to the rubber surface during UV treatment. The changes in wetting and adhesion of UV radiation or corona discharge surface-treated polymers have been studied [15,16]. It has been established that additive surface migration or exudation and reorientation of oxidized functionalities away from the surface region can adversely affect the adhesion properties of the treated polymer [13,15–17]. On the contrary, Wu [18] found that low-molecular-weight additives may improve adhesion of polymers by promoting interfacial flow and interdiffusion.

To analyze the effect of different additives (oils, lubricants, fillers) on the surface properties and adhesion of SBS rubbers, UV-radiation surface treatment has been carried out in three SBS rubbers (SBS0, SBS1, SBS2) prepared using the same base rubber polymer but containing different additives such as oils, lubricants, or fillers in their formulations. The influence of the length of UV radiation treatment on the surface modifications and adhesion of the different rubbers were compared.

2. EXPERIMENTAL

2.1. Materials

The base SBS rubber polymer used in this study was pellets of thermoplastic Kraton D-4270CS rubber (it contains tiny amounts of talc to avoid agglomeration), which was supplied by Synthelast S.A. (Elche, Alicante, Spain). It is an oil-extended (45 phr nonstaining paraffin oil) radial block styrene–butadiene–styrene copolymer containing 32 wt% styrene. All SBS rubber test samples (25 mm wide, 150 mm long, 5 mm thick) contain 0.3 wt% phenolic antioxidant and were prepared by Synthelast S.A. by injection molding in a heated mold (150°C).

The formulation of the SBS0 rubber contains only the base Kraton D-4270CS rubber. Some properties of the SBS0 rubber were obtained using standardized UNE Spanish procedures: density (20°C) = $0.94\,g/cm^3$, tensile strength = 12 MPa, maximum elongation at break = 1100%. The SBS1 rubber formulation contains the base Kraton D-4270CS rubber, 20 parts per hundred parts rubber (phr) paraffinic/naphthenic oils (70/30 ratio by weight), and 0.2 phr lubricants (zinc soaps). The SBS2 rubber formulation contains the base Kraton D-4270CS rubber, 10 phr calcium carbonate, and other additives (Table 1). Some properties of the SBS2 rubber were obtained using standardized UNE Spanish procedures: hardness = 60°Shore A, density (20°C) = $0.97\,g/cm^3$, tensile strength = 4.7 MPa, maximum elongation at break = 520%, tear resistance = 10.1 kN/m. The three rubber formulations (SBS0, SBS1, SBS2) were selected by considering the most typical formulations for soles in the shoe industry.

To determine the adhesion properties, UV-treated SBS rubber/polyurethane adhesive/leather joints were prepared. A bovine chromium-tanned leather without finishing was used in this study. This leather has a tensile strength of 22 MPa, an elongation at break of 52%, and chromium content lower than 5 wt%. The adhesive solution was prepared by dissolving 18 wt% polyurethane pellets

TABLE 1 Composition of the SBS2 Rubber

Ingredient	Percentage (phr)[a]
Kraton D-4270CS rubber	100
Paraffin plasticizer	10
Polystyrene	20
Diesteramide	0.1
Antioxidant (Irganox 565)	0.2
Calcium carbonate	10
Carbon black	1.1

[a] Data are expressed in parts per hundred parts of rubber (phr).

(Desmocoll 540, Bayer, Leverkusen, Germany) and 10 wt% fumed silica (Aerosil 200, Degussa, Hanau, Germany) in an acetone/toluene (80:20, w:w) mixture. To facilitate the dispersion of the fumed silica in the polyurethane and to avoid further settling, the adhesive was prepared in two consecutive steps: 1) the fumed silica was mixed with a small amount of the solvent mixture at 2500 rpm for 15 min in a laboratory mixer to facilitate dispersion; 2) the polyurethane pellets were added to the solvent-fumed silica mixture simultaneously with all the solvent; the mixture was stirred in the laboratory mixer at 2000 rpm for 2.30 h until a homogeneous solution was obtained. The viscosity of the solution obtained in a rotational rheometer (Rheolab MC 100 Physica, Stuttgart, Germany) was 4.4 Pa·s at 25 s^{-1}.

2.2. Experimental Techniques

UV Radiation Treatment Unit

The UV radiation source was a medium-pressure vapor grid mercury lamp, manufactured by American Ultraviolet (Upland, CA, USA). The lamp, made of fused quartz, provided a radiation intensity of 10 mW/cm^2 measured at a distance of 2 in. (5 cm) from the lamp. The lamp emits UV radiation mainly at 254 and 185 nm. Ozone is formed at 185 nm and decomposed into radicals and atomic oxygen because of the absorption by ozone of the radiation at 254 nm. The UV lamp was placed inside a UV protective polycarbonate box. The box has an extraction unit to avoid high concentrations of ozone inside the chamber during treatment. Because mercury lamps are notorious for heating up the substrate from IR emissions, it was cooled down by air directed away from the substrate. The UV lamp was turned on directly on the substrate and, prior to treatment, was allowed to come to equilibrium for 10 min to reach steady-state conditions. The length of treatment varied from 10 s to 30 min. In a previous paper [19], the influence of the distance between the UV source and the rubber sample was varied, and it was concluded that 2 cm provided a good balance between the extent of surface modifications and reasonable heating of the substrate. Therefore, in this study the distance between the UV source and the rubber sample was set to 2 cm.

Contact-Angle Measurements

The wettability of the as-received and UV-radiation-treated rubbers was evaluated from contact-angle measurements using a Ramé-Hart 100 goniometer (Ramé-Hart, Inc., Mountain Lakes, NJ). Drops (4 μl) of ethylene glycol test liquid were placed on the rubber surfaces using a micrometric syringe (Hamilton Instruments, Reuo, NV, USA). Ethylene glycol (purity higher than 99 wt%) provided by Merck-Schuchardt (Barcelona, Spain) was used as received and was selected because of its adequate balance between dispersive and polar components of surface energy. Furthermore, none of the rubbers were dissolved by contact with ethylene glycol during contact-angle measurements, and no swelling of the rubber surface was noticed. Contact angles were measured immediately after UV treatment and immediately after the ethylene glycol drop was placed on the treated rubber surfaces. At least three drops on two identically treated samples were measured and averaged. The experimental error was ±2°.

ATR-IR Spectroscopy

A Bruker Vector 22 (Bruker Optik GmbH, Madrid, Spain) FTIR spectrometer was used to obtain the ATR-IR spectra and to analyze the chemical modifications produced within a distance of approximately 3 μm (the penetration depth of the infrared radiation in these ATR experiments) of the surface of the treated rubbers. The incident angle of the IR radiation was 45°, and a KRS-5 (thallium bromoiodide) prism was used to obtain the ATR-IR spectra of the SBS0 and SBS1 rubber surfaces. A germanium crystal was used for the SBS2 rubber spectra because of the presence of carbon black in the formulation. Two hundred scans were obtained and averaged with a resolution of 4 cm^{-1}.

Considering that the lack of adhesion in adhesive joints of formulated rubbers is mainly caused by migration of low molecular moieties to the rubber–adhesive interface, the use of ATR-IR spectroscopy to interpret the loci of failure in the adhesive joints is sound. Therefore, to assess the locus of failure of the joints, the failed surfaces obtained after a T-peel test were characterized by ATR-IR spectroscopy.

X-ray Photoelectron Spectroscopy (XPS)

Chemical modifications produced in the outermost approximately 5 nm of the treated rubber surfaces were obtained using XPS. A VG Scientific Microtech Multilab spectrometer (VG Scientific Microtech, Surrey, UK), with an Mg Kα X-ray source (1253.6 eV) operating at 15 keV and 300 W was used. A 45° incidence angle was selected. Prior to analysis, samples were outgassed in a vacuum chamber to a pressure lower than 5×10^{-8} Torr. The analysis was performed on 5×2 mm pieces of the treated rubbers at a residual pressure below 10^{-8} Torr. For each sample, a survey scan encompassing the region 0–1200 eV was first obtained. Multiplex scanning of all observed photopeaks in the survey scan were carried out in a 20 eV range. Binding energies of all photopeaks were referenced to the C 1s photopeak position for C−C and C-H (hydrocarbons) species at 285.0 eV. The FWDH (full width at half maximum) for the C 1s photopeak was 1.8 eV. Atomic concentration calculations were carried out using a VGX900-W system.

Scanning Electron Microscopy (SEM)

The morphological modifications produced on the treated rubber surfaces were analyzed using a JEOL JSM-840 SEM system (Izasa, Alcobendas, Madrid, Spain). The rubber samples were coated with gold before analysis, and the energy of the electron beam was 20 kV.

T-peel Tests

UV surface-treated rubber/polyurethane adhesive/leather joints were prepared to measure the adhesive strength. Immediately after UV radiation treatment of the SBS rubbers, 0.8 ml of adhesive solution was applied by brush. The leather surface was roughened to expose the corium in a Superlema S.A. (Zaragoza, Spain) instrument operating at 2800 rpm. A P100 aluminum oxide abrasive cloth was used to produce roughening, and about 0.5 mm of leather was removed. Adhesive solution (0.8 ml) was applied by brush to the roughened leather surface, and 30 min later an additional 0.8 ml of adhesive was applied to assure the adequate penetration of the adhesive into the leather pores. Once the adhesive solution was applied, the solvent was allowed to evaporate for 45 min. The dried solid adhesive films (about 100 μm thick) on the surfaces of the two substrates were melted at 80°C under IR irradiation and immediately placed into contact under a pressure of 0.8 MPa for 10 s. T-peel tests (72 h after joint formation) were carried out using an Instron 4411 instrument (Instron Limited, Barcelona, Spain). A peeling rate of 0.1 m/min was used. Five replicates for each length of treatment were tested, and the peel strength values were averaged. The error was less than 0.7 kN/m.

3. RESULTS AND DISCUSSION

The contact-angle values on the as-received and UV-treated rubber surfaces are given in Figure 1. The as-received rubbers show high contact-angle values (87, 73, and 77° for the SBS0, SBS1, and SBS2 rubber surfaces, respectively), due to their nonpolar nature. The rubbers containing additives in the formulation show lower contact-angle values as compared with that for SBS0 (without additives). The UV treatment produces a marked decrease in the SBS0 rubber contact-angle value; the decrease in the contact-angle value is less for the rubbers containing additives. The UV treatment carried out for only 30 s produces a decrease in the contact-angle values in all three rubbers; this decrease is more marked by increasing the length of treatment. The effects of the UV treatment are always more noticeable for SBS0 (*i.e.,* improved wettability) and less marked for SBS2 because of the presence of additives that tend to decrease the effectiveness of the UV treatment. Nevertheless, for UV treatment times of more than 5–10 min, the wettability on all rubber surfaces is almost complete,

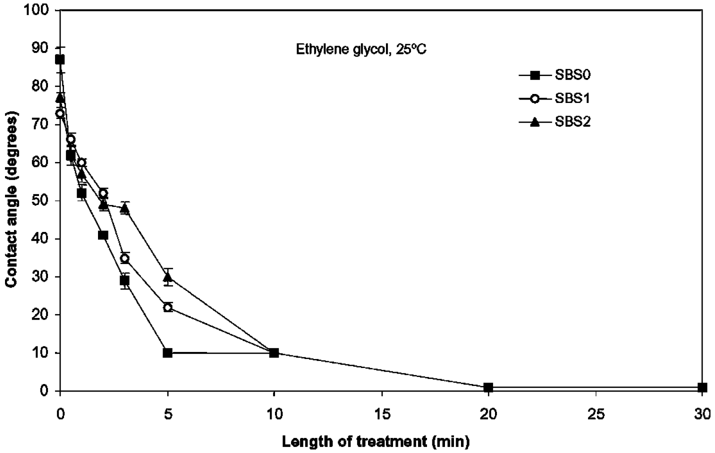
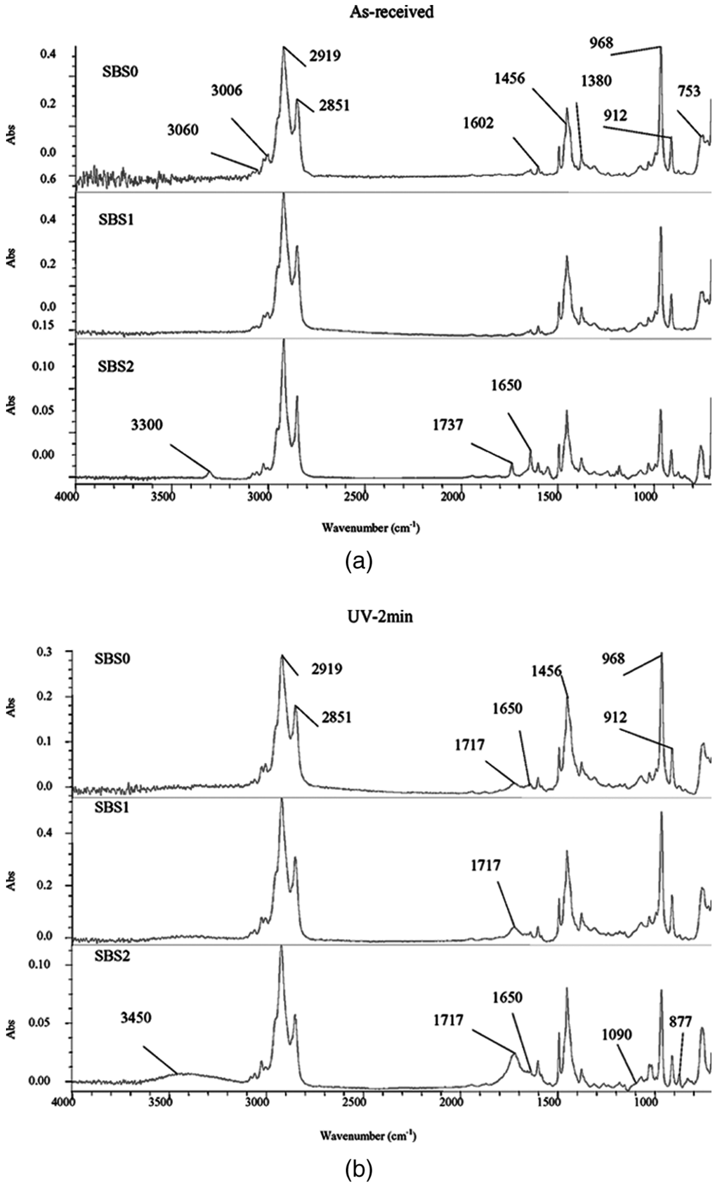


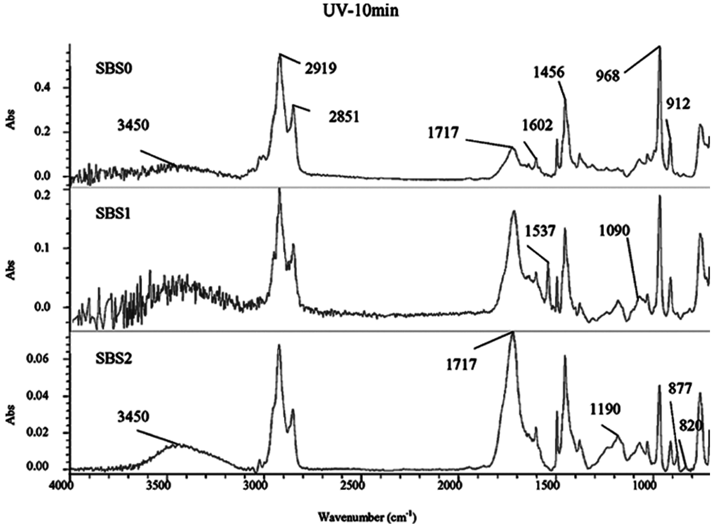
FIGURE 1 Contact angle values (ethylene glycol, 25°C) on the as-received and UV-treated SBS0, SBS1, and SBS2 rubber surfaces for different lengths of treatment.



(a)

(b)

FIGURE 2 ATR-IR spectra of the SBS0, SBS1, and SBS2 rubbers: a) as-received; b) treated with UV radiation for 2 min; c) treated with UV radiation for 10 min.



(c)

FIGURE 2 Continued.

independent of their composition, because the contact-angle values obtained are lower than 5°.

The ATR-IR spectra of the as-received rubbers are given in Figure 2a. The ATR-IR spectrum of the SBS0 rubber (Figure 2a) shows bands due to butadiene and styrene. Bands at 2919 and 2851 cm^{-1} correspond to C–H stretching (CH_2 groups) from butadiene and other butadiene absorption bands are CH_2 in-plane deformation (1456 cm^{-1}), $-CH_2$ wagging motion (1380 cm^{-1}), C–H out-of-plane bending in *trans*-1,4-C=C (968 and 912 cm^{-1}), and a small band at 3006 cm^{-1} (=CH stretching). Styrene absorption occurs at 753 (C–H out-of-plane deformation) and 1602 cm^{-1} (aromatic C–C stretching). The band at 3060 cm^{-1} is due to aromatic C–H stretching. The ATR-IR spectrum of the as-received SBS1 rubber (Figure 2a) shows the same bands as in the as-received SBS0 rubber, except for the higher intensity of the C–H bands in CH_2 groups (2919 and 2851 cm^{-1}) due to the paraffinic/naphthenic oils in the formulation. The ATR-IR spectrum of the as-received SBS2 (Figure 2a) shows bands similar to those of SBS0 and also additional bands at 3300 cm^{-1} due to N–H deformation in $-NH_2$ (due to the lubricant in the rubber formulation) and at 1737 and 1650 cm^{-1} due to C=O stretching and C=C in O–C=C groups, respectively (due to the lubricant and/or to surface aging in air). The intensity of the C–H bands at 2919 and 2851 cm^{-1} is even higher than for the SBS1 rubber because of its higher content of hydrocarbon moieties. It should be indicated that the C–O stretching ($1450\,\mathrm{cm}^{-1}$) and bending ($877\,\mathrm{cm}^{-1}$) bands due to calcium carbonate filler cannot be distinguished in the ATR-IR spectrum of SBS2 rubber, indicating that the filler particles are covered by hydrocarbon moieties that migrate to the surface, in agreement with the high-contact angle value measured on the as-received SBS2 rubber (Figure 1).

Figure 2b shows the ATR-IR spectra of the SBS0, SBS1, and SBS2 rubbers treated with UV radiation for 2 min, the time at which a noticeable decrease in contact-angle values is produced in all rubbers (Figure 1). As a consequence of the UV treatment, new bands at $1717\,\mathrm{cm}^{-1}$ (C=O stretching), $3450\,\mathrm{cm}^{-1}$ (O–H stretching), and $1090\,\mathrm{cm}^{-1}$ (CCO out-of-phase of an alcohol) are observed in the ATR-IR spectra to a greater extent for SBS2 rubber. Furthermore, the intensity of the C–H bands at 2919 and $2851\,\mathrm{cm}^{-1}$ decreases, and a small band at $877\,\mathrm{cm}^{-1}$ due to calcium carbonate filler appears in the ATR-IR spectrum of SBS2 rubber, indicating the removal of hydrocarbon moieties covering the filler particles and the greater modification produced by UV treatment. Therefore, the treatment with UV radiation for 2 min produces oxidation of the rubbers to a greater extent for SBS2.

Increase in the length of treatment to 10 min enhances the modifications produced by UV treatment; *i.e.*, higher intensity of the bands due to oxidized moieties (3450, 1717, and $1090\,\mathrm{cm}^{-1}$) is produced in all rubbers (Figure 2c). On the other hand, the UV radiation treatment leads to a decrease in the intensity of the bands ascribed to butadiene (2919, 2851, 968, and $912\,\mathrm{cm}^{-1}$). In fact, almost complete wettability is obtained in all rubbers by UV treatment for 10 min (Figure 1). The effects of the UV treatment are more noticeable in SBS2 rubber, and thus, new bands at $820\,\mathrm{cm}^{-1}$ (=CH deformation out of plane in C=C–C=O groups) and $1190\,\mathrm{cm}^{-1}$ (C–O bending) are observed; furthermore, the band at $877\,\mathrm{cm}^{-1}$ due to the calcium carbonate becomes more intense than for UV treatment for 2 min (Figure 2c). The ATR-IR spectrum of the SBS1 rubber treated for 10 min with UV radiation shows a band at $1537\,\mathrm{cm}^{-1}$ due to zinc compounds, (stearate soaps) in the SBS1 rubber formulation. The presence of this zinc compound can be ascribed either to an ablation process (*i.e.,* removal of rubber surface layers) that exposes stearate soaps on the SBS1 surface or to the increase in surface energy of the SBS1 rubber that favors the migration of stearate soaps from the bulk to the surface.

During UV radiation treatment, the temperature on the rubber surfaces measured by a noncontact digital IR thermometer increased to

40–50°C, depending on the length of treatment. Likely, this increase in temperature will favor the migration of low molecular moieties from the bulk to the rubber surface. Furthermore, cross-linking of the rubber surface may occur.

XPS measurements were also carried out to investigate the surface modifications produced on the outermost (about 5 nm) rubber surfaces treated with UV radiation. Tables 2a–c show the atomic percentages of elements on the SBS0, SBS1, and SBS2 rubber surfaces. The as-received rubber surfaces are mainly constituted of carbon corresponding to C–C and C–H species (binding energy = 285.0 eV) (Tables 3a–c, Figures 3a–c), indicating the presence of antiadhesion moieties. Small amounts of oxygen moieties (3.6 to 6.1 atomic%) as C–O (binding energy = 286.4 eV) are also found on the as-received rubber surfaces due to aging under open air. For the as-received SBS2, a small amount of nitrogen (likely from the diesteramide in the formulation) is detected on the surface (Figure 3c). The UV

TABLE 2a Atomic Percentages (XPS) of Elements (at%) on the As-Received and SBS0 Rubber Surface Treated with UV Radiation for Different Lengths of Treatment

Element	Binding energy (eV)	As-received SBS0 (at%)	Length of treatment (min)		
			0.5 (at%)	2 (at%)	30 (at%)
C1s	285.0	94.0	91.7	89.5	75.4
O1s	532.2	6.0	7.9	10.5	23.7
N1s	401.0	—	0.4	—	0.9
O/C		0.06	0.09	0.12	0.31

TABLE 2b Atomic Percentages (XPS) of Elements (at%) on the As-Received and SBS1 Rubber Surface Treated with UV Radiation for Different Lengths of Treatment

Element	Binding energy (eV)	As-received SBS1 (at%)	Length of treatment (min)		
			0.5 (at%)	2 (at%)	30 (at%)
C1s	285.0	94.3	93.8	86.9	74.0
O1s	532.2	5.6	6.0	12.8	24.8
N1s	401.0	—	—	0.3	1.0
Zn2p3/2	1023.0	0.1	0.2	—	1.2
O/C		0.06	0.06	0.15	0.34

TABLE 2c Atomic Percentages (XPS) of Elements (at%) on the As-Received and SBS2 Rubber Surface Treated with UV Radiation for Different Lengths of Treatment

Element	Binding energy (eV)	As-received SBS2 (at%)	Length of treatment (min) 0.5 (at%)	2 (at%)	30 (at%)
C1s	285.0	94.7	94.3	89.1	79.7
O1s	532.2	3.1	4.5	9.2	19.0
N1s	401.0	2.2	1.2	1.7	1.1
S2p3/2	165.0	—	—	—	0.2
O/C		0.03	0.05	0.10	0.24

radiation treatment produces a decrease in the atomic percentage of carbon and an increase in the atomic percentage of oxygen, more marked as the length of treatment increases. Independent of the length of treatment, the oxygen percentage on the treated SBS2

TABLE 3a Percentage of Species (at%) Obtained from the C1s Curve Fitting on the As-Received and SBS0 Rubber Surface Treated with UV Radiation for Different Lengths of Treatment

Species	Binding energy (eV)	As-received SBS0 (at%)	Length of treatment (min) 0.5 (at%)	2 (at%)	30 (at%)
C–H, C–C	285.0	96.4	92.3	87.3	67.3
C–O	286.4	3.6	7.7	11	16.6
C=O	287.9	—	—	0.9	6.9
COO^-	289.3	—	—	0.8	9.2

TABLE 3b Percentage of Species (at%) Obtained from the C1s Curve Fitting on the As-Received and SBS1 Rubber Surface Treated with UV Radiation for Different Lengths of Treatment

Species	Binding energy (eV)	As-received SBS1 (at%)	Length of treatment (min) 0.5 (at%)	2 (at%)	30 (at%)
C–H, C–C	285.0	95.3	89.8	89.2	63.5
C–O	286.4	4.7	10.1	10.7	22.1
C=O	287.9	—	0.1	0.1	5.2
COO^-	289.3	—	—	—	9.2

TABLE 3c Percentage of Species (at%) Obtained from the C1s Curve Fitting on the As-Received and SBS2 Rubber Surface Treated with UV Radiation for Different Lengths of Treatment

Species	Binding energy (eV)	As-received SBS2 (at%)	Length of treatment (min) 0.5 (at%)	2 (at%)	30 (at%)
C−H, C−C	285.0	93.9	92.9	83.9	71.8
C−O	286.4	6.1	7.1	13.5	17.0
C=O	287.9	—	—	2.1	4.6
COO^-	289.3	—	—	0.5	6.6

rubber surface (Table 2c) is lower than for the UV-treated SBS0 and SBS1 rubber surfaces, which is in agreement with the lower wettability found in contact-angle values (Figure 1); however, it is not in agreement with the ATR-IR spectra (Figures 2a–c). Thus, the modifications produced by UV radiation treatment seem to be extended into the SBS2 rubber bulk to a greater extent than for SBS0 and SBS1 rubbers; *i.e.*, the UV treatment is not restricted to the rubber surface.

The greatest modifications are produced when the UV radiation treatment is carried out for 30 min, regardless of the rubber, as evidenced by the incorporation of nitrogen moieties (binding energy = 400 eV) on the surface (Tables 2a–c). The presence of zinc on the 30 min UV-treated SBS1 rubber surface is also observed (Table 2b, Figure 3b), in agreement with ATR-IR spectra. XPS experiments do not show the presence of calcium carbonate on the 30 min UV-treated SBS2 rubber surface (Table 2c, Figure 3c) although it appears in the ATR-IR spectrum (Figure 2c). Because ATR-IR spectroscopy analyses a larger depth (3 μm) than XPS, it seems that the calcium carbonate particles are not exposed to the surface but are covered by a thin layer of rubber.

The oxygen introduced on the rubber surfaces after UV-radiation treatment corresponds to different carbon–oxygen species depending on the length of treatment. The C1s curve fitting results are given in Tables 3a–c and Figures 4a–c. On the UV-treated SBS0, SBS1, and SBS2 rubber surfaces, the percentage of C−O moieties (286.4 eV) increases as the length of treatment increases. Moreover, the formation of more oxidized moieties for UV treatment longer than 2 min is also observed (C=O at 287.9 eV and COO^- at 289.3 eV).

The mechanism of the photo-oxidation reaction of *cis*-1,4-polyisoprene can be used to understand the effects of UV radiation on SBS rubbers [5].

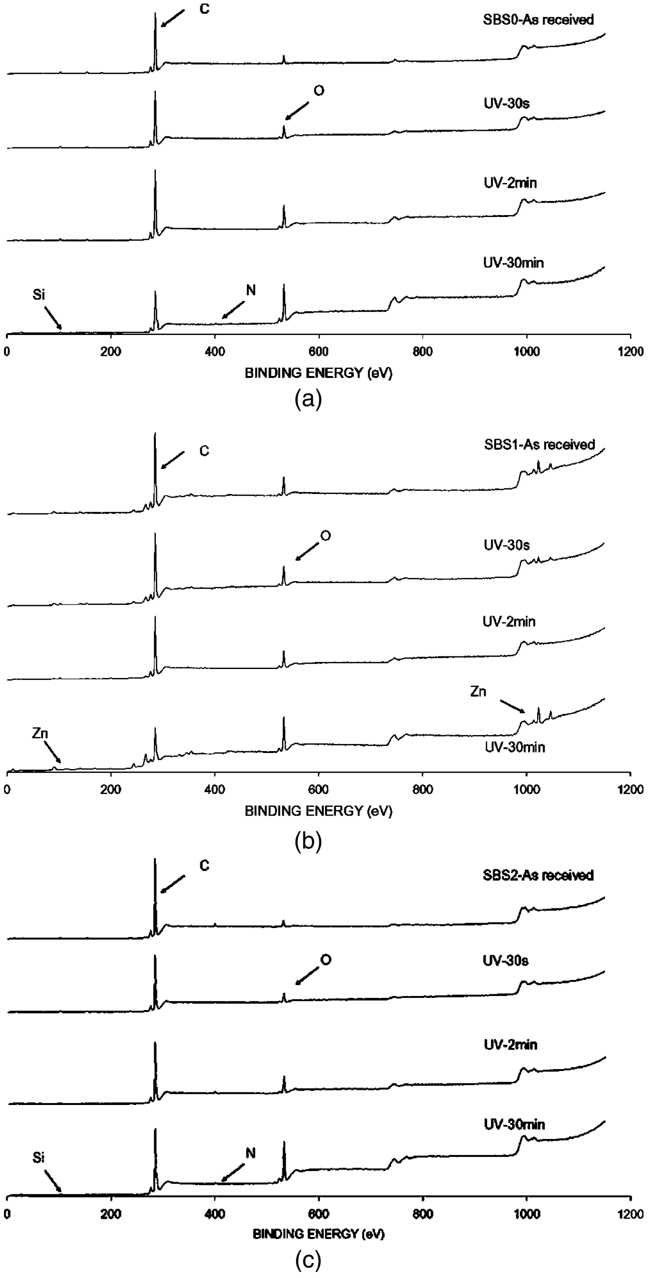


FIGURE 3 XPS survey spectra of as-received and UV-radiation treated rubber for different lengths of treatment: a) SBS0 rubber; b) SBS1 rubber; c) SBS2 rubber.

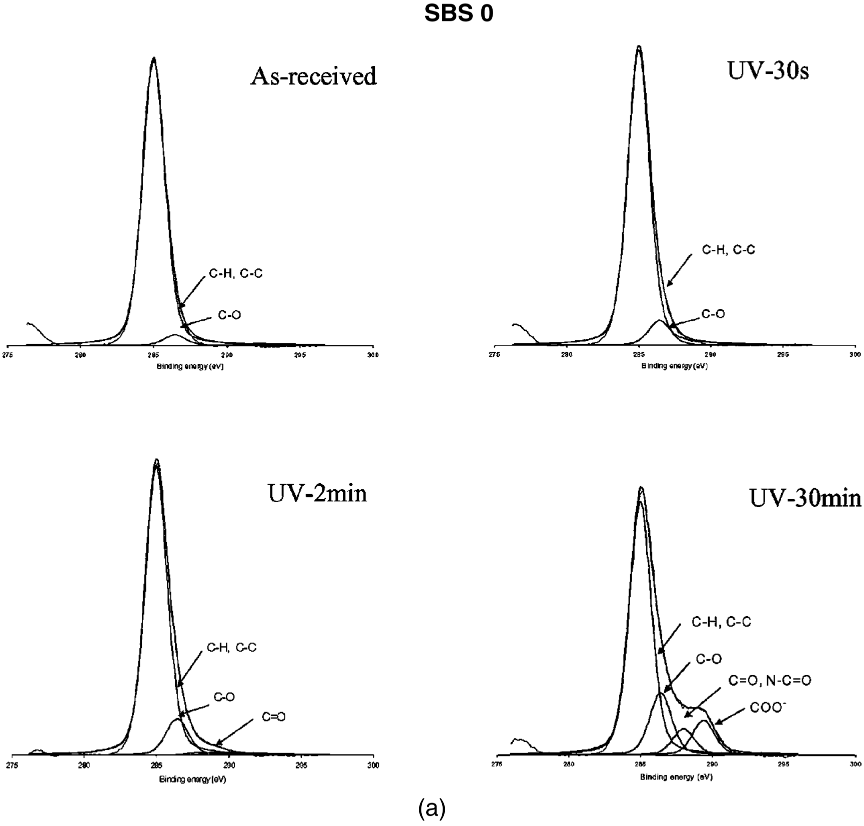
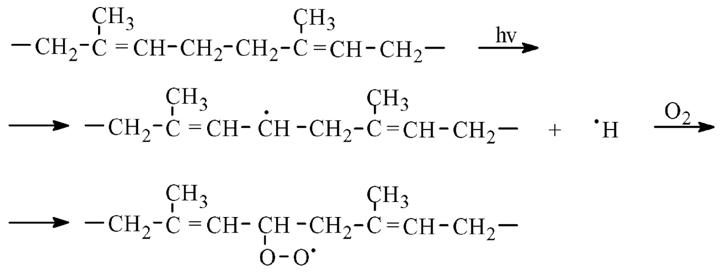


FIGURE 4 Curve fitting of C1s photopeak (XPS) of as-received and UV-radiation treated rubber for different lengths of treatment: a) SBS0 rubber; b) SBS1 rubber; c) SBS2 rubber.



$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \xrightarrow{h\nu}$$

$$\longrightarrow -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\overset{\bullet}{C}H-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \quad + \quad {}^{\bullet}H \xrightarrow{O_2}$$

$$\longrightarrow -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{O-O^{\bullet}}{\underset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$$

The peroxy radicals may react intramolecularly with a C=C double bond to form a cyclic peroxide, which may react with another oxygen

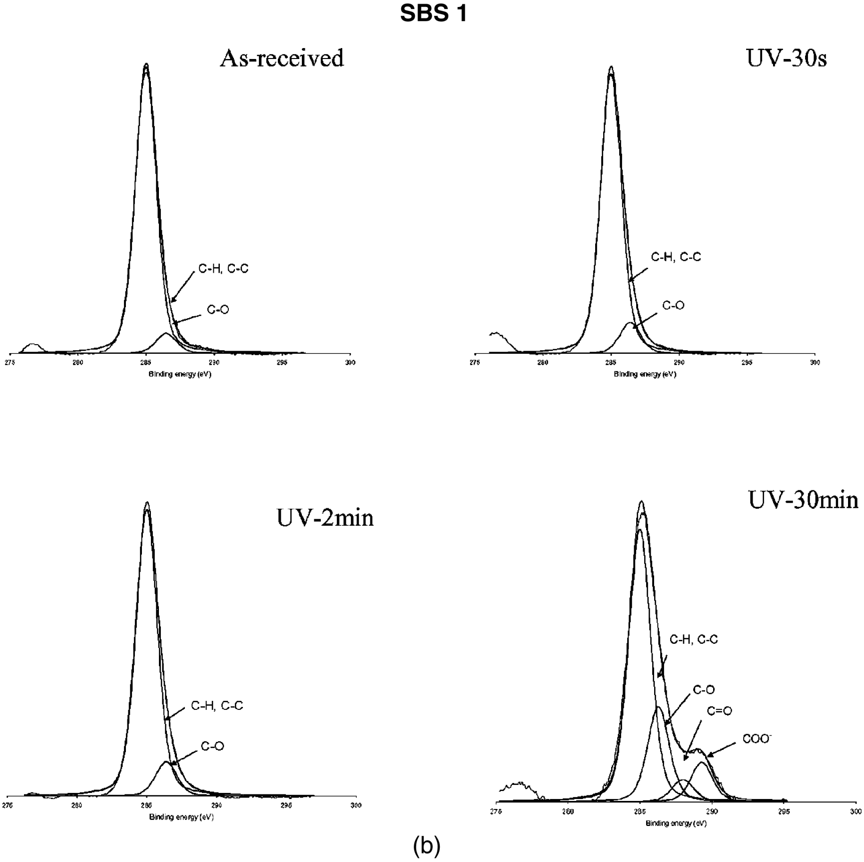
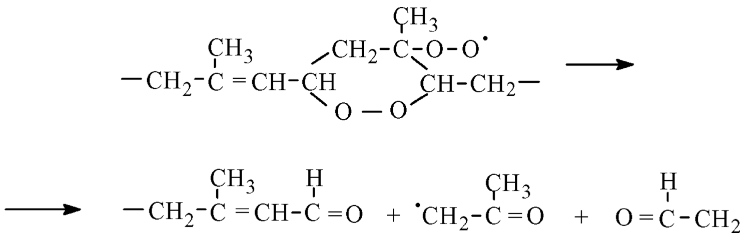


FIGURE 4 Continued.

molecule to form a peroxy radical. This radical is destroyed by UV radiation.



$$\longrightarrow -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\overset{H}{\overset{|}{C}}=O + {}^{\bullet}CH_2-\overset{CH_3}{\overset{|}{C}}=O + O=\overset{H}{\overset{|}{C}}-CH_2$$

The alkyl, alkoxy, and peroxy radicals produced by UV radiation may react with each other to produce cross-linking of the polymer at

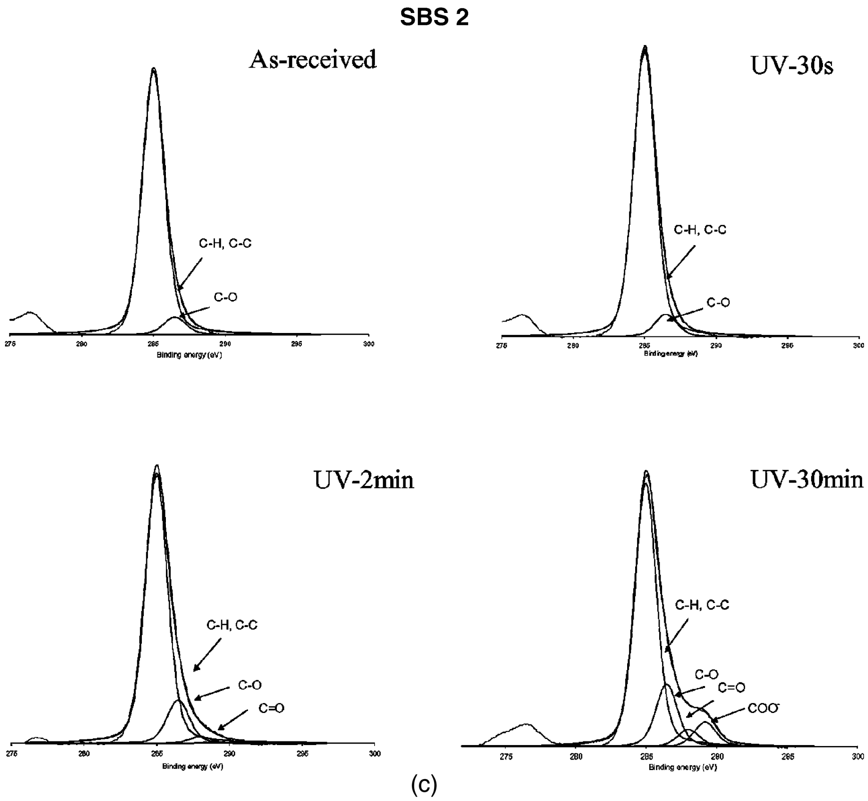
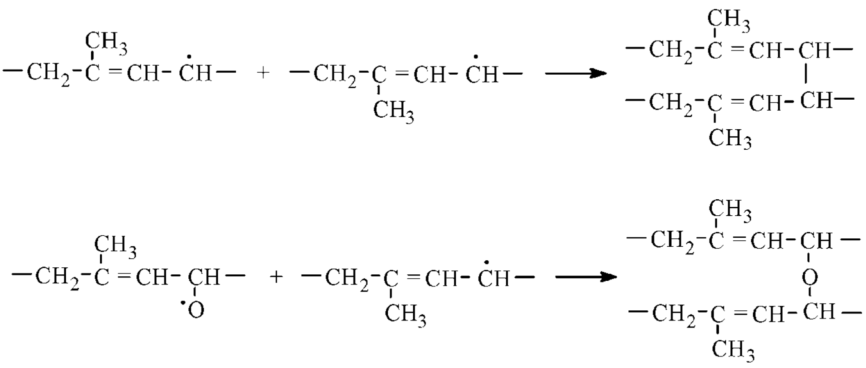


FIGURE 4 Continued.

the surface.

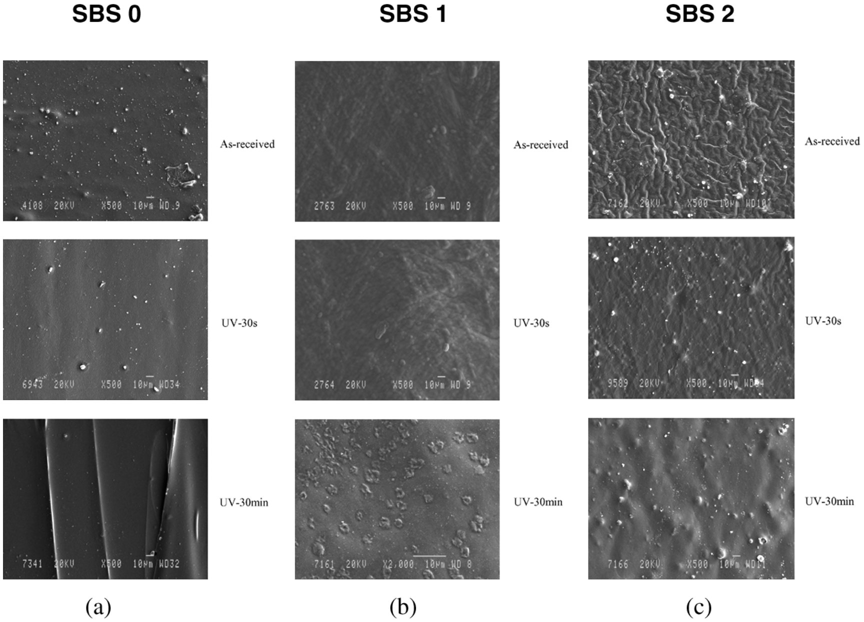


$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H- \; + \; -CH_2-\underset{CH_3}{\underset{|}{C}}=CH-\dot{C}H- \longrightarrow \begin{array}{l} -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH- \\ \qquad\qquad\qquad\quad | \\ -CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH- \end{array}$$

$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\cdot O}{\underset{|}{C}H}- \; + \; -CH_2-\underset{CH_3}{\underset{|}{C}}=CH-\dot{C}H- \longrightarrow \begin{array}{l} -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH- \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad O \\ \qquad\qquad\qquad\quad | \\ -CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH- \end{array}$$

Some differences in chemistry between the UV-treated SBS0 and SBS1 rubbers are observed in Tables 3a and 3b and Figures 4a and 4b. Although the C-O content in the 2-min UV-treated rubbers is similar (11 atomic% for SBS0 and 10.7 atomic% for SBS1), C=O and COO^- groups (0.9 and 0.8 atomic%, respectively) only appear on the treated SBS0 rubber surface. Thus, more extended oxidation on the SBS0 rubber surface is produced for lower treatment time than for SBS1 rubber. In fact, in a recent study dealing with the corona discharge treatment of two polyolefins with and without oil additives in their formulations [20], it has been shown that for lower corona discharge energies, the oxidation degree is higher for the polyolefin without oil additives.

The SEM micrographs of the as-received SBS0 and SBS1 rubbers (Figures 4a and 4b) shows a relatively flat surface, whereas a cord-like structure is found in the as-received SBS2 rubber (Figure 5c). For the as-received SBS0 and SBS2 rubbers, some small, round, white particles that correspond to silicon appear on the surface (evidenced by EDX–X-Ray Dispersive Energy, Model Link QX-20, Röntec, GmbH,



(a) (b) (c)

FIGURE 5 SEM micrographs of the as-received and UV-radiation treated rubber for different lengths of treatment: a) SBS0 rubber; b) SBS1 rubber; c) SBS2 rubber.

Berlin, Germany). These particles could be contaminants from the anticaking agent (talc) in the Kraton D-4270CS rubber, and by extending the length of the UV treatment, they are gradually covered by a thin layer of hydrocarbon moieties that migrates from the bulk to the rubber surface. The morphological modifications produced by UV treatment are different in the three rubbers.

- UV-treated SBS0 rubber (Figure 5a). The UV-radiation treatment produces the covering of silica particles by a thin hydrocarbon layer that migrates from the bulk to the rubber surface. Furthermore, a gradual elimination of external rubber layers (ablation process), creating extended thin cracks all along the surface, occurs.
- UV-treated SBS1 rubber (Figure 5b). The UV-radiation treatment produces some surface ablation, less marked than for SBS0 rubber, and a gradual migration of compounds—more evidenced in the 30 min UV-treated rubber—allowing the blooming of oils and/or lubricants (stearate soaps) and creating round blossom heterogeneities on the treated surface. Because of the migration of additives, the extent of ablation is less important and the degree of oxidation is lower in SBS1 rubber than in SBS0.
- UV treated SBS2 rubber (Figure 5c). The UV-radiation treatment destroys the cord-like structure and produces the covering of silica particles on the SBS2 rubber surface by a thin layer of hydrocarbon moieties that migrates from the bulk to the rubber surface. Furthermore, small white, calcium carbonate particles that seem to be covered by a thin rubber layer appear on the surface.

The adhesive strength of the UV-treated rubbers was obtained from T-peel tests (Figure 6). The nonpolar nature and the presence of antiadhesion moieties on the as-received rubber surfaces are clearly evidenced by the low adhesive strength obtained (about 0.5 kN/m) in all of the as-received SBS rubber/polyurethane adhesive/leather joints. A marked increased in adhesive strength is obtained by treatment with UV radiation, due to improved wettability, creation of polar moieties, and ablation. In general, the adhesive strength for the joints produced with the UV-treated rubbers follows the order SBS2 > SBS0 > SBS1, although the trend varies depending on the length of the treatment. The lower adhesive strength in the joints produced with the UV-treated SBS1 rubber (Figure 6) can be due to the presence of low-molecular-weight oils and lubricants, which migrate to the rubber surface, creating a weak boundary layer. It is not likely that the solvent mixture (80 parts ketone + 20 parts toluene) in the polyurethane adhesive favors the migration of low-molecular-weight

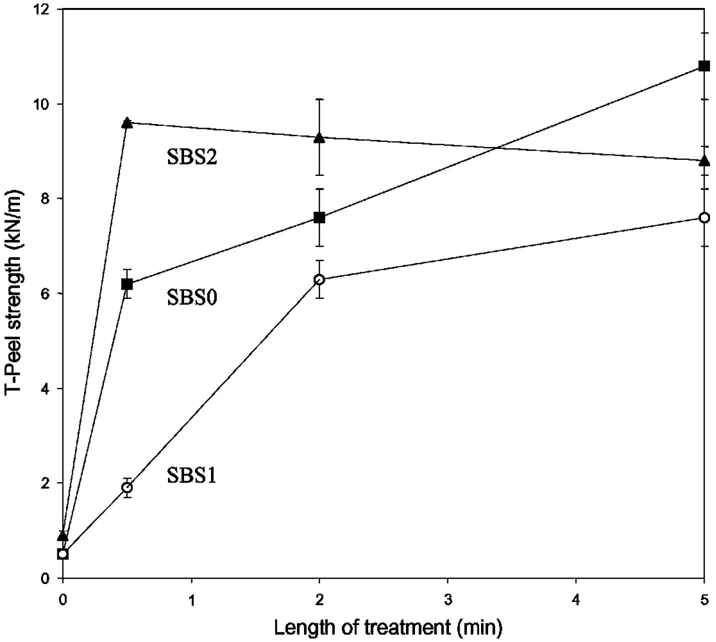


FIGURE 6 T-peel strength values of as-received and UV-treated SBS0, SBS1, and SBS2 rubber/polyurethane adhesive/leather joints.

moieties to the rubber–polyurethane interface, because these organic additives are not soluble in that mixture. On the other hand, the increase in adhesive strength as a function of the length of UV treatment is more marked in the joints produced with SBS0 rubber and irrelevant to the length of treatment; relatively similar adhesive strengths are obtained in the joints produced with the UV-treated SBS2 rubber. The greatest differences in adhesive strength between the joints produced with the UV-treated SBS0, SBS1, and SBS2 rubbers correspond to the treatment of 30 s.

The trends in adhesive strength of the different UV-treated rubbers cannot be fully explained from the variations in contact-angle values and the modifications in surface chemistry observed by ATR-IR and XPS spectroscopy. For the joints produced with the UV-treated SBS1 rubber, the lower adhesive strength obtained could be ascribed to the creation of weak boundary layers, whereas the greater values of the UV-treated SBS2 rubber joints with respect to the UV-treated SBS0 rubber joints can be ascribed to its lower tensile strength (4.7 MPa for SBS2 rubber *vs.* 12 MPa for SBS0 rubber), which allows less energy dissipation during peel tests.

To provide further evidence to justify the trends in adhesive strength of the different joints, their loci of failure were assessed by analyzing the ATR-IR spectra of the failed surfaces after the peel test. In this study, the failed surface that visually corresponds to the adhesive surface has been named the A surface, and the one that visually corresponds to the rubber has been called R surface. Figure 7 shows the ATR-IR spectrum of the polyurethane (PU) adhesive before joint formation, in which typical absorption bands different from those of the rubbers (Figures 2a to 2c) can be distinguished: N–H stretching absorption at 3350 cm^{-1}, C–H stretching bands of CH_2 and CH_3 groups in the polyurethane (2860, 2939 cm^{-1}), C=O stretching in the urethane at 1730 cm^{-1}, N–C=O symmetric stretching absorption at 1531 cm^{-1}, and C–O stretching band at 1177 cm^{-1}. On the other hand, the ATR-IR spectrum (not shown) of the leather used to make the joints shows bands due to N–H stretching (3310 cm^{-1}), C–H stretching in CH_2 and CH_3 (2930, 2853 cm^{-1}), C=O stretching (1650 cm^{-1}), N–H in-plane bending and C–N stretching (1545 cm^{-1}), C–N stretching (1242 cm^{-1}) and C–O stretching (1030 cm^{-1}).

Figure 8 shows the ATR-IR spectra of the failed surfaces obtained after peel testing of the as-received SBS0 rubber/polyurethane

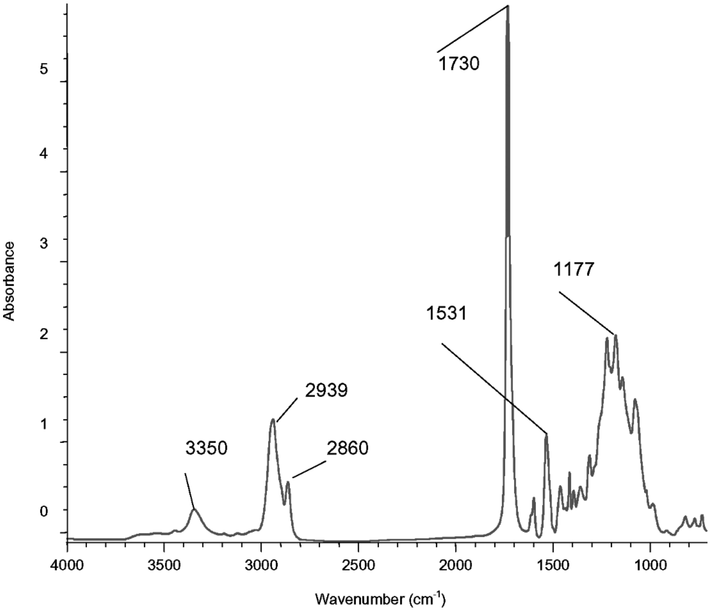


FIGURE 7 ATR-IR spectrum of the polyurethane adhesive.

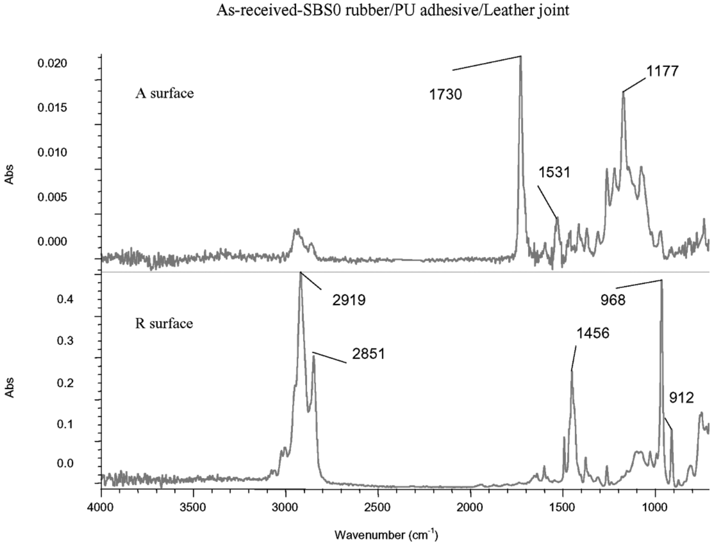


FIGURE 8 ATR-IR spectra of the failed surfaces obtained after peel test of the as-received SBS0 rubber/polyurethane adhesive/leather joint. A surface: failed surface that visually corresponds to the adhesive; R surface: failed surface that visually corresponds to the rubber.

adhesive/leather joint. The ATR-IR spectrum of the R surface is similar to that of the as-received SBS0 rubber, and the ATR-IR spectrum of the A surface shows typical polyurethane adhesive absorptions (1730, 1531, and 1177 cm^{-1}) indicating that an interfacial failure is produced. For the joints produced with the SBS0 rubber treated with UV radiation for 30 s or 2 min, a similar interfacial failure is produced between the SBS0 rubber and the PU adhesive, but the adhesive strength is 15 times as high (0.5 and 7.6 kN/m) for the joints prepared with the as-received and 2 min UV-treated SBS0 rubber, respectively, which is likely due to the increase in wettability and creation of polar moieties produced by UV treatment. In fact, for the joint produced with the 5 min UV-treated SBS0 rubber, a cohesive failure in the rubber is obtained during peel test.

Figure 9a shows the ATR-IR spectra of the failed A and R surfaces of the as-received SBS1 rubber/polyurethane adhesive/leather joint. For the joint produced with the as-received SBS0 rubber, an interfacial failure between the polyurethane adhesive and the rubber is obtained. However, similar ATR-IR spectra for the A and R failed surfaces are obtained (Figure 9b) in the joint produced with the

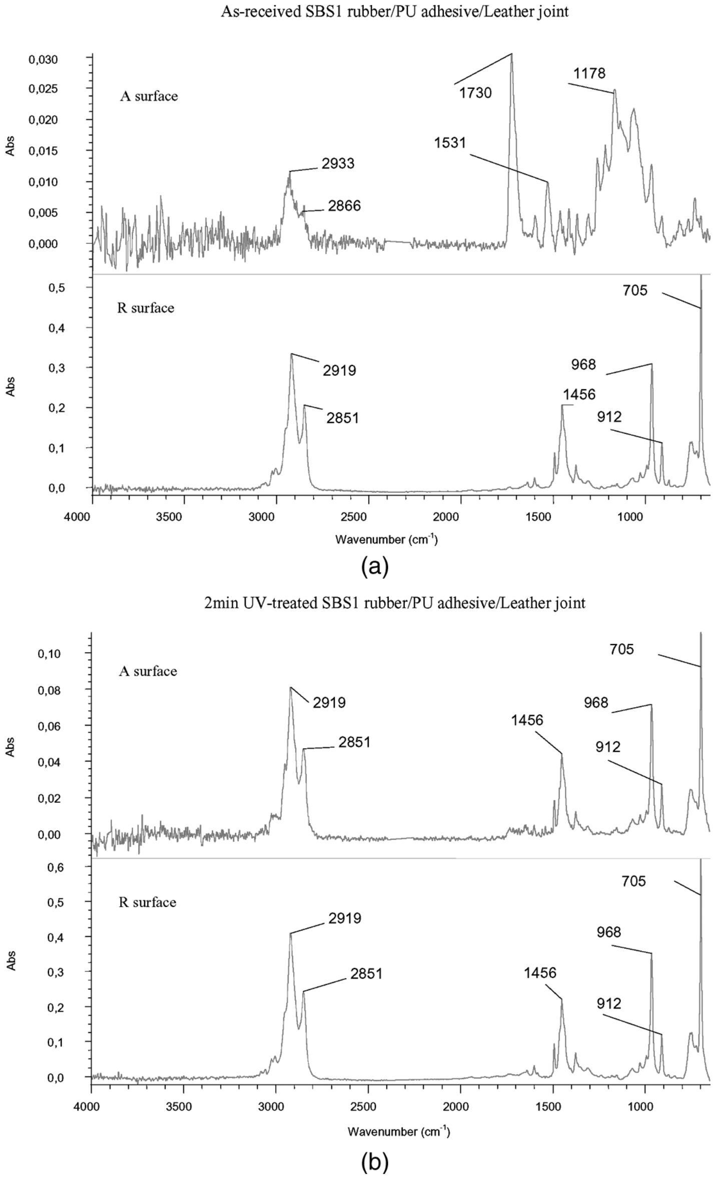


FIGURE 9 ATR-IR spectra of the failed surfaces obtained after peel test: a) As-received SBS1 rubber/polyurethane adhesive/leather joint; b) 2 min UV-treated SBS1 rubber/polyurethane adhesive/leather joint.

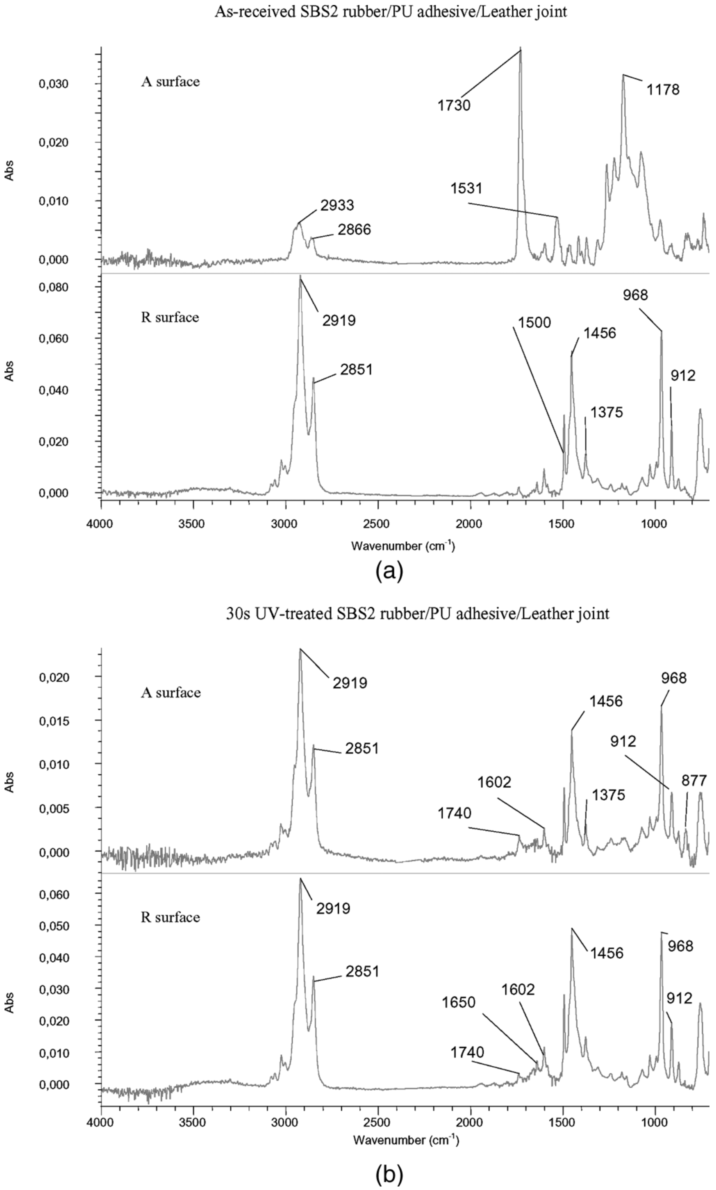


FIGURE 10 ATR-IR spectra of the failed surfaces obtained after peel test: a) As-received SBS2 rubber/polyurethane adhesive/leather joint; b) 30 s UV-treated SBS2 rubber/polyurethane adhesive/leather joint.

2 min UV-treated SBS1 rubber, and both show the absorption bands of the as-received rubber (2919, 2851, 1456, 968, 912, and 705 cm^{-1}). Because the oxidation bands on the UV-treated SBS1 rubber are not observed, we conclude that a cohesive failure in the rubber is produced. For the joint made with the 5 min UV-treated SBS1 rubber, a cohesive failure in the rubber is also obtained during peel testing.

An interfacial locus of failure between the polyurethane adhesive and the SBS2 rubber in the as-received SBS2 rubber/polyurethane adhesive/leather joint is produced (Figure 10a). The ATR-IR spectra of the failed surfaces corresponding to the 30 s UV-treated SBS2 rubber/polyurethane adhesive/leather joint (Figure 10b) are very similar and correspond to the ATR-IR spectrum of the as-received SBS2 rubber (2919, 2851, 1456, 968, 912 cm^{-1}). However, the ATR-IR spectrum of the A failed surface shows the band at 877 cm^{-1} due to calcium carbonate and bands at 1740 and 1602 cm^{-1} corresponding to surface oxidation. Therefore, although a cohesive failure in the rubber is produced, it is located close to the oxidized rubber layer. For the joints produced with the 30 s UV-treated SBS0 or SBS1 rubbers, an interfacial failure between the rubber and the adhesive is obtained, indicating that the UV treatment of SBS2 rubber is more efficient for a short length of treatment. The loci of failure of the joints produced with the 2 and 5 min treated SBS2 rubber were fully cohesive in the rubber.

4. CONCLUSIONS

The UV radiation treatment on the SBS0, SBS1, and SBS2 rubber surfaces produced an increase in wettability, creation of carbon–oxygen polar moieties, and ablation. The extent of the surface modifications and the adhesion properties were negatively affected by the presence of oils and lubricant additives in the formulation of SBS rubbers, mainly when an extended UV-radiation treatment was carried out. The migration of additives competed with the oxidation produced by the UV-radiation treatment. For short treatment times, the UV-treated SBS2 rubber showed better adhesion as compared with that for the joints produced with UV-treated SBS0 and SBS1 rubbers.

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