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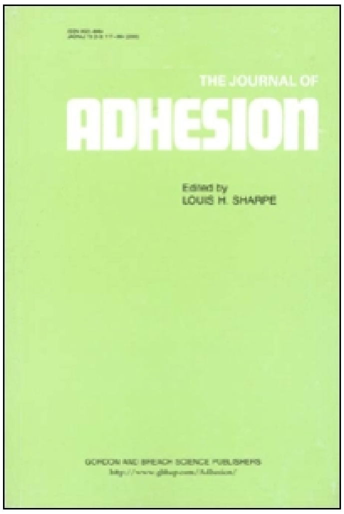

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SURFACE MODIFICATIONS AND ADHESION OF VULCANIZED SBR RUBBER TREATED WITH RF PLASMAS OF DIFFERENT GASES

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SURFACE MODIFICATIONS AND ADHESION OF VULCANIZED SBR RUBBER TREATED WITH RF PLASMAS OF DIFFERENT GASES

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The surface modifications produced by treatment of a synthetic vulcanized styrene-butadiene rubber (R1) with oxidizing (oxygen, air, carbon dioxide) and nonoxidizing (nitrogen, argon) RF plasmas have been assessed by ATR-IR and XPS spectroscopy, SEM, and contact angle measurements. The effectiveness of the treatment depended on the gas atmosphere used to generate the RF plasma. In general, acceptable adhesion values of treated R1 rubber were obtained for all plasmas, except for the nitrogen plasma treatment during 15 min, due to the creation of weak layers of low molecular weight moieties on the outermost R1 rubber layer. A toluene wiping of the 15 min N_2-plasma–treated R1 rubber surface removed those moieties, and increased adhesion was obtained. On the other hand, the air, carbon dioxide, and oxygen plasmas produced ablation of the R1 rubber surface, whereas mechanical degradation was not produced by treatment with the Ar plasma.

Keywords: Low-pressure gas RF plasma; Vulcanized styrene-butadiene rubber; Surface treatment; Contact angle; ATR-IR spectroscopy; SEM; XPS; T-peel strength

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INTRODUCTION

Synthetic rubbers require a surface treatment to achieve a satisfactory level of adhesion. If a surface treatment is not carried out, poor adhesion is usually produced due to the lack of chemical interaction between the nonpolar rubber surface and the polar adhesive. Besides, migration of low molecular weight moieties in the formulation (antioxidants, mold-release agents) from the bulk to the rubber surface produces a weak boundary layer that prevents interaction between the rubber surface and the adhesive. Traditionally, chemical surface treatments (mainly halogenation) were used in the footwear industry to improve the adhesion of rubber to polyurethane (PU) adhesives [1–4]. The improvement in adhesion of rubber by halogenation treatment is due to the removal of antiadherent moieties from the surface, the creation of surface heterogeneities, and the formation of C-Cl and C-O polar moieties [4]. However, halogenation involves the use of organic solvents, the chlorinating solutions have a limited stability, and evolution of chlorine is a potential threat. Considering environmental and health issues, enforced reduction of volatile organic compounds (VOCs) due to legislation is envisaged, and an environmentally friendly alternative to the traditional solvent-based halogenation surface treatment of rubber should be developed.

Low-pressure plasmas were developed in the 1960s by the microelectronic industry for the deposition of thin films [5], but some studies have shown the effectiveness of radio frequency (RF) plasma treatment to enhance the adhesion of different rubbers [6–8]. The plasma is generated by applying a high-energy dose (in the range of RF in this study), enough to ionize the gas molecules. This yields a mixture of electrons, charged particles, free radicals, atoms, and molecules in excited states and UV radiation, as a result of the inelastic collisions between the particles [9]. The energetic environment of the plasma creates surface free radicals as well as cleaning, ablation, crosslinking, and chemical modifications on the rubber surface. However, these effects are greatly affected by the gas used to generate the plasma [10, 11]. The application of inorganic and organic plasmas to modify polymer surfaces have been described, and oxidizing (O_2, CO_2, air) or nonoxidizing (He, Ar, N_2) inorganic plasmas have been effective [9]. Typically, the plasmas created with an inert gas produce scission and crosslinking of polymeric chains and rearrangement of radical species on the material surface [12], whereas the oxidizing gas plasmas create chemical species and roughness, and considerable oxidation and degradation of the material surface is also obtained. Some studies dealing with surface modifications produced by both

TABLE 1 Wavelength (nm) and Energy (kcal/mol) of Photons Emitted by Different Plasmas

Plasma	Ar	N_2	O_2	CO_2
λ (nm)	334–529	337	210–400	10600
E (kcal/mol)	85–54	85	135–71	2.7

Data taken from NIST Atomic Spectra Database [20].

oxidizing and nonoxidizing plasmas on polypropylene [13–15], polymethylmethacrylate and polyethyleneterephtalate [16], and polycarbonate [10, 17–19] have been reported.

In this study, a synthetic vulcanized styrene–butadiene rubber was treated with different RF oxidizing and nonoxidizing plasmas. The plasmas were produced in argon, nitrogen, air, oxygen, and carbon dioxide atmosphere. The energy of the radiation emitted from Ar, nitrogen, air, and O_2 plasmas is in the UV region (Table 1), whereas CO_2 plasma emits in the IR region [20]. The surface modifications and adhesion properties of the treated rubber surfaces were studied.

EXPERIMENTAL

Materials

A sulfur-vulcanized synthetic styrene–butadiene rubber (R1) (Caster, Elda(Alicante), Spain) was used in this study. The formulation of the rubber is given in Table 2. This rubber contains carbon black and silica

TABLE 2 Formulation of the R1 Synthetic Vulcanized Styrene–Butadiene Rubber

Component	Percentage (phr)
SBR1502	65
SBR 1904	35
Carbon black N-330	23
Precipitated silica	25
Hydrocarbon resin	3.5
Sulfur	1.8
N-cyclohexyl-2-benzothiazole-sulphenamide	1.1
Tetramethylthiuram disulfide	0.2
Stearic acid	0.8
Zinc oxide	3.8
Phenolic antioxidant	0.8
Poly(ethylene glycol) (M_W = 4000)	1.1

as fillers, as well as zinc oxide and stearic acid; these compounds react during vulcanization to produce zinc stearate, a compound that generally provides antiadherent properties [21]. Some properties of the R1 rubber were obtained using standardized procedures: Hardness = 93° Shore A; density (20°C) = $1.2\,\mathrm{g\,cm^{-3}}$; tensile strength = 18.0 MPa; maximum elongation-at-break = 397%; tear resistance = $19.9\,\mathrm{kN\,m^{-1}}$.

The R1 rubber was treated with low-pressure RF plasmas for 1–15 min in a Pyrex glass barrel-type March Plasmod Instruments reactor (19 cm long and 14 cm diameter) (March Instruments Concord, CA, USA) at 13.56 MHz. The samples were placed on a floating aluminum plate inside the reactor. The plasma reactor has upper and lower external electrodes and is sealed with a flat silicone gasket, which sits against a raised lip placed on the inner chamber. The gas delivery tube feeds through the back of the plasma reactor. The bottom of the plasma reactor is connected to the vacuum hose by a glass tube. The reaction chamber was evacuated to mild vacuum (<0.2 Torr) by means of a rotary vacuum pump. Then, the gas used to generate the plasma was introduced over the specimen to be treated in the plasma reactor, increasing the pressure to 1 Torr. A March GCM-200 Gas Control unit provided with a flow meter and a pressure gauge was used to control the gas flow into the plasma reactor. Argon, nitrogen, air, oxygen and carbon dioxide (99.999% minimum purity) used to generate the plasmas were supplied by Abelló Linde S.A. (Valencia, Spain). Care was taken to pump down and purge the plasma reactor for at least 10 min prior to activating the RF field. The discharge power was set at 50 W. Before plasma treatment, the rubber samples were wiped with 2-butanone and the solvent was allowed to evaporate for 30 min. All bonding operations were performed within 1–2 min after plasma treatment to minimize surface molecular rearrangement and contamination from the atmosphere.

To determine the T-peel strength, thermoplastic polyester–urethane pellets (Desmocoll 540) manufactured by Bayer AG (Leverkusen, Germany) was used. This polyester–urethane has a high crystallization rate and a short open time. The adhesive was prepared by dissolving 17 wt% polyurethane pellets in 2-butanone in a laboratory mixer (850 rpm for 3 h). The adhesive solution obtained had a Brookfield viscosity of 4040 mP.s (23°C). To produce adequate adhesion, 5 wt% thionophosphoric acid-tris-(p-isocyanatephenil ester) (Desmodur RFE, provided by Bayer AG, Leverkusen, Germany) was added to the polyurethane adhesive solution just before the adhesive joint was produced.

Adhesive joints were made using two rubber strip test pieces (150 mm × 30 mm) that had been similarly treated. The polyurethane adhesive + 5 wt% isocyanate was applied 2 min after mixing using a brush (150 mg of adhesive was applied on each rubber strip). After allowing the solvent to evaporate for 2 h, the dried adhesive film was melted at 100°C under IR radiation. The coated rubber specimens were placed into contact immediately under a pressure of 0.8 MPa. The thickness of the adhesive layer was about 0.5 mm. The adhesive joints were maintained at 23°C and 50% relative humidity before undergoing the T-peel test. Adhesion was measured 45 min (immediate adhesion) and 24–72 h (final adhesion) after joint formation.

Experimental Techniques

Contact Angle Measurements

The surface-treated rubber pieces were introduced into the thermostatted chamber of a Ramé Hart 100 goniometer (Ramé Hart, Mountain Lakes, NJ, USA). The chamber was previously saturated with the vapor of the test liquid at 25°C for at least 10 min before placing a liquid drop on the surface of the treated rubber. The contact angle values on the surface-treated rubber were measured immediately after placing 4 μl drops of doubly distilled deionized water. The experimental error was ±2 degrees.

Fourier Transformed Infrared Spectroscopy (FTIR)

The ATR-IR spectra of plasma-treated R1 rubber were obtained using a Nicolet FTIR 205 spectrophotometer (Thermo Nicolet, Madison, WI, USA). To avoid deep penetration of the IR radiation into the sample, the attenuated total multiple reflection method was employed (ATR-IR), a germanium crystal was used; the incident angle was 45°. Two-hundred scans were obtained and averaged at a resolution of $4\,\mathrm{cm}^{-1}$. The chemical modifications produced in about 2 μm R1 rubber surface depth were obtained using this technique.

X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was used to determine the modifications produced on the outermost (50–100 Å) R1 rubber surface. The plasma-treated R1 rubber was analyzed using a *V.G. Scientific Microtech Multilab* spectrometer with a Mg K_α achromatic X-ray source (1253.6 eV) operating at 15 keV and 300 W (Thermo Electron Corp., Madrid, Spain). The pressure inside the analysis chamber was held below 5×10^{-8} Torr (6.6×10^{-6} Pa) during the course of the analysis. Square sample pieces (5 mm × 5 mm) were used, although the dimensions of the analyzed areas on the samples were 5 mm × 2 mm. The measurements were taken using a takeoff angle of 45°. Survey scans were taken in the range 0–1100 eV, and high-resolution scans were obtained for all significant peaks in the survey spectra. Binding energies of all photopeaks were referenced to the C 1 s photopeak position for C-C and C-H species at 285.0 eV, and were curve fitted using Gaussian peak shape function with a full-width-at-half maximum (FWHM) of $1.8 + 0.1$ eV.

Scanning Electron Microscopy

A JEOL JSM-840 (JEOL, Peabody, MA, USA) scanning electron microscope (SEM) was used to obtain the micrographs of the as-received and plasma-treated R1 rubber samples. The samples were secured onto copper mounts using silver paint and coated with gold in a Polaron sputter coater (Quorum Technologies Ltd., Hailsham, E. Sussex, UK) to obtain enough contrast in the SEM micrographs.

T-Peel Strength Measurements

The adhesion of the adhesive joints was determined using a T-peel test in an Instron 4411 instrument (peel rate = 0.1 m/min) (Instron, Cerdañola (Barcelona), Spain). Four experimental determinations for each experimental variable were obtained. The standard deviation was less than 0.7 kN/m.

In order to determine precisely the locus of failure in the joints, the failed surfaces obtained after T-peel tests were analyzed using ATR-IR spectroscopy and SEM.

RESULTS AND DISCUSSION

As-received R1 rubber shows (Figure 1) a high contact angle value, indicating a poor wettability, which can be partially due to the presence of zinc stearate (IR absorption bands of C=O stretching at 1540 cm^{-1}, and C–H stretching at 2850 and 2920 cm^{-1}) (Figure 2) on its surface. The ATR-IR spectrum of the as-received rubber also shows the bands due to silica (broad band at 1080 cm^{-1}), butadiene (968 cm^{-1}), and styrene (696, 760, 915, and 3040 cm^{-1}). Treatment of R1 rubber with oxidizing and nonoxidizing RF plasmas for 1 min produces a noticeable decrease in contact angle values (Figure 1), and the increase in the length of plasma treatment slightly increases the wettability. this increase is quite noticeable for Ar plasma treatment.

The improved wettability of plasma-treated R1 rubber is due to the creation of chemical moieties. Thus, ATR-IR spectroscopy (Figure 2)

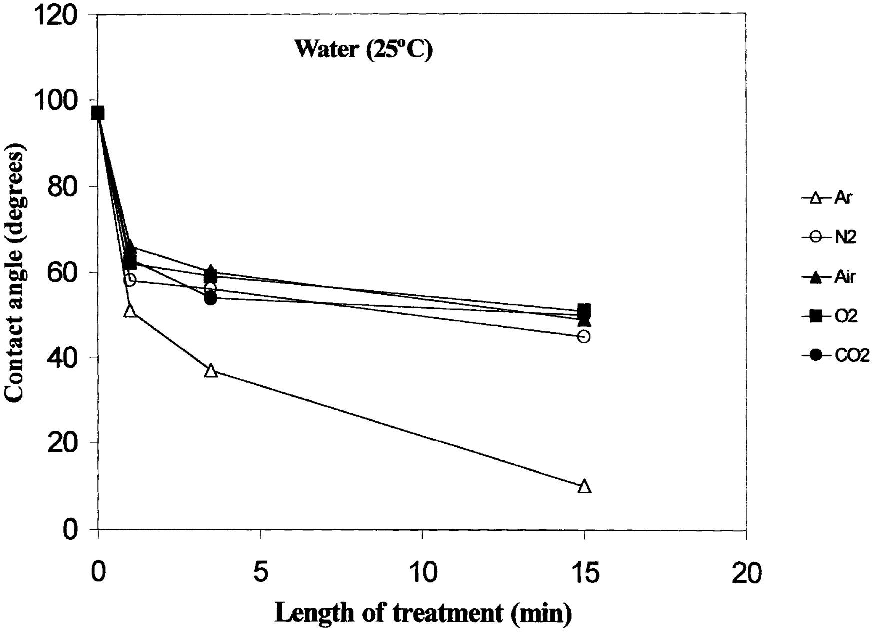


FIGURE 1 Contact angle values (water, 25°C) on as-received and RF plasma-treated R1 rubber.

shows as a typical example that treatment with nonoxidizing Ar and N_2 plasmas for 3.5 min produces removal of zinc stearate (a low molecular weight species of the rubber formulation, which migrated from the bulk to the outermost surface of the as-received rubber). Thus, there is a noticeable decrease in the relative intensity of the bands at 1540, 2850, and 2920 cm^{-1}. In addition to zinc stearate removal, oxidation of the R1 rubber surface is produced, as indicated by the creation of the $C{=}O$ stretching absorption band at 1600–1700 cm^{-1}. According to the ATR-IR spectra, the treatment with oxidizing plasmas (O_2, air, and CO_2) produces a more effective removal of zinc stearate from the rubber surface, but a less important degree of oxidation is produced compared with the treatment with nonoxidizing plasmas (Ar and N_2).

To restrict the depth of analysis to approximately the outermost 5 nm of the R1 rubber surface, XPS was used. From XPS measurements, Ar and N_2 plasma treatments produce noticeable surface oxidation (noticeable increase in oxygen and a significant decrease in carbon, *i.e.*, an important increase of O/C ratio; Table 3a), which

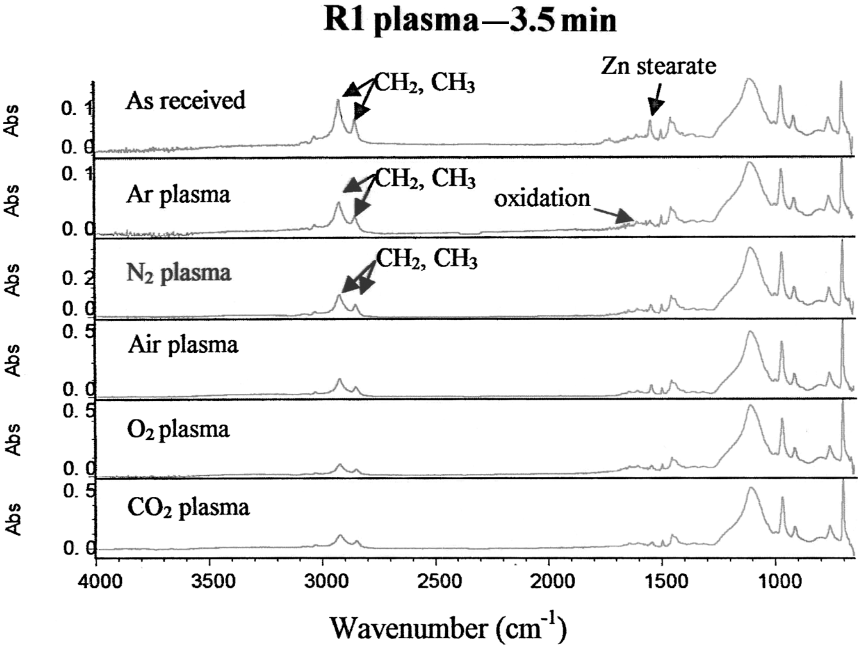


FIGURE 2 ATR-IR spectra of as-received and RF plasma-treated R1 rubber for 3.5 min.

is mainly due to the creation of C-O, C=O, and RO-C=O moieties on the R1 rubber surface (Figure 3 and Table 3b). However, O_2, air and CO_2 plasma treatments produce a decrease in O and lower O/C ratio, but they also produce a greater increase in silicon concentration (from

TABLE 3a XPS Percentages (Atomic%) on As-Received and Plasma-Treated R1 Rubber (3.5 min)

			Plasma treatment for 3.5 min				
Binding energy (eV)	Element	As received	Ar	N_2	Air	O_2	CO_2
285.0	C 1s	82.5	71.0	71.0	87.0	85.6	86.9
532.0	O 1s	12.4	23.0	22.8	7.1	8.3	7.5
398.3	N 1s	0.7	1.0	1.6	0.3	0.4	0.3
99.6	Si 2p	2.2	3.3	2.9	4.3	3.9	3.7
1021.9	Zn $2p_{3/2}$	0.9	0.6	1.3	0.2	0.4	0.3
164.5	S 2p	1.3	1.1	0.4	1.1	1.4	1.3
532.0/285.0	O/C	0.15	0.32	0.32	0.08	0.10	0.09

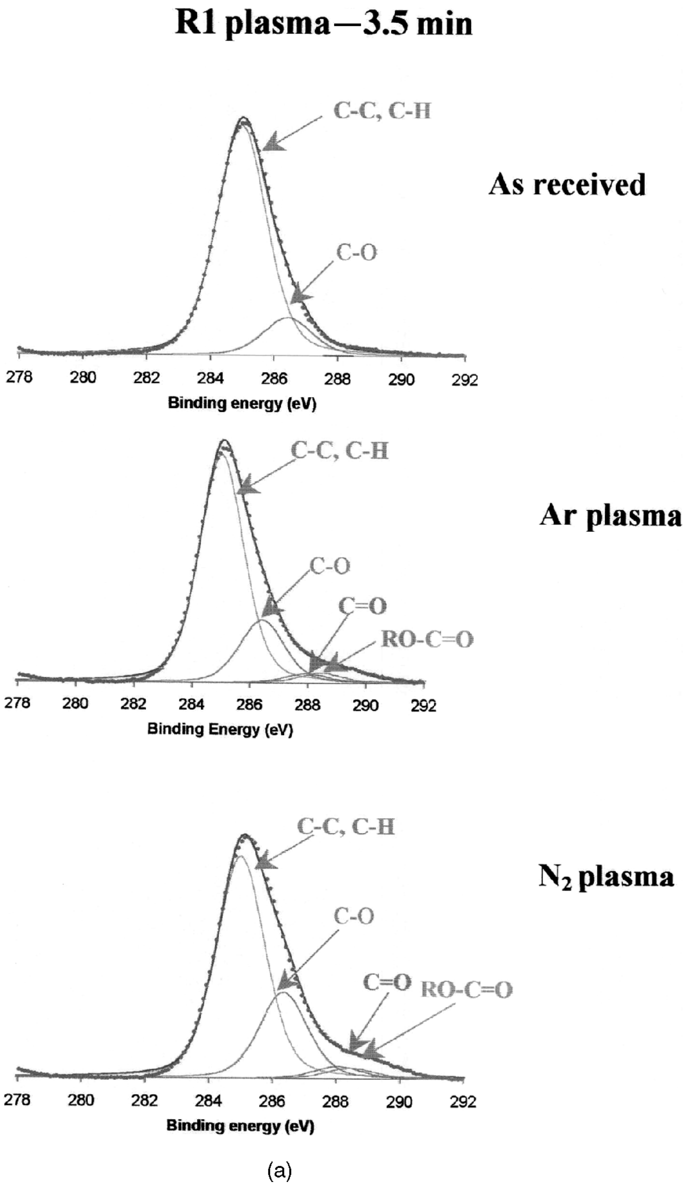


FIGURE 3 C 1 s curve fitting of as-received and RF plasma-treated R1 rubber for 3.5 min. (*Continued.*)

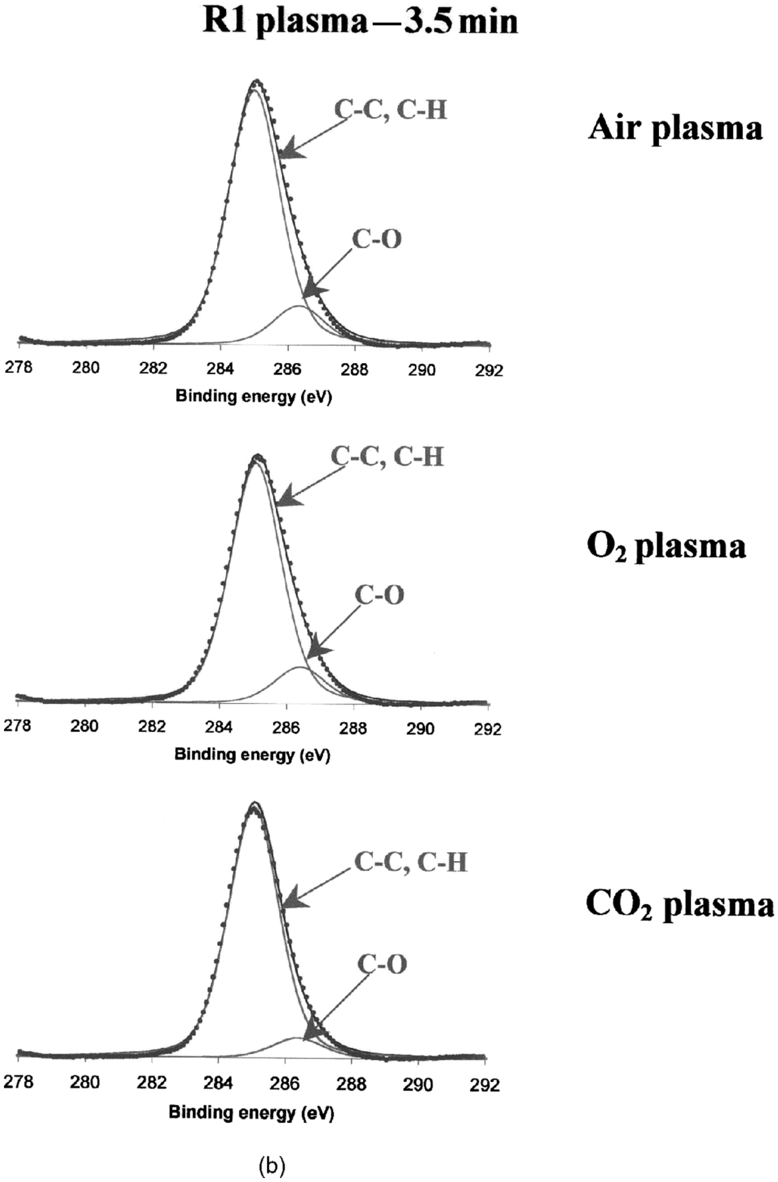


FIGURE 3 (Continued).

TABLE 3b XPS Percentages (Atomic%) of C1s Curve Fitting on As-Received and Plasma-Treated R1 Rubber (3.5 min)

			Plasma treatment for 3.5 min				
Binding energy (eV)	Species	As received	Ar	N_2	Air	O_2	CO_2
285.0	C-C, C-H	86.1	73.6	67.2	86.7	86.7	92.5
286.5	C-O	13.8	20.3	25.9	13.3	13.3	7.5
288.0	C=O	0.1	2.9	3.7	—	—	—
289.2	RO-C=O	—	3.2	3.2	—	—	—

the silica filler) compared with the treatment with nonoxidizing plasmas of the R1 rubber (Table 3a). These findings suggest the ablation of the R1 rubber surface produced by oxidizing plasmas. Besides, the atomic percentage of Zn (from zinc stearate) is reduced, which is in agreement with the removal of the zinc-stearate–rich outermost surface layer. In fact, ablation is shown in the SEM micrographs of the R1 rubber treated with oxidizing plasmas (Figure 4).

The variation in wettability of the R1 rubber treated with Ar plasma for different lengths of treatment differs with respect to the other plasma treatments (Figure 1). In fact, the increase in the length of the treatment of R1 rubber with the Ar plasma shows the gradual removal of zinc stearate (favored by surface ablation produced by an extended Ar plasma treatment), but oxidation is not greatly increased (Figure 5a). By comparison, the treatment of R1 rubber with a CO_2 plasma (Figure 5b) shows greater removal of zinc stearate and a noticeable decrease in CH_2 and CH_3 absorption bands in the ATR-IR spectra by increasing the length of the treatment. However, for a 15 min treatment zinc stearate from the bulk reappears on the rubber surface, indicating that an important degree of ablation is produced. Thus, the nonoxidizing plasma treatment with Ar requires longer treatments than the oxidizing CO_2 plasma to produce ablation and removes zinc stearate from the rubber surface. On the other hand, CO_2 plasma easily ablates the zinc-stearate–rich outermost rubber surface, and an extended treatment produces a deeper ablation so the zinc stearate from the bulk shows up on the ablated rubber surface.

Adhesion was evaluated from T-peel test measurements in plasma-treated R1 rubber/polyurethane adhesive/plasma-treated R1 rubber joints (Figure 6), and the loci of failure of the joints were assessed by using ATR-IR spectroscopy (the absorption bands of the raw materials (Figure 7) were compared with those of the failed surfaces

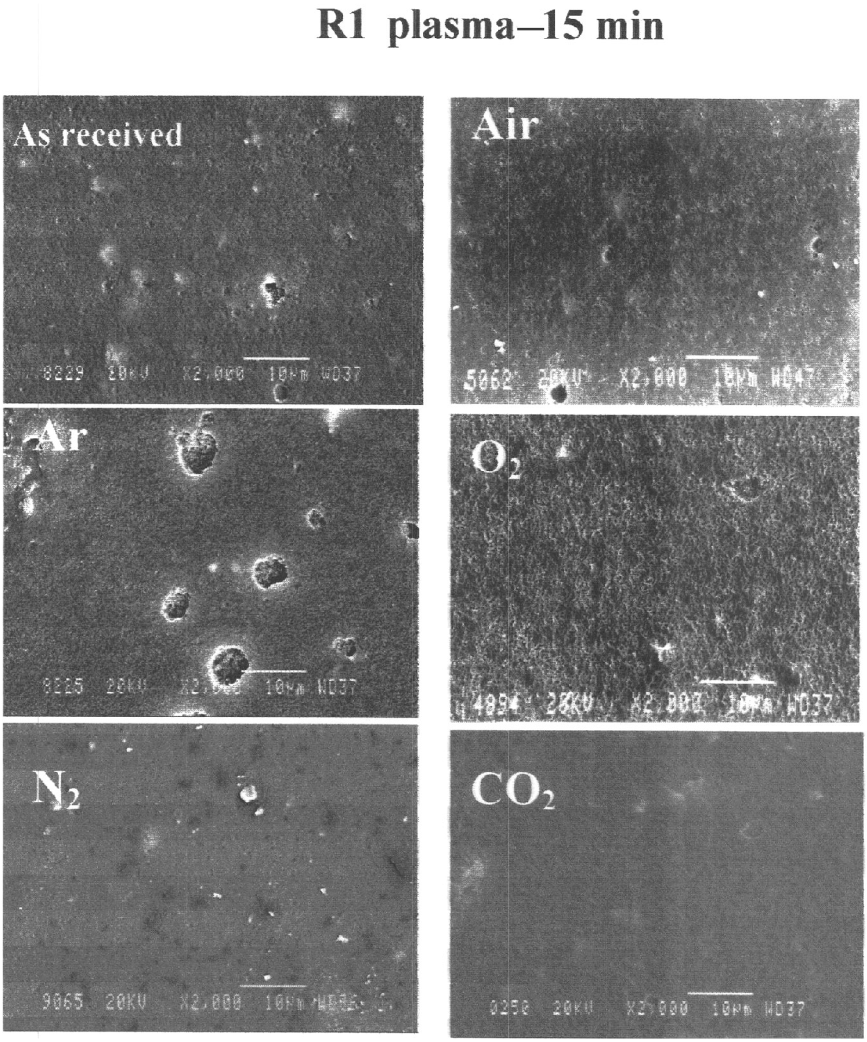
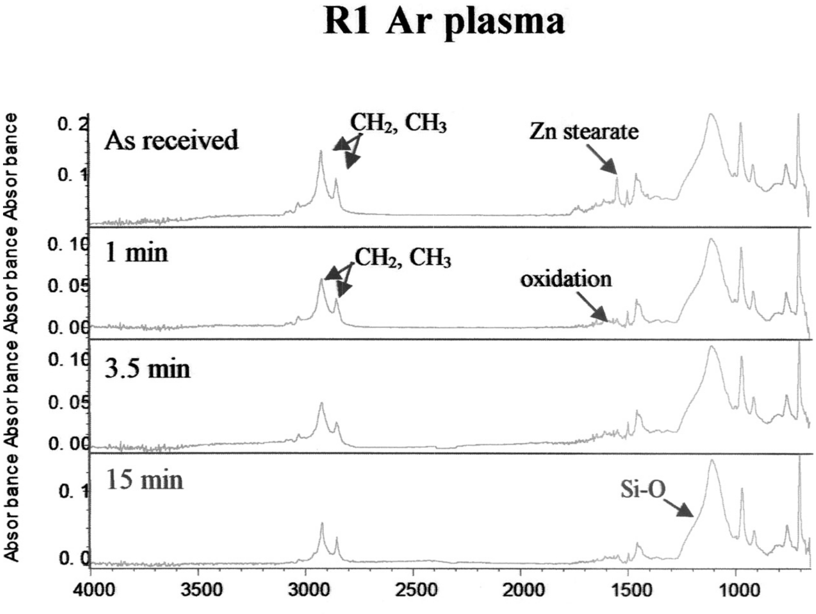


FIGURE 4 SEM micrographs of as-received and RF plasma-treated R1 rubber for 15 min.

after the peel test (Figure 8)). The ATR-IR spectrum for the polyurethane adhesive + 5 wt% isocyanate film (Figure 7) shows typical polyurethane absorption bands: C–H stretching (2939, 2860 cm^{-1}), N-H bending and N–C=O symmetric stretching (1533 cm^{-1}), C=O stretching (1717 cm^{-1}), C–O stretching (bands at 1100–1240 cm^{-1}), C–N stretching (1240 cm^{-1}), and N-H out-of-plane deformation



(a)

FIGURE 5 ATR-IR spectra of **(a)** RF Ar-plasma–treated and **(b)** CO_2-plasma–treated R1 rubber as a function of the length of treatment. (*Continued.*)

($\sim 700\,cm^{-1}$). No absorption bands from the isocyanate (*e.g*, N=C=O stretching at $2270\,cm^{-1}$) are present; this suggests that the isocyanate added to the polyurethane just before adhesive application on the R1 rubber surface has completely reacted with the polyurethane. To assess the locus of failure in the joints, the A-surface will correspond to the failed surface that visually looks like the adhesive, and the R-surface refers to the failed surface that visually corresponds to the rubber.

A low peel-strength value was obtained in the adhesive joint produced with the as-received R1 rubber due to the absence of surface chemistry and the presence of antiadherent moieties on its surface. All plasma treatments for 1 min effectively increased the adhesion of R1 rubber and a cohesive failure in the rubber was obtained, *e.g*, the two ATR-IR spectra of the failed surfaces in Figure 8a are similar and correspond to the ATR-IR spectrum of the as-received R1 rubber. Higher peel-strength values are obtained for the adhesive joint

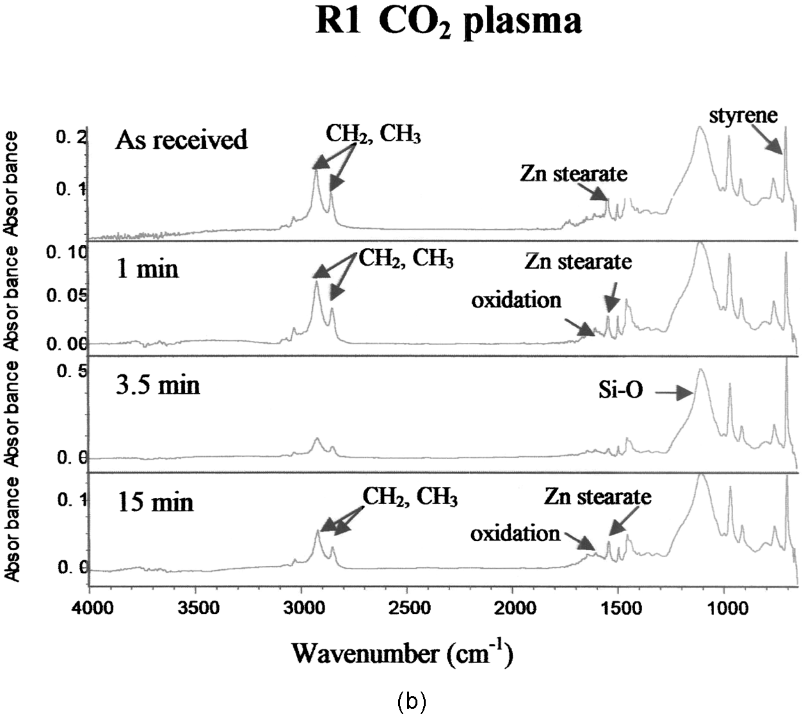


FIGURE 5 (Continued).

produced with R1 rubber treated with oxidizing plasmas compared with those obtained with nonoxidizing plasmas. This is not in agreement with the trend obtained in wettability and surface chemistry, indicating that roughness and surface ablation produced with oxidizing plasmas favor the adhesion of plasma-treated R1 rubber. Furthermore, the poor adhesion of joints produced with nonoxidizing plasma-treated R1 rubber could also be attributed to the formation of more oxidized low molecular weight species at the rubber surface creating a weak boundary layer. The surface oxidation of R1 rubber upon treatment with nonoxidizing Ar and N_2 plasmas may occur after exposure of the plasma-treated rubber surface to air. In fact, Table 4a shows that 15 min treatment of R1 rubber with nitrogen plasma generated species that can be partially removed by toluene wiping, and toluene wiping improved the T-peel strength of the joints (Figure 9).

The T-peel values are similar when the length of treatment was increased for all plasmas, and a cohesive failure in the rubber was

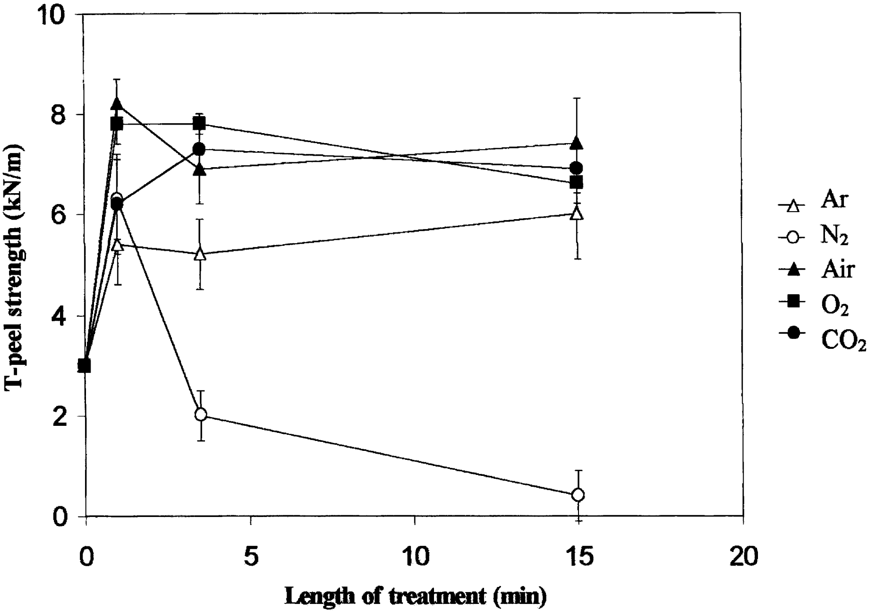


FIGURE 6 T-peel strength values (72 h after joint formation) of as-received and RF plasma-treated R1 rubber/polyurethane adhesive + 5 wt% isocyanate joints.

always obtained. The joints produced with R1 rubber treated with the N_2 plasma are an exception because an important decrease in adhesion is obtained by increasing the length of treatment (Figure 6). This decrease in adhesion could be ascribed to a surface degradation produced by the extended N_2 plasma treatment. In fact, the surface chemistry of the N_2-plasma–treated R1 rubber surface for 15 min (Table 4a) is less developed than with a treatment for 3.5 min (Table 3a). However, a more detailed explanation is necessary.

The loci of failure of the adhesive joint produced with a nitrogen-plasma–treated R1 rubber for 15 min is partly cohesive in the adhesive and partly located within the degraded R1 rubber surface, as the ATR-IR spectra of the failed surfaces (Figure 8b) show both the polyurethane adhesive and the R1 rubber bands. Besides, the SEM micrographs of the cross sections of the failed surfaces of the joint produced with R1 rubber treated with N_2 plasma for 15 min (Figure 10) show the presence of an adhesive layer about 15 μm thick on both failed surfaces. This kind of failure is somewhat difficult to understand.

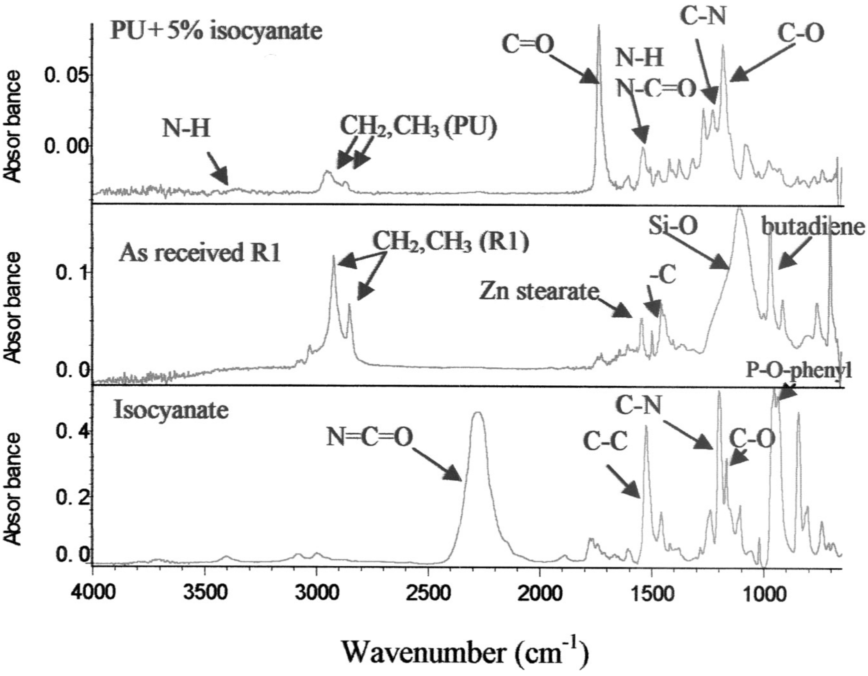
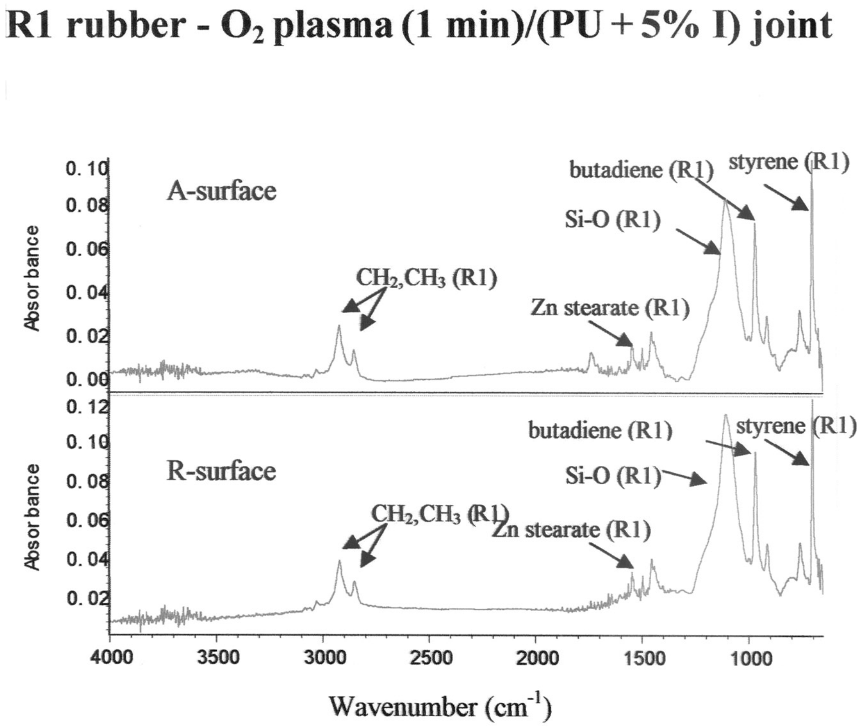


FIGURE 7 ATR-IR spectra of as-received R1 rubber, polyurethane adhesive + 5 wt% isocyanate, and isocyanate.

Toluene is an appropriate solvent for cleaning the R1 rubber surface. Therefore, after the N_2 plasma treatment and prior to bonding, the surface of R1 rubber was wiped with toluene to remove the degraded outermost R1 rubber layer. The toluene wiping does not affect the chemistry of the as-received R1 rubber (Tables 4a and 4b), but a decrease in oxygen and an increase in carbon atomic percentages are obtained on the nitrogen-plasma–treated (15 min) R1 rubber, *e.g.*, a decrease in the O/C ratio is obtained. Table 4a also shows a decrease in the percentage of silicon, suggesting that the toluene wiping partially removes the degraded outermost R1 rubber surface after the N_2 plasma treatment. Table 4b shows the decrease in C-O, C=O, and RO-C=O moieties on the R1 rubber surface after toluene wiping.

Figure 9 shows the peel strength values of adhesive joints produced with R1 rubber treated with a nitrogen plasma before and after toluene wiping. Toluene produces the swelling of the as-received R1 rubber surface so the T-peel strength value obtained after toluene



(a)

FIGURE 8 ATR-IR spectra of the failed surfaces obtained after peel test of **(a)** oxygen-plasma–treated R1 rubber (1 min)/polyurethane adhesive + 5 wt% isocyanate joint and **(b)** nitrogen-plasma–treated R1 rubber (15 min)/ polyurethane adhesive + 5 wt% isocyanate joint. (*Continued.*)

wiping (2.1 kN/m) is lower than that of the nonwiped, as-received R1 rubber (4.8 kN/m). A short nitrogen plasma treatment (1 min) produces an adequate wettability and sufficient degree of oxidation without rubber surface degradation, so a toluene wiping dissolved the outermost modified rubber surface, decreasing its chemistry and leaving an unmodified rubber surface. Thus, a decrease in adhesion is obtained (1.9 kN/m) (Figure 9). However, by increasing the length of treatment in the nitrogen plasma, surface degradation is favored and toluene seems to partially dissolve low molecular weight moieties on the degraded oxidized outermost R1 rubber surface. As a consequence, adhesion is increased (3.4 kN/m). The failure mode of the adhesive joint produced with 15 min N_2-plasma–treated R1 rubber

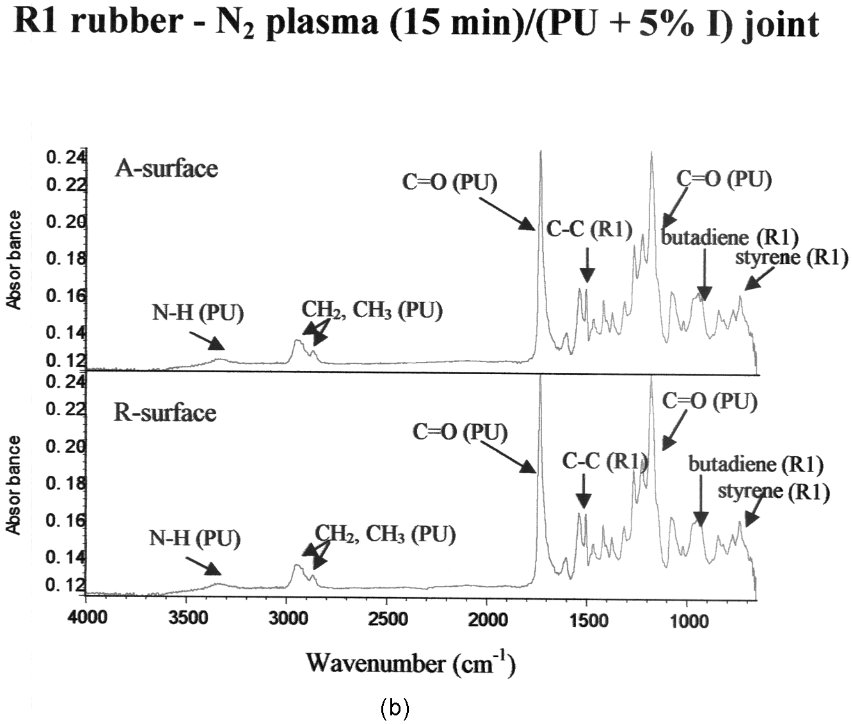


FIGURE 8 (Continued).

TABLE 4a XPS Percentages (Atomic%) on As-Received and Nitrogen-Plasma–Treated (15 min) R1 Rubber Before and After Toluene Wiping

Binding energy (eV)	Element	As received		N_2 plasma treatment (15 min)	
		No toluene	Toluene	No toluene	Toluene
285.0	C 1s	82.5	81.5	73.0	78.3
532.0	O 1s	12.4	12.9	20.6	17.0
398.3	N 1s	0.7	0.9	1.8	1.4
99.6	Si 2p	2.2	2.4	2.6	1.2
1021.9	Zn $2p_{3/2}$	0.9	0.9	1.1	1.2
164.5	S 2p	1.3	1.4	0.9	0.9
532.0/285.0	O/C	0.15	0.16	0.28	0.22

TABLE 4b XPS Percentages (Atomic%) of C1s Curve Fitting on As-Received and Nitrogen-Plasma–Treated R1 Rubber (15 min) Before and After Toluene Wiping

Binding energy (eV)	Species	As received		N_2 plasma treatment (15 min	
		No toluene	Toluene	No toluene	Toluene
285.0	C-C, C-H	86.1	84.6	68.5	72.3
286.5	C-O	13.8	15.1	24.0	22.3
288.0	C=O	0.7	0.3	4.7	2.9
289.2	RO-C=O	—	—	2.8	2.5

(Figure 11) is mixed, being more cohesive in the R1 rubber when a toluene wiping is performed.

These findings suggest that for a short time (1 min) N_2 plasma produces an adequate degree of oxidation of the R1 rubber surface so that adhesion towards polyurethane adhesive is enhanced. However, an

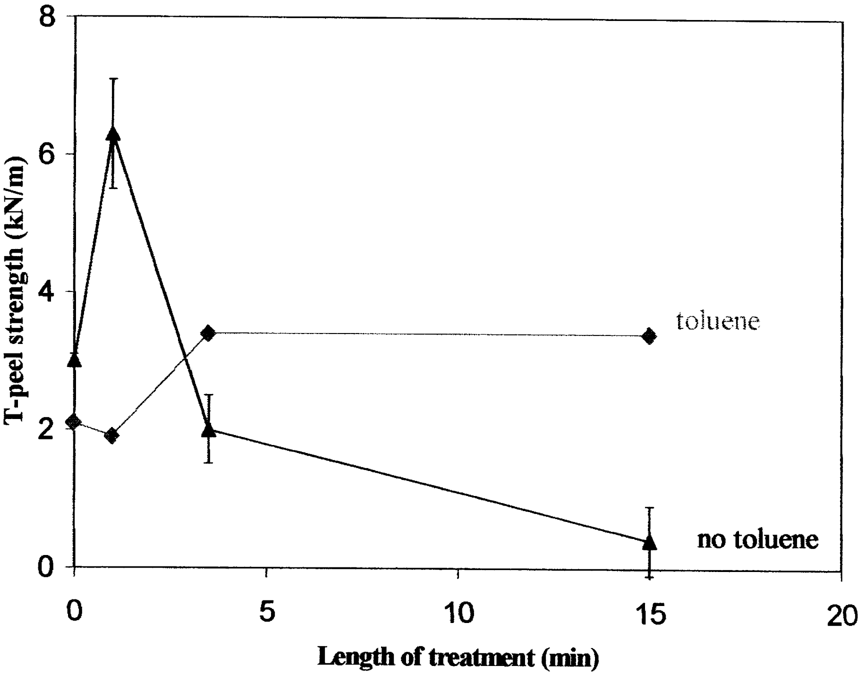


FIGURE 9 T-peel strength values (72 h after joint formation) of as-received and nitrogen-plasma–treated R1 rubber/polyurethane adhesive + 5 wt% isocyanate joints. Influence of toluene wiping.

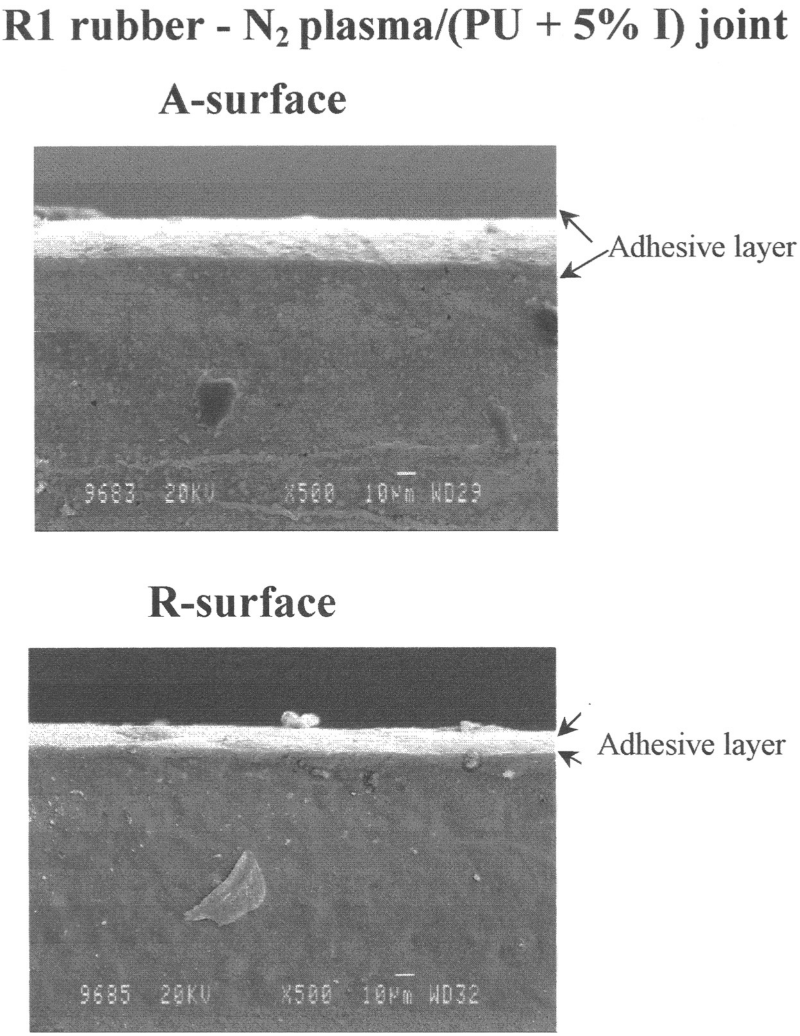


FIGURE 10 SEM micrographs of sections of the failed surfaces obtained after peel test of nitrogen-plasma–treated R1 rubber (15 min)/polyurethane adhesive + 5 wt% isocyanate joint.

extended N_2 plasma treatment degrades the outermost R1 rubber surface, and the failure of the joint is produced in this mechanically damaged thin R1 rubber surface. This degraded rubber surface can be partially removed by toluene wiping.

For the other plasmas (argon, air, oxygen, and carbon dioxide) ablation of the R1 rubber surface is produced, so the mechanically weak

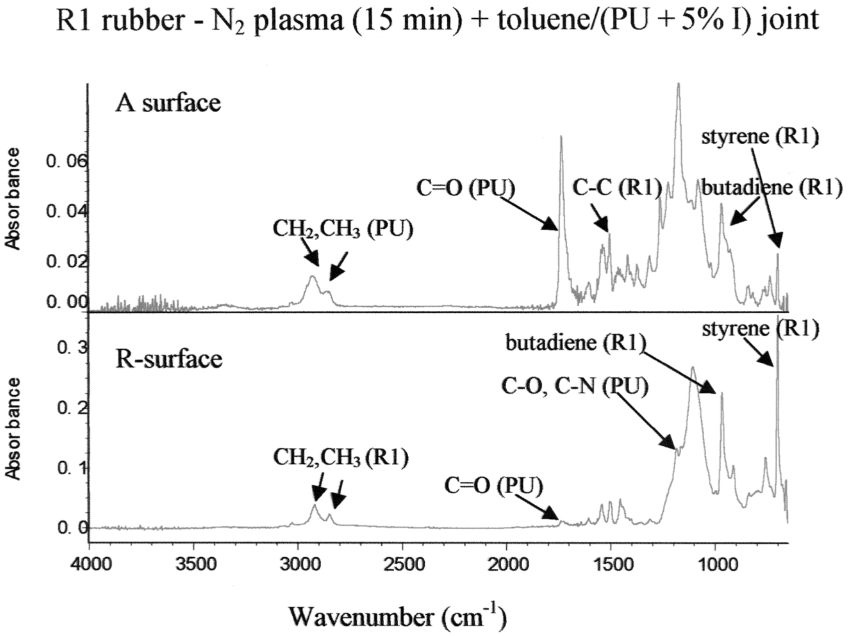


FIGURE 11 ATR-IR spectra of the failed surfaces obtained after peel test of nitrogen-plasma–treated R1 rubber (15 min)-toluene wiped/polyurethane adhesive + 5 wt% isocyanate joint.

degraded R1 rubber layer is not present when the joint is produced. Besides, the energetic environment in the plasma reaction chamber produces an oxidation without degradation. Thus, an improvement in adhesion and a cohesive failure in the R1 rubber is obtained.

CONCLUSIONS

The effectiveness of the plasma treatment of R1 rubber depends on the gas atmosphere used to generate the plasma. In general, acceptable adhesion values are obtained in all joints produced with R1 rubber treated with inorganic plasmas (oxygen, nitrogen, air, and carbon dioxide), except for nitrogen plasma when the duration of the treatment is longer that 1 minute, due to the degradation of the outermost R1 rubber layer. In this case, a toluene wiping of the N_2-plasma–treated R1 rubber surface removes low molecular weight moieties and increases adhesion.

Air, carbon dioxide, and oxygen plasmas-treatments performed for 3.5 min or more produce ablation of the R1 rubber surface, removing the degraded outermost layer. Thus, adhesion is increased. On the other hand, Ar plasma activates the R1 rubber surface so that subsequent exposure of this activated surface to the air after Ar plasma treatment-produces oxidation of the rubber surface. The degree of oxidation achieved is enough to increase the polarity of the rubber surface, and enhanced adhesion is obtained even when the rubber is treated for up to 15 min.

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