FULL PAPER

PLASMA PROCESSES
AND POLYMERS

Improvement of the adhesive capacity of SBR for footwear outsoles by surface activation and coating deposition with atmospheric pressure plasma

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Abstract
Looking for a cleaner alternative to halogenation in the preparation of rubber for bonding with leather in footwear, atmospheric pressure plasma treatments were applied on styrene–butadiene rubber (SBR). Its adhesive capacity was improved and the highest bond strength standards for footwear were met. Two optimal processes were identified: (1) Plasma polymerization of (3-aminopropyl) triethoxysilane coatings on flat SBR and (2) plasma-activation of mechanically roughened SBR. The improvement on coated, flat SBR was mainly due to its surface chemistry having greater concentrations of polar carbon–oxygen species than the untreated SBR. For plasma-activated, mechanically roughened SBR, combined contributions of mechanical roughening and roughening by plasma irradiation were found. Coating flat SBR at 100 mm/s showed the best balance between improved bond strength and durability.
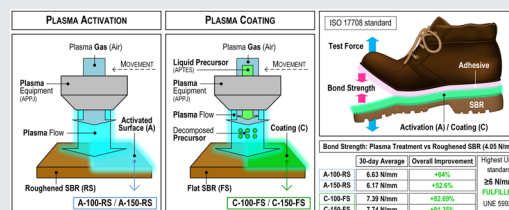
KEYWORDS
adhesion, aging, aminopropyltriethoxysilane, atmospheric pressure plasma polymerization, SBR

1 | INTRODUCTION

To provide the user's feet with durable protection and comfort in harsh environments, it is important for footwear products to possess a strong adhesion between their outsoles and upper parts. Outsoles are frequently made of vulcanized rubbers because of the superior physical properties of these materials, such as good traction and durability, as well as their ability to be molded in different colors. Among these materials, styrene–butadiene rubber (SBR) is considered the main polymer for the manufacture of footwear outsoles because of its availability, low cost, and high filler tolerance.[1] However, vulcanized rubbers have poor adhesive properties unless

they are properly prepared. This lack of adhesion is due to the nonpolar nature of the rubber and low molecular weight of additives, such as antiozonant paraffin wax and processing oils, which are used in its manufacture, and tend to migrate from the bulk to the rubber surface after vulcanization and generate a weak boundary layer.[2–4]

The most traditional procedure to prepare SBR for bonding consists of applying a halogenation process. Halogenation of SBR using trichloroisocyanuric acid as the chlorinating agent improves the adhesion of joints obtained with polyurethane (PU) adhesives by increasing the surface energy of the rubber, removing antiadherent moieties, creating morphological heterogeneities that improve mechanical adhesion, and creating polar groups on the rubber that improve chemical interaction.[5,6] Nevertheless, halogenation has drawbacks, such as long processing times and the production of chlorine-containing residues, which are harmful to the environment and may cause human health problems.[2,7,8] Another commonly used approach for the preparation of rubber consists of applying a mechanical roughening to generate an adherent morphology.[9] However, the effectiveness of this approach can be limited by the entrapment of residual particles in the morphological features of the roughened surface and by possible migration of low molecular weight moieties from the bulk to the surface as time passes after the mechanical roughening.[10–12]

In the seek for cleaner procedures to prepare the surface of rubber materials for specific applications, plasma treatments have become an interesting solution over the last decades because they do not rely on the use of hazardous chemicals and the gases that they emit to have a low impact on the environment.[13] Focusing on the improvement of the adhesive capacity of rubber surfaces, plasma treatments have been proved beneficial by removing low molecular weight moieties, inducing roughness, and providing polar species to the surface chemistry.[4,14] Ortíz-Magán et al.[15] used oxidizing (air, CO_2 and O_2) and nonoxidizing (Ar and N_2) low-pressure plasmas to treat SBR. The plasma treatments produced removal of low molecular weight species by surface ablation as well as oxidation by the creation of C–O, C=O, and RO–C=O moieties. Whereas oxidizing plasmas were more effective at producing ablation, nonoxidizing plasmas generally resulted in more noticeable surface oxidation. Except for N_2 plasma treatments for longer times than 1 min, the T-peel strength of SBR/PU adhesive/SBR joints was improved from the low values obtained with as-received SBR (~3 kN/m) to acceptable values that ranged approximately between 5 and 8 kN/m for the plasma-treated SBR. Cantos-Delegido and Martín-Martínez[2] treated vulcanized styrene–butadiene/natural rubber for shoe outsoles that intentionally contained an excess of processing oils with Ar-O_2 low-pressure plasma. An increase in the surface energy, especially in its polar component, was observed for the plasma-treated rubber. Chemical characterization indicated that plasma treatments partially removed the nonpolar species of antiozonant wax and oils, which was in agreement with the partial removal of wax crystallites, which was observed by scanning electron microscopy (SEM). As the treatment time increased, more effective removal of wax and oils took place and roughness was generated. In spite of these modifications on the rubber surface, an improvement in the adhesion of the plasma-treated rubber to waterborne PU adhesive was not obtained because of the migration of wax and oil to the rubber–adhesive interface after joint formation. Nevertheless, applying a thermal treatment to the rubber before the plasma treatment enhanced the extent of the surface modifications, thus causing an improvement in the adhesion.

In spite of their favorable effects on the preparation of SBR surfaces, low-pressure plasma technologies require the use of vacuum, which makes them difficult to implement for industrial purposes. To overcome this drawback, atmospheric pressure plasma has been proposed as a more suitable alternative for in-line production. To improve the adhesion of footwear joints formed by SBR and roughened leather parts bonded by means of PU adhesive, Carreira et al.[13] treated the surface of vulcanized SBR parts with atmospheric pressure plasma. Compared to the untreated SBR, the plasma-treated SBR showed improved wettability, which confirmed that an increase in the surface energy of the SBR had been caused by the atmospheric pressure plasma treatment. Ablation of the plasma-treated SBR surface was also identified, which caused changes in its topography and an increase in its roughness. A 10- to 12-fold increase in the T-peel strength of the untreated SBR joints was achieved by the plasma-treated SBR. The effect of aging of the plasma-treated SBR on the T-peel strength of the joints was also studied, and it was shown that the aforementioned T-peel strength improvement was maintained after 1-month aging.

Atmospheric pressure plasma technologies are also capable of depositing functional coatings when a liquid precursor is added to the plasma. The properties of the obtained coatings depend on the chemical composition of the precursor and its flow rate during the deposition process, as well as on the parameters of the plasma generation such as the type of gas used and the power setting.[16] For instance, Moreno-Couranjou et al.[17] used an atmospheric pressure plasma torch to treat natural vulcanized rubber to improve its adhesion to a silicone adhesive in a study that considered two types of

treatments: (1) Using only plasma from an N_2–O_2 mixture and (2) coating the rubber by using N_2 plasma associated with organic precursors. T-peel tests of rubber/ silicone adhesive/silicone sheet joints revealed that the treated rubbers reached greater T-peel strength values than the untreated rubber. Furthermore, the greatest improvement in the T-peel strength was achieved by rubber that had been coated using allyl alcohol as a precursor, which resulted in a 10-fold increase in the T-peel strength of the untreated rubber. This improvement was attributed to the increase in the oxygen content and the formation of mainly C–O bonds at the surface of the coated rubber that were identified by chemical characterization.

In the present study, an atmospheric pressure plasma jet (APPJ) system was used for the application of surface activation treatments by plasma irradiation and coating treatments by plasma-polymerization on flat and mechanically roughened SBR to improve the bond strength of SBR/PU adhesive/leather joints for footwear. For the coating treatments, the liquid precursor (3-aminopropyl) triethoxysilane (APTES) was selected because it contains amine groups (NH_2), which can be favorable for improving the adhesive properties of materials,[18–21] and it has been previously used by some of the authors of the present study to successfully coat elastomeric substrates by atmospheric pressure plasma polymerization.[22–25] Compared to previous studies where low-pressure plasma technologies were used,[2,15] the atmospheric pressure plasma system that is used in the present study has the competitive advantage of not requiring vacuum equipment, which makes it relatively inexpensive and easier to be implemented for large-scale production. Furthermore, this study aims to fill the gaps existing in the bibliography regarding the use of atmospheric pressure plasma for the improvement of the adhesive capacity of vulcanized rubbers. Compared to previous studies where SBR surfaces were treated only by exposure to the plasma,[13] the present study also considers the deposition of coatings by plasma polymerization. On the contrary, compared to previous studies that studied the plasma-deposition of coatings on vulcanized rubber,[17] the present study makes a more extensive study by addressing the aging of the activation and coating treatments, it uses compressed air as the gas for generating the plasma, which is an inexpensive alternative to the use of N_2 and O_2 from different flows, and it also uses materials that better resemble the ones in footwear joints (i.e., SBR, PU adhesive, and leather). Furthermore, different from the discussed literature and considering the commonly used practice of mechanically roughening the rubber surfaces for footwear joints, the present study initially uses both flat and mechanically roughened SBR

for all the studied cases (i.e., untreated, plasma-activated, and coated) to identify the most promising combinations for industrial implementation.

2 | MATERIALS AND METHODS

2.1 | Materials

Test pieces of $120 \times 25 \times 3$ mm were prepared by vulcanizing SBR that was supplied by Cauchos Arnedo S.A. In the experiments of the present study, the SBR test pieces were used in two different conditions: (1) As-prepared (flat samples) and (2) after having undergone a mechanical roughening process (roughened samples) that imitated the usual conditioning technique for rubber surfaces in the footwear industry. An EM 91 (Euromeccanica) roughening machine operating at 2850 rpm and a 100-grit abrasive belt of aluminum oxide were used three times to roughen each SBR test piece.

Leather test pieces of $150 \times 30 \times 1.3$ mm were taken from the chromium-tanned bovine split that was supplied by Curtidos Martínez Leal S.L.U. using a cutting die. The animal hair layer of all the leather test pieces was removed by roughening them two times with the same equipment and speed that were used for the SBR test pieces.

The commercial PU adhesive Obrador 900 from Colas y Adhesivos Obrador S.A with a 5% (v/v) of the TDI-based hardener Desmodur RC from Covestro AC was used for bonding the SBR and leather test pieces that were submitted to peel tests.

The liquid APTES purchased from Sigma-Aldrich Chemie GmbH was used in the plasma polymerization treatments as a precursor of the deposited coatings.

2.2 | Treatment of SBR surfaces by atmospheric pressure plasma

Surface activation and coating treatments were applied on the SBR samples using the APPJ system Plasma-Spot500® (MPG) as shown in Figure 1. The APPJ system used has two cylindrical electrodes, one grounded and the other one connected to a high-voltage source operating at 68 kHz, which are mounted in a coaxial arrangement with an Al_2O_3 dielectric barrier between them. The plasma was generated from an airflow that passed between the electrodes. The airflow rates that were used respectively for the activation and coating treatments were 100 and 80 slm, and their respective power settings for plasma generation were 500 and 300 W. During the plasma treatments, the SBR samples
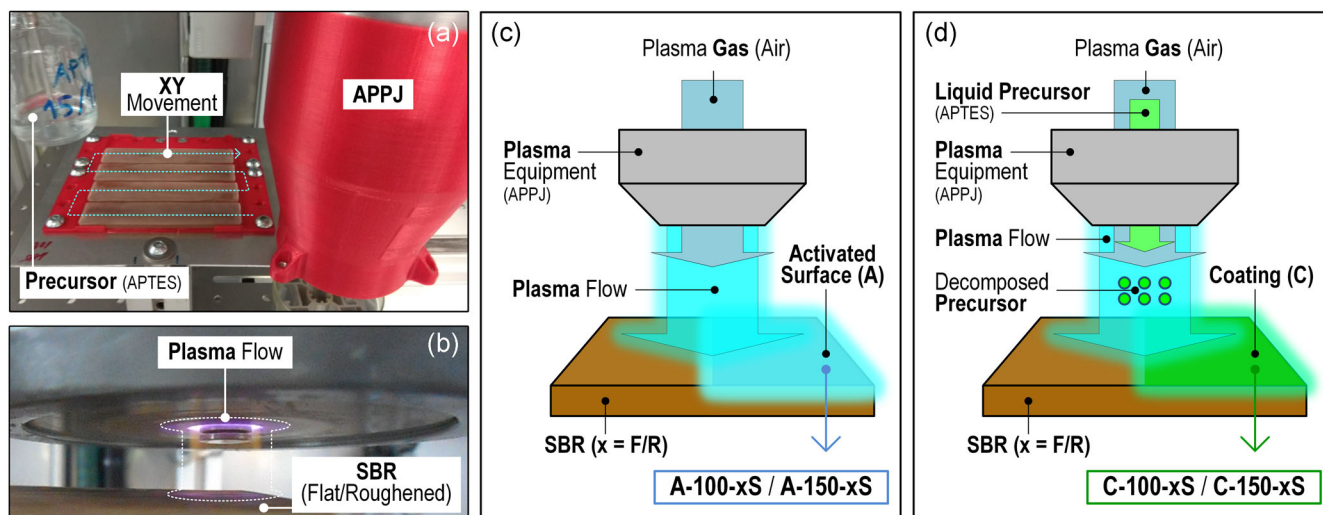
FIGURE 1 Plasma treatment processes: (a) Setup overview, (b) close view of treatment, (c) scheme of the plasma activation treatments, and (d) scheme of the plasma polymerization treatments

were placed on an X–Y table that performed a scanning movement with a 2-mm track pitch under the APPJ, keeping a gap of 3 mm between the SBR surface and the tip of the inner electrode. Scanning speeds of 100 and 150 mm/s were used for both activation and coating treatments of flat and mechanically roughened SBR samples, which were named as shown in Table 1.

The activation treatments were performed by exposing the SBR samples to the APPJ in one pass. The coating treatments were performed in two stages. First, the SBR surfaces were preactivated by one pass of plasma exposure without adding the liquid precursor. Second, the deposition of a coating by plasma polymerization was carried out by performing one scanning pass, using the same treatment parameters as in the preactivation stage, while adding the liquid precursor APTES to the APPJ. The transport of the precursor from its vessel to the APPJ in the form of an aerosol was made by using a 2-slm flow rate of air as the carrier gas and an atomizer (model 3076; TSI Inc.).

2.3 | Joint preparation

Before performing the peel tests, a 95/5 adhesive: hardener mix was uniformly applied to the SBR and leather parts using a brush. It was let dry for 30 min and, after the solvent was evaporated, a heat IR (infrared) radiation flash lamp Muver 5073 was used for 12 s to reactivate the adhesive. Then, SBR and leather parts were bonded using a pneumatic press Muver 5056 that applied pressure of 4.58 MPa for 16 s. Finally, the samples were let to cure for 48 h so that proper adhesive bonding was ensured.

2.4 | Peel tests

The joints were tested using a method that was based on the ISO 17708 standard[26] to measure their bond strength. An Instron model 4302 tensile-testing machine with a 1-kN load cell was used for this purpose. The samples were clamped between the jaws of the machine, then the SBR and leather parts were separated at 100 ± 10 mm/min and the force/deformation curve was recorded. From this curve, the average separation force

TABLE 1 Nomenclature of samples according to the distinctive characteristics of their respective substrate and treatment

Sample	Plasma treatment type	Scanning speed (mm/s)	Initial substrate conditions
A-100-FS	Activation	100	Flat
A-100-RS	Activation	100	Roughened
A-150-FS	Activation	150	Flat
A-150-RS	Activation	150	Roughened
C-100-FS	Coating	100	Flat
C-100-RS	Coating	100	Roughened
C-150-FS	Coating	150	Flat
C-150-RS	Coating	150	Roughened
Flat SBR	–	–	Flat
Roughened SBR	–	–	Roughened

Abbreviation: SBR, styrene–butadiene rubber.

was obtained and it was divided by the average sample width. Thus, the bond strength expressed in N/mm was calculated. The samples were tested in duplicate for each measurement of the bond strength presented in this study.

In an initial approach, all the sample types that were designated in Table 1 were subjected to preliminary peel tests. These preliminary tests were performed on samples that had been plasma-treated and bonded to the leather parts on the same day. From the preliminary bond strength values that were obtained from these tests, the most promising sample types were selected for a deeper study concerning the effect of aging on the adhesive capacity of the plasma-treated samples. For this study, peel tests were performed on plasma-treated SBR parts that were stored in the dark, in individual zip-locked polyethylene bags at room temperature for 0, 1, 2, 3, 6, 14, 21, and 30 days immediately after the plasma treatment and before being bonded to the leather parts. The morphology and chemistry of the selected samples were also studied as described in the following subsections.

2.5 | Morphological characterization

Atomic force microscopy (AFM) three-dimensional (3D) images of regions of $40 \times 40\,\mu m$ from the surfaces of the studied samples that had not been mechanically roughened were obtained using a Multimode atomic force microscope (Bruker) with a Nanoscope V controller, working in tapping mode. Three independent regions of each sample type were imaged and the average roughness (R_a) of each sample was obtained as the mean R_a value of its three AFM images using the software NanoScope Analysis 1.40 (Bruker). The R_a of the studied samples that had been mechanically roughened and the thicknesses of the plasma-polymerized coatings were obtained through contact profilometry. A Surtronic 25 (Taylor Hobson) profilometer set at 4 mm evaluation length and $100\,\mu m$ range was used for these purposes. To obtain the average roughness of the mechanically roughened samples, five independent surface profiles were measured for each sample type and their R_a values were averaged. The measurement of the coating thickness was done as follows. Before the coating treatment, the flat SBR surface was partially covered with a mask. Then, the coating treatment was applied and the mask was removed. Thus, a step between the surface of the coating and the uncoated SBR was obtained. The thickness of each coating was obtained as the average of five measurements of its respective step's height that was taken by the contact profilometer. Furthermore, the deposition rate of each coating was obtained by dividing its

average thickness by its deposition time (i.e., the time for performing one pass of plasma polymerization on an SBR test piece). Scanning electron microscopy (SEM) images were also obtained with an S-2400 microscope (Hitachi) operating at 18 kV for additional qualitative characterization. Before SEM imaging, the studied samples were made conductive by sputtering of gold-palladium.

Portions of $10 \times 10 \times 3$ mm of each sample type were used for AFM and SEM. This was done to comply with the limitations of space inside devices that were used for these analyses.

2.6 | Chemical characterization

X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR) were used for analyzing the chemical composition of the untreated SBR substrates and plasma-treated samples that had been stored for 0, 3, 6, and 30 days immediately after the plasma treatment and before being subjected to the chemical characterization analyses. These samples were stored in the same conditions as the ones that were used in the peel tests of the aging study (i.e., in the dark, in individual zip-locked polyethylene bags at room temperature). Thus, the identification of possible correlations between the aging of the bond strength and the aging of the chemistry was enabled.

The XPS analysis of the surface chemistry was performed using an AXIS Supra spectrometer (Kratos Analytical) that was equipped with a monochromatic Al-Kα X-ray source operating at 225 W (15 mA/15 kV), keeping the pressure within the chamber below 10^{-9} Torr. The device was set to hybrid lens mode and slot mode, thus covering an analysis area of approximately $700 \times 300\,\mu m$. XPS spectra of each analyzed sample type were acquired at three different regions of its surface. Pieces of $4 \times 2 \times 2$ mm of each sample type were used for the XPS analysis so that the vacuum in the chamber was facilitated. The survey spectra for the quantification of the atomic percentages of the elements at the surface of the samples were acquired at pass energy of 160 eV. The high-resolution spectra of the regions that corresponded to specific elements were acquired at pass energy of 20 eV. A correction was applied to the binding energies of all the XPS spectra by setting the highest peak of the carbon component (C 1s) at 285 eV. The correction of the binding energy and the quantification of the atomic percentages of the elements at the surface of the samples was done with the software CasaXPS 2.3.19 (Casa Software). The atomic percentages were obtained from the areas under the photoelectron peaks of their respective

elements in the survey XPS spectra after subtracting a Shirley-type background. The deconvolution of the high-resolution spectra corresponding to the C 1s region of the analyzed samples was done with the software PeakFit 4.12 (SPSS Inc.), allowing variable widths for the peaks that composed the deconvolution and fitting them with Gaussian–Lorentzian sum functions.

For more insight on the chemistry of the analyzed samples, ATR-FTIR spectra with a $4\,cm^{-1}$ resolution were obtained performing 32 scans with a Spectrum Two FT-IR spectrometer (PerkinElmer). Automatic baseline correction was done with the software Spectrum 10.4.3.339 (PerkinElmer).

3 | RESULTS AND DISCUSSION

3.1 | Preliminary peel tests and process optimization

Preliminary tests were performed to measure the bond strength between all the sample types that were considered in this study and the leather parts (Table 2). For these tests, plasma treatment of the SBR samples and bonding were performed within the same day. Greater bond strength values were obtained for any of the plasma-treated SBR samples than for the untreated substrates (i.e., flat and roughened SBR). Furthermore, some of the treated samples reached bond strength values that met the most restrictive adhesion requirement for footwear in the UNE standards (i.e., $\geq 6\,N/mm$ in school shoes).[27] Such degree of adhesion was achieved by all of the coated samples (either flat or roughened), as well as by those plasma-activated samples that had been previously roughened (samples A-100-RS and A-150-RS). These results suggested that to make it as simple as possible for its industrial implementation, the process for obtaining high degrees of adhesion between SBR and leather parts could be optimized in two ways: (1) Applying a plasma polymerization treatment to a flat SBR surface like in samples C-100-FS and C-150-FS (thus avoiding the mechanical roughening) or (2) mechanically roughening the SBR surface and applying a plasma activation treatment like in samples A-100-RS and A-150-RS (thus avoiding the coating stage). Therefore, as discussed in the following sections, a more thorough study was conducted focusing on those two ways by selecting their corresponding samples, analyzing the effects of aging in their adhesive capacities, and characterizing their chemistry and morphology. Flat and mechanically roughened SBR samples with no plasma treatment were also taken into account to better understand the changes that the plasma-treated samples had undergone.

3.2 | Morphological characterization

To measure the R_a and study the morphology of the selected samples, 3D images of their surfaces were acquired by AFM. However, the diamond tip of the microscope failed at capturing the surface features of the mechanically roughened samples, so representative AFM images and roughness measurements could be obtained only for the samples with flat SBR substrates (Figure 2). The hills and valleys that were clearly distinguishable in the AFM images of the flat SBR substrate became less evident in those of the coated samples, which also showed the formation of a fine grainy texture on the surface of the coatings. According to the R_a results obtained from the AFM images (Figure 3a), the coated samples (C-100-FS and C-150-FS) were smoother than the flat SBR substrate. Furthermore, sample C-100-FS was smoother than sample C-150-FS. These results suggest that the lower scanning speed that was used for sample C-100-FS (100 mm/s) than for sample C-150-FS (150 mm/s) during the plasma-polymerization treatment allowed a greater amount of precursor to be deposited on sample C-100-FS, thus filling the valleys of the topography of the flat SBR substrate and smoothening its surface to a greater extent. The deposition of a greater amount of material on the sample that was coated at 100 mm/s than on the sample that was coated at 150 mm/s was confirmed by measuring the thickness of their coatings through contact profilometry. The coating thickness of sample C-100-FS (117 ± 25 nm) was higher than that of sample C-150-FS (83 ± 17 nm). When the coating thicknesses of sample C-100-FS and sample C-150-FS were divided by their deposition times, deposition rates of 4.67 and 4.97 nm/s were obtained, respectively. Therefore, the deposition rate of these treatments was practically

TABLE 2 Preliminary bond strength results of all the styrene–butadiene rubber (SBR) samples

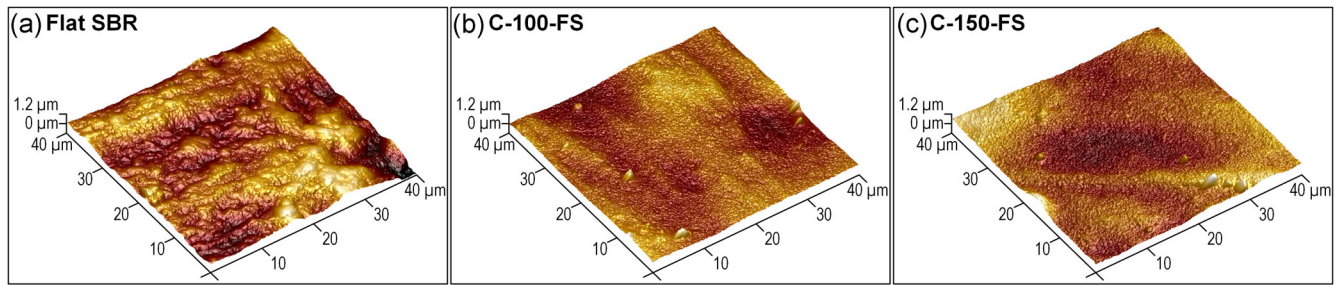| Sample	Bond strength (N/mm)
A-100-FS	5.10 ± 0.40
A-100-RS	8.22 ± 0.03
A-150-FS	4.80 ± 0.06
A-150-RS	9.40 ± 0.20
C-100-FS	10.30 ± 1.05
C-100-RS	9.10 ± 0.50
C-150-FS	10.40 ± 0.20
C-150-RS	9.70 ± 0.70
Flat SBR	0.32 ± 0.04
Roughened SBR	3.82 ± 0.03

FIGURE 2 Atomic force microscopy images of the flat styrene–butadiene rubber (SBR) substrate and the coated samples
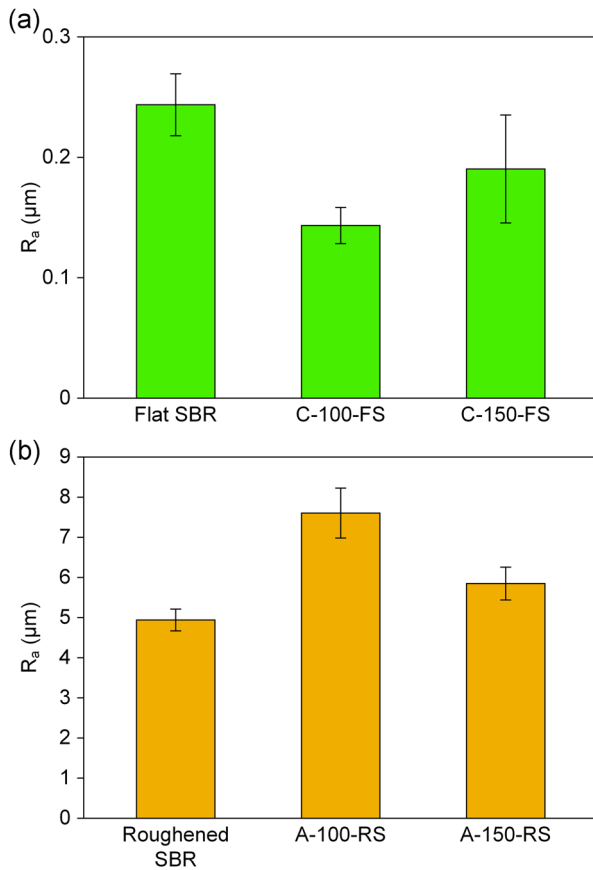

FIGURE 3 Average roughness (R_a) of the studied samples: (a) Flat styrene–butadiene rubber (SBR) substrate and coated samples and (b) mechanically roughened SBR and plasma-activated samples

the same regardless of the scanning speed and the thickness of the coatings was directly related to the deposition time. The R_a of the samples with mechanically roughened SBR substrates (Figure 3b) was obtained by contact profilometry. The plasma-activated samples (A-100-RS and A-150-RS) showed higher R_a values than the mechanically roughened SBR substrate, with sample A-100-RS being rougher than sample A-150-RS. This suggests that the plasma-activation treatments caused further roughening of the mechanically roughened SBR

substrate. Furthermore, it seems that using a lower scanning speed for sample A-100-RS (100 mm/s) than for sample A-150-RS (150 mm/s) roughened the SBR surface to a greater extent, which may have been due to longer exposure of the rubber to the plasma during the activation treatment at the lowest scanning speed.

A qualitative morphological analysis was also performed by SEM (Figures 4 and 5). In this case, proper images of both flat and mechanically roughened samples were obtained.

The flat SBR substrate showed fibrous structures, most of them oriented in the same direction. Furthermore, this substrate showed patches (white circles in Figure 4a–c) that were distributed all over its surface, which probably were crystallites of paraffin wax.[2,14] With the deposition of coatings on samples C-100-FS and C-150-FS, most of the fibrous features of the flat SBR substrate became less evident and lumpy features of 40–50 μm in diameter (white circles in Figures 4d, 4g, and 4h) grew over the aforementioned patches. SEM images at a magnification of ×5000 of the lumpy features (Figures 4e and 4i) and of the regions between them (Figure 4f) revealed that the plasma polymerization treatments had coated the substrate with small particles (<1 μm in diameter) that were formed by gas-phase plasma reactions,[28,29] thus generating a texture like the one that was observed in the AFM images (Figure 2b,c).

On the contrary, the mechanically roughened samples (Figure 5) showed very different morphologies and rougher surfaces than the flat samples (Figure 4). The roughened SBR substrate (Figure 5a) showed ridges that had been generated by elastomer deformation of the abraded rubber.[30] The plasma-activated samples (Figure 5b–e) looked even rougher than the mechanically roughened SBR substrate, which is in agreement with the profilometry results (Figure 3b). This roughening effect could have been due to a surface ablation by the plasma irradiation, as observed by other authors,[13] and seemed to affect both the ridges and the areas between them. The plasma activation treatments of samples A-100-RS and A-150-RS also generated cracks (white arrows in
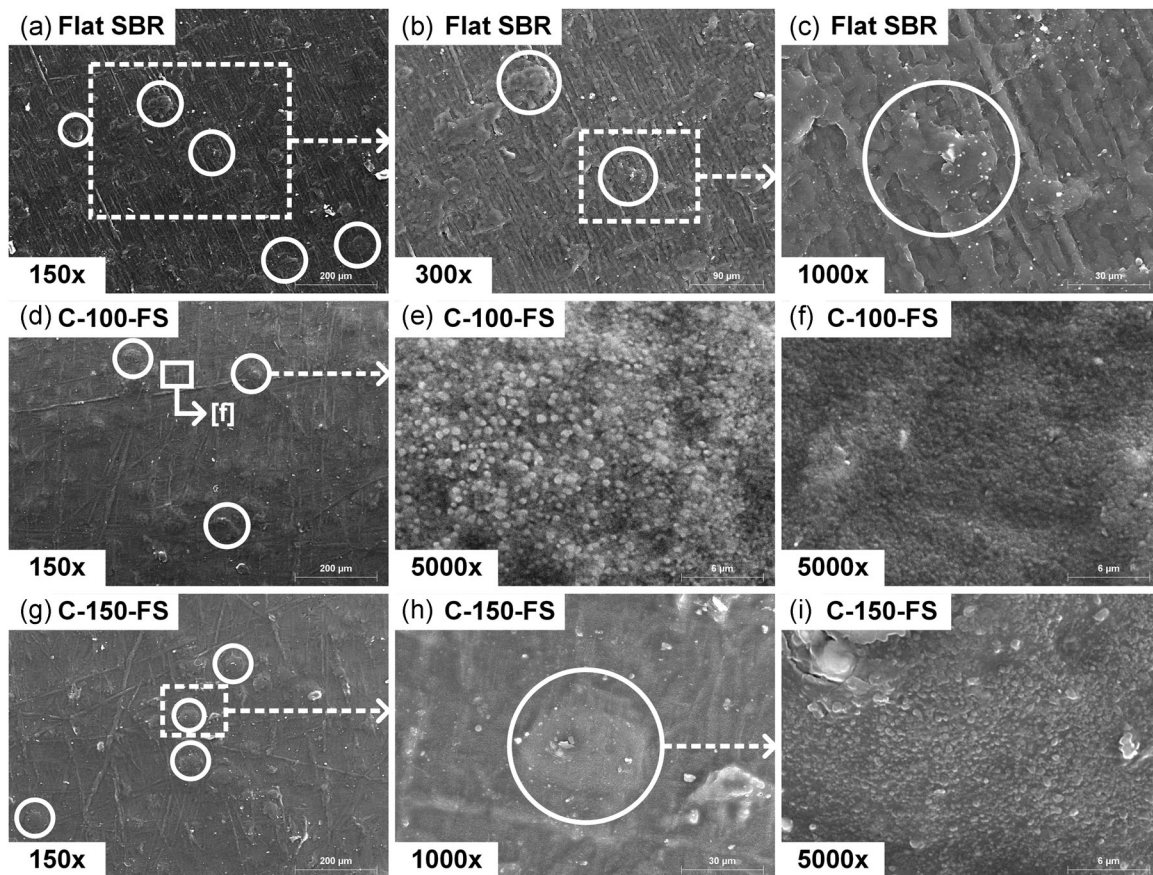
FIGURE 4 Scanning electron microscopy images of flat samples: (a–c) Flat styrene–butadiene rubber (SBR) substrate, and coated samples, (d–f) C-100-FS, and (g–i) C-150-FS

Figure 5b–e). It is known that ultraviolet (UV) radiation and ozone can cause surface cracking of rubber materials.[7,31] For instance, Moyano and Martín-Martínez[7] applied treatment with UV-ozone on SBR to improve its adhesion to PU adhesive for footwear applications and observed the formation of cracks on the treated surface. As UV radiation and ozone were produced with the air APPJ that was used in the present study, these were probably the causes of the formation of cracks at the surfaces of the plasma-activated samples A-100-RS and A-150-RS. Those cracks may have contributed to the improvement of the adhesive capacity of samples A-100-RS and A-150-RS by further roughening the surface of the mechanically roughened SBR substrate. Furthermore, a greater amount of cracks seemed to have been formed on sample A-100-RS than on sample A-150-RS. This was probably caused by the longer exposure to the plasma of sample A-100-RS, which was treated at a lower speed than sample A-150-RS. These observations are also in agreement with the results of contact profilometry (Figure 3b), which suggested that the roughening effect of the plasma activation treatment affected sample A-100-RS to a greater extent than sample A-150-RS.

3.3 | Chemical characterization

The selected samples were analyzed by XPS at different ages of the plasma treatments (0, 3, 6, and 30 days). The XPS analysis revealed that the surface chemistries of the samples were composed mainly of carbon, nitrogen, oxygen, and silicon (Table 3). At the age of 0 days, the most notable changes in the surface chemical compositions of the plasma-treated samples in comparison with those of the untreated SBR substrates were the decrease in the concentration of carbon and the increase in the concentration of oxygen. These facts suggest that a surface oxidation took place as a result of the plasma treatments. According to the lower carbon concentrations and higher oxygen concentrations that were found on the coated samples than on the activated ones, it seems that the surfaces of the coatings obtained by plasma polymerization of APTES were more oxidized than those of the SBR samples that were activated by air plasma irradiation. As the treated samples aged during storage, these changes were partially reverted.

As polar carbon–oxygen species, such as C–O, C=O, and COO−, have been identified as functional groups

FIGURE 5 Scanning electron microscopy images of mechanically roughened samples: (a) Roughened styrene–butadiene rubber (SBR) substrate, and plasma-activated samples, (b, c) A-100-RS, and (d, e) A-150-RS
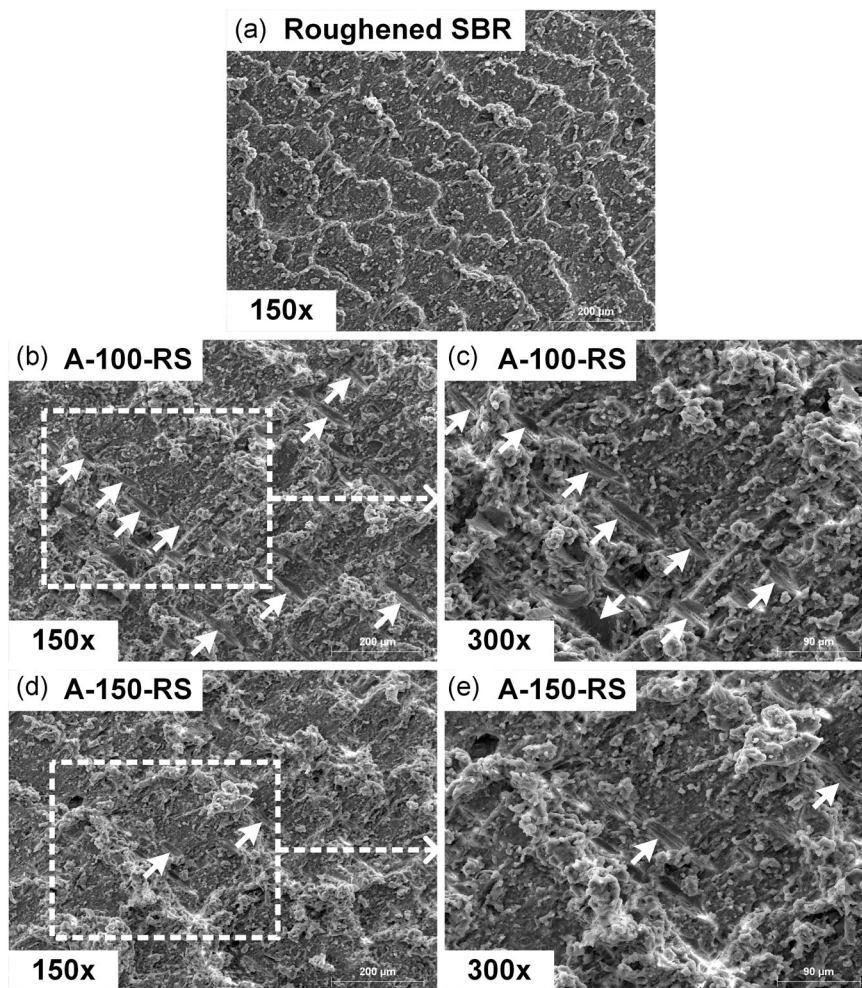
that are produced by the oxidation of rubbers and promote their adhesive capacity,[7,8,32] the high-resolution carbon region (C 1s) of the XPS spectra of the studied samples was deconvoluted to calculate the concentrations of those functional groups. The deconvolution consisted of four components, which were C–C/C–H at ~285 eV, C–O at ~286.4 eV, C=O at ~288 eV, and COO⁻ at ~289.2 eV.[32] Figure 6 shows the sum of the percentages of the oxygen-containing components as a measure of the concentration of surface polar carbon–oxygen species. The plasma-treated samples had greater concentrations of carbon–oxygen species than the untreated SBR substrates during practically all the aging study. Generally, the increments in the concentration of carbon–oxygen species in the plasma-treated samples were most notable at the age of 0 days. The fact that the greatest of such increments were in the coated samples (C-100-FS and C-150-FS) would be due mainly to the use of APTES as a precursor for the coatings, which provided carbon and oxygen for the plasma polymerization process. On the contrary, the less prominent increments observed for the plasma-activated samples (A-100-RS and

A-150-RS) were due to the interaction of the rubber surface and the plasma that was generated from the air.[14]

It is known that the aging of plasma-treated surfaces in nonpolar media like air may cause the surface polar species to reorientate into the subsurface, resulting in a reduction of the surface density of functional groups.[33] This was likely the reason why the surface carbon–oxygen species in all of the plasma-treated samples of this study generally decreased as the storage time increased.

According to the literature, amines (NH_2) are functional groups that can promote the adhesive properties of materials.[18–21] In a recent study by Inoue et al.,[19] a crucial role of amine functionalization of glass substrates in the improvement of the adhesion between glass and PU was identified, which was attributed to the enhanced adhesion of hydrophilic PU to amine-functionalized surfaces. ATR-FTIR analyses of the selected samples at different ages of the plasma treatments (0, 3, 6, and 30 days) were carried out to identify and evaluate the presence of

TABLE 3 Atomic concentrations of the main surface components of the studied samples

Sample	Age (days)	Surface chemical composition (at %)			
		C 1s	N 1s	O 1s	Si 2p
Flat SBR	–	94.10 ± 0.32	0.42 ± 0.14	4.94 ± 0.32	0.54 ± 0.12
Roughened SBR	–	97.59 ± 0.41	–	2.08 ± 0.25	0.33 ± 0.16
A-100-RS	0	86.54 ± 0.23	0.92 ± 0.35	11.53 ± 0.52	1.01 ± 0.13
	3	91.85 ± 1.26	0.55 ± 0.51	6.45 ± 0.57	1.14 ± 0.19
	6	94.14 ± 0.41	–	4.72 ± 0.32	1.14 ± 0.15
	30	96.35 ± 0.15	0.66 ± 0.23	2.49 ± 0.21	0.50 ± 0.12
A-150-RS	0	90.08 ± 0.25	0.62 ± 0.24	8.29 ± 0.42	1.01 ± 0.17
	3	91.67 ± 0.40	0.73 ± 0.27	5.91 ± 0.08	1.70 ± 0.24
	6	94.05 ± 0.41	–	4.77 ± 0.38	1.17 ± 0.05
	30	94.44 ± 0.35	1.12 ± 0.15	3.68 ± 0.31	0.76 ± 0.15
C-100-FS	0	69.23 ± 0.44	4.05 ± 0.27	22.27 ± 0.39	4.45 ± 0.21
	3	65.17 ± 0.21	5.83 ± 0.37	24.26 ± 0.47	4.75 ± 0.15
	6	67.01 ± 0.27	5.42 ± 0.24	22.88 ± 0.16	4.69 ± 0.07
	30	85.05 ± 1.11	1.90 ± 0.37	10.31 ± 0.67	2.74 ± 0.33
C-150-FS	0	70.48 ± 0.67	3.64 ± 0.23	21.23 ± 0.37	4.64 ± 0.12
	3	67.70 ± 0.67	5.04 ± 0.27	22.59 ± 0.62	4.67 ± 0.39
	6	71.90 ± 0.33	4.27 ± 0.25	19.34 ± 0.25	4.49 ± 0.04
	30	85.22 ± 1.11	1.98 ± 0.11	10.09 ± 1.00	2.71 ± 0.21

Abbreviation: SBR, styrene–butadiene rubber.

amine groups. The ATR-FTIR spectra of the plasma-treated samples did not change significantly with the passing of time, so Figure 7a shows the spectra of these samples at the age of 0 days, along with those of the untreated SBR substrates, to establish a comparison between different sample types.

The FTIR spectra show peaks that are caused by styrene at ~698 cm^{-1} (Figure 7a1)[7] and butadiene at ~908 and ~963 cm^{-1} (Figure 7a2),[2,7] which are characteristic of the SBR substrate and indicate that the penetration of the ATR-FTIR analysis (~1 μm) reached the substrate also in the coated samples (C-100-FS and C-150-FS). The peaks at ~718, ~1458, ~1643, ~2841, and ~2909 cm^{-1} (Figure 7a3) are due to the CH$_2$ groups of the rubber substrate, as well as those of the paraffinic oil and wax that are used as additives in the preparation of SBR.[2,3,7] The band at ~1101 cm^{-1} (Figure 7a4) that appeared in the FTIR spectra of all the studied samples was caused by the presence of silica filler in the SBR substrates. An additional reason for the presence of the CH$_2$ peaks (Figure 7a3) and silica band (Figure 7a4) in the FTIR spectra of the coated samples is that these were components of the coatings because they were provided by the APTES that was used as precursor. The decrease in the intensity of the peaks that correspond to CH$_2$ (Figure 7a3) from the FTIR spectrum of the flat SBR substrate to that of the mechanically roughened SBR substrate and those of the plasma-treated samples suggests that paraffin oil and wax were removed to some extent from the surface of SBR by the mechanical roughening and the plasma treatments. Furthermore, those low molecular weight substances seem to have been removed more effectively by the plasma treatments, whether the substrate was flat or roughened than by only applying a mechanical roughening to the SBR. The higher absorbance in the plasma-treated samples than in the untreated SBR substrates within the range of 1650–1700 cm^{-1} (Figure 7b) may be a sign of N–H bending,[34] which could have two possible origins: (1) The nitrogen from the air that was used to generate the plasma jet in all of the treatments and (2) the amines from the APTES that was added to the plasma specifically for the coating treatments of samples C-100-FS and C-150-FS. Nevertheless, absorbance in this range can also increase because the presence of C═O originated from the oxidation of the treated SBR.[7] Therefore, considering the possible overlapping of C═O and N–H in the FTIR spectra, along with the low atomic percentages of nitrogen (<6%) that were measured in the XPS analyses (Table 3), the results of the chemical characterization suggest that the presence of amine groups was not high enough to have a relevant effect in the adhesive capacity of the studied samples.
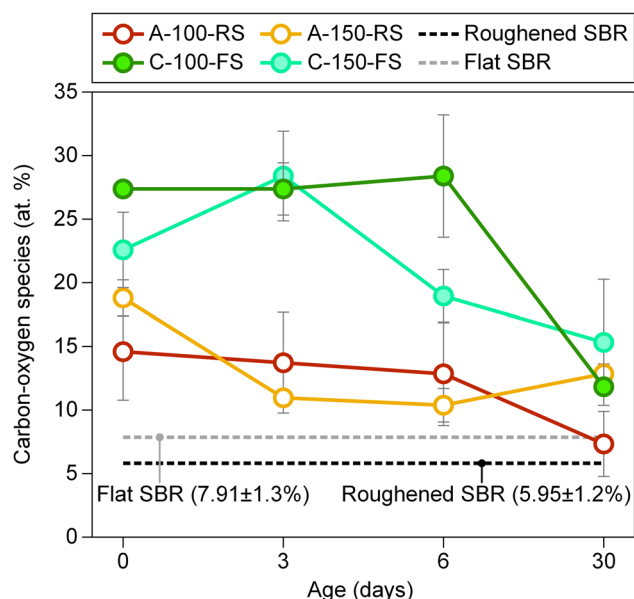

FIGURE 6 Concentration of surface carbon–oxygen species (sum of C–O, C═O, and COO$^-$) in the studied samples at different ages of the plasma treatments. SBR, styrene–butadiene rubber
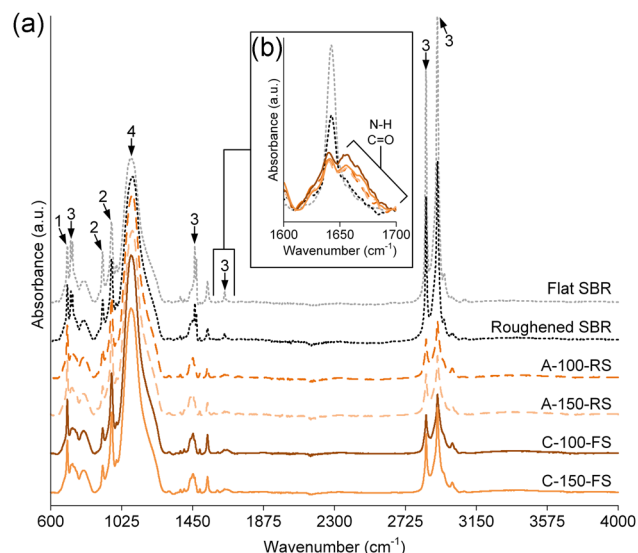

FIGURE 7 (a) ATR-FTIR spectra of the studied samples and (b) close view in the range of 1600–1700 cm^{-1}. For the sake of clarity, only the spectra at 0-day age are presented for the plasma-treated samples. ATR-FTIR, Fourier-transform infrared spectroscopy with attenuated total reflectance; SBR, styrene–butadiene rubber

3.4 | Effect of aging in the adhesive capacity of plasma-treated SBR

Samples A-100-RS, A-150-RS, C-100-FS, and C-150-FS were treated and stored for up to 30 days to study how the effectiveness of their plasma treatments was affected by aging

(Figure 8). Untreated SBR substrates (flat and mechanically roughened) that were bonded to leather parts on the same days as the plasma-treated ones were also included in this study. The bond strength was practically the same in all the tests that were performed on flat SBR substrates (~0.30 N/mm), whereas a greater variability was observed for the roughened SBR substrate, which gave bond strengths ranging between 2.60 and 4.90 N/mm. Although the mechanical roughening improved the adhesive capacity of untreated SBR, it seems that its effect was not always the same, which induced some variability in the bond strength results.

For each age of the treatments, all of the plasma-treated samples showed greater bond strengths than those of the untreated SBR substrates that were bonded on the same day. The unexpectedly low results of samples A-100-RS and A-150-RS at the beginning of this study (Figure 8, 0-day age), which were considerably lower than those obtained under the same conditions in the preliminary peel tests (Table 2), may have been due to the variability of the mechanical roughening.

Generally, the adhesive capacity of the plasma-treated samples tended to decrease as the treatments aged. This tendency is in agreement with the reduction in the concentration of carbon–oxygen functional groups that was observed in the chemical characterization (Figure 6), thus indicating that the surface chemistry was a factor that influenced the adhesive capacity of the plasma-treated samples. During the first days of aging, when the concentrations of carbon–oxygen species in the plasma-treated samples were higher than in later ages, a more effective contribution of the surface chemistry of the plasma-treated samples could be observed, thus resulting in higher bond strengths. As the concentration of carbon–oxygen species lowered with aging, the effectiveness of the surface chemistry of the plasma-treated samples was reduced, thus resulting in lower bond strength values.

The results that are shown in Figure 8 suggest that, for the first 2 days of aging, the coated samples C-100-FS and C-150-FS had greater adhesive capacities than the rest of the studied samples and were able to reach bond strength values that were clearly superior to 6 N/mm until the ages of 21 and 14 days, respectively. For longer storage times, their bond strength became lower than the 6 N/mm standard. Compared to the roughened SBR substrate with no plasma treatment, the coated samples showed improvements of 146.3% (C-100-FS) and 119.5% (C-150-FS) at the age of 0 days and, after 30-day aging, they still showed improvements of 21.9% (C-100-FS) and 75% (C-150-FS). Taking into account the average values of all the results obtained during the whole period of the study, whereas the roughened SBR substrate showed an average bond strength of 4.05 ± 0.8 N/mm, the coated samples showed average bond strengths of 7.39 ± 1.74 N/mm (C-100-FS) and 7.74 ± 1.47 N/

FIGURE 8 Bond strength values of the untreated styrene–butadiene rubber (SBR) substrates and the selected plasma-treated samples at different periods of storage after the plasma treatments: (a) Activated samples and (b) coated samples. The ages are the amounts of days during which the samples were stored between the application of the plasma treatments and the bonding with the leather parts

mm (C-150-FS). Therefore, overall improvements of 82.69% (C-100-FS) and 91.35% (C-150-FS) in the bond strength of the coated samples can be considered in comparison with the bond strength of the mechanically roughened SBR substrate for the 30 days that followed the coating treatments. Considering that roughening is one of the effects of mechanical and chemical preparation methods that improve the adhesive capacity of rubber surfaces, a contribution of the morphologies of the coated samples C-100-FS and C-150-FS in their improved bond strength seems unlikely because they were smoother than the flat SBR substrate (Figure 3a). Nevertheless, these samples showed the highest concentrations of polar carbon–oxygen species at almost any age in the XPS analyses (Figure 6). Therefore, it can be concluded that the improvement of the adhesive capacity of the flat SBR substrates that were coated by plasma-polymerization (i.e., samples C-100-FS and C-150-FS) was mainly due to the modification of their surface chemistry.
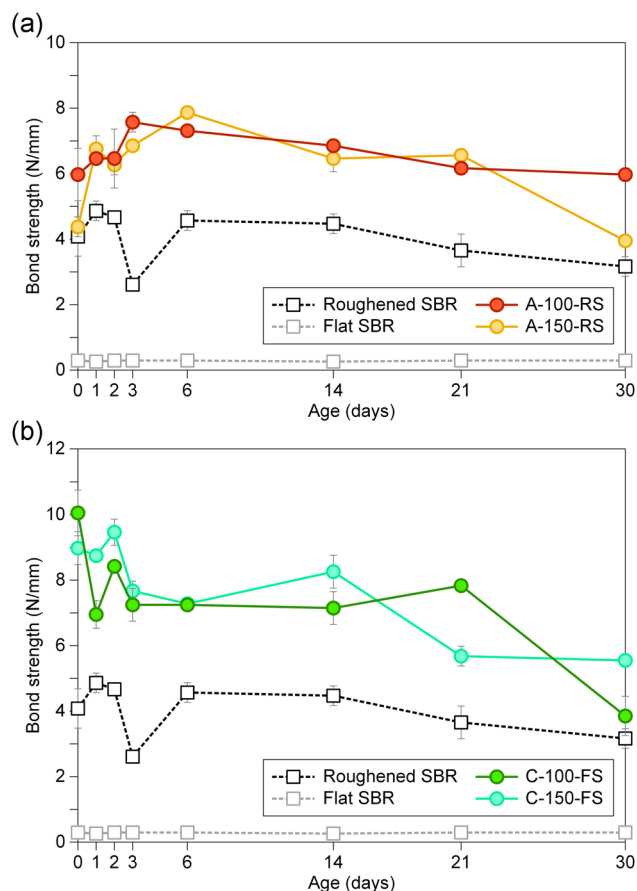
Regarding the plasma-activated samples A-100-RS and A-150-RS, they could meet the 6 N/mm or above standard until the age of 21 days and their average bond strength values for the whole study were 6.63 ± 0.6 N/mm (A-100-RS) and 6.17 ± 1.32 N/mm (A-150-RS), thus reaching overall improvements of 64% (A-100-RS) and 52.6% (A-150-RS) in the average bond strength of the roughened SBR substrate. As observed in their profilometry results (Figure 3b) and SEM images (Figure 5), samples A-100-RS and A-150-RS were rougher than the mechanically roughened SBR substrate as a result of an additional roughening induced by ablation and cracking effects of the plasma irradiation. Furthermore, these samples also showed higher concentrations of polar carbon–oxygen species than the mechanically roughened SBR substrate in the results of the XPS analyses (Figure 6). Therefore, one can conclude that both morphological and chemical modifications contributed to the improvement of the adhesive capacity of the mechanically roughened SBR substrates that were treated by plasma activation (i.e., samples A-100-RS and A-150-RS).

By comparing the results of the activated and coated samples with each other, one can see that the improvements in the adhesive capacity of the activated samples were not as high as those obtained with the coated samples. Furthermore, the possibility of activated samples giving bond strengths less than 6 N/mm at the age of 0 days (Figure 8) has been observed. Considering these facts, it can be concluded that the application of coatings by plasma polymerization on flat SBR (i.e., samples C-100-FS and C-150-FS) was more effective and had a clearer capacity of meeting high adhesion standards than the plasma activation of mechanically roughened SBR (i.e., samples A-100-RS and A-150-RS).

4 | CONCLUSIONS

In this study, the application of atmospheric pressure plasma treatments on SBR parts before bonding with leather parts improved the adhesion of the joint when these materials were bonded with each other by means of PU adhesive. The adhesive capacity of the plasma-treated SBR seemed to be favored by two factors: (1) The increase of roughness that was due to surface morphological changes and (2) the increase in the concentration of polar carbon–oxygen species that was due to the modification of the surface chemistry. Depending on whether the SBR substrate was mechanically roughened before the plasma treatment (flat or roughened SBR), the type of treatment that was applied (activation by plasma irradiation or coating by plasma-polymerization) and the time that passed between the plasma treatment and the bonding with the leather parts, each of the two mentioned factors

(i.e., morphological and chemical factors) contributed to a greater or lesser extent in improving the adhesion.

From preliminary peel tests that combined both types of plasma treatments (activation and plasma polymerization) with flat and mechanically roughened SBR substrates, two ways of optimizing the processing of the SBR parts for the sake of simplicity and industrial applicability were identified and further studied: (1) Applying plasma polymerization treatments to flat SBR substrates or (2) mechanically roughening the SBR substrates and applying plasma activation treatments.

For coated, flat SBR (i.e., samples C-100-FS and C-150-FS), which was smoother than the flat SBR substrate, a contribution of the morphological factor in the improvement of its adhesive capacity seems unlikely. Therefore, the chemical factor would be the main cause of its improved adhesive capacity because of the concentration of polar carbon–oxygen species in its surface chemistry, which was generally greater than for the rest of the studied cases.

For plasma-activated, mechanically roughened SBR (i.e., samples A-100-RS and A-150-RS), it can be concluded that both morphological and chemical factors contributed to improve the adhesive capacity. Regarding surface morphology, the changes that are caused by the mechanical roughening process improve the adhesive capacity of the roughened SBR substrate, in comparison with the flat SBR substrate. Furthermore, the subsequent plasma treatment causes surface ablation and generates cracks that seem to further roughen the SBR surface and, hence, further improve its adhesive capacity. Regarding the surface chemistry, an increase in the concentration of polar carbon–oxygen species is produced in the plasma-activated SBR compared to the untreated substrates, which is especially notable during the first days after the plasma treatments and favors the adhesive capacity.

As observed for all the studied samples, both the concentration of carbon–oxygen species and the adhesion tend to decrease as the plasma treatments age. Therefore, it can be concluded that the longer the time that passes between the plasma treatments and the bonding with the leather parts, the lesser the contribution of the chemical factor in the improvement of the adhesive capacity of the SBR parts. Thus, during the first days of aging of the plasma-treated SBR (when the surface chemistry was most effective) greater bond strength values were generally reached than after 30-day aging (when the effectivity of the surface chemistry was diminished).

Finally, it was concluded that the plasma-polymerization of coatings on flat SBR was more effective at improving the adhesive capacity of SBR and had a clearer capability of meeting high adhesion standards than the plasma activation of mechanically roughened SBR. More specifically, the

coating treatment at 100 mm/s on flat SBR (i.e., sample C-100-FS) is considered the most favorable in this study. Compared to the common industrial solution of using a mechanically roughened SBR substrate, this coating treatment achieved an overall improvement of 82.69% in the bond strength when the SBR part was bonded to the leather part within the 30 days following the treatment. Furthermore, it was able to meet the most restrictive requirement in the UNE standards regarding the bond strength between outsoles and upper parts of footwear (≥6 N/mm for school footwear)[27] until 21 days after coating deposition. This suggests longer suitability for high-performance applications than the 14 days that were measured for the coating that was deposited at 150 mm/s.

In future research, in a closer approach to the conditions of footwear manufacturing, similar treatments will be applied to real SBR outsoles by adapting the treatment setup to their geometry.

CONFLICT OF INTERESTS
The authors have declared that there are no conflict of interests.

DATA AVAILABILITY STATEMENT
Research data are not shared.

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