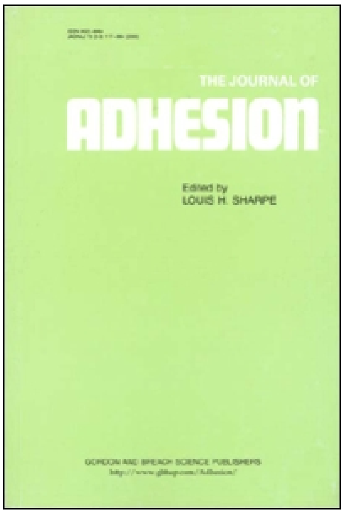

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Treatment of vulcanized styrene-butadiene rubber (SBR) with mixtures of Trichloroisocyanuric Acid and Fumaric Acid

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TREATMENT OF VULCANIZED STYRENE-BUTADIENE RUBBER (SBR) WITH MIXTURES OF TRICHLOROISOCYANURIC ACID AND FUMARIC ACID

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In this study, mixtures of trichloroisocyanuric acid (TCI) and fumaric acid (FA) solutions were applied to a difficult-to-bond, vulcanized styrene-butadiene rubber (R2) to analyze the combined effect of both surface treatments. The treated R2 rubber surfaces were characterized using advancing contact angle measurements, ATR-IR and XPS spectroscopy, and SEM. T-peel tests of treated R2 rubber/polyurethane adhesive/leather joints have been obtained in order to quantify the adhesion properties. The wettability of R2 rubber was improved by treatment with 3 wt% TCI/EA (ethyl acetate) or 0.5 wt% FA/EtOH, and lower contact angles were obtained by treatment with both 3 wt% TCI/EA and 0.5 wt% FA/EtOH. The improved wettability was ascribed to the creation of carbon-chlorine moieties, the removal of zinc stearate and paraffin wax, and the creation of surface roughness on the R2 rubber surface. Treatment of R2 rubber with 3 wt% TCI/EA before or after treatment with 0.5 wt% FA/EtOH, or with a solution containing 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture produced a noticeable increase in peel strength. Always, the effects of the treatment of R2 rubber with 3 wt% TCI solution were dominant over those produced by treatment with 0.5 wt% FA solution in ethanol (FA/EtOH). On the other hand, the treatment of R2 rubber with 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture was more effective than the treatment with 0.5 wt% TCI/EA+ 2 wt% FA/EtOH because the lower amount of chlorinating agent in this mixture.

Keywords: Vulcanized SBR rubber; Treatment with trichloroisocyanuric acid; Treatment with fumaric acid; Contact angle measurements; ATR-IR spectroscopy; XPS; SEM Peel strength

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INTRODUCTION

It has been previously established [1, 2] that the treatment of synthetic vulcanized styrene-butadiene rubber (SBR) with fumaric acid (FA) solutions avoids the migration of antiadherent moieties to the surface, giving improved adhesion to polyurethane adhesive. On the other hand, the treatment with trichloroisocyanuric acid (TCI) solutions has been proved [3, 4] to be effective in enhancing the adhesion of several rubbers to epoxy and polyurethane adhesives.

Halogenation with trichloroisocyanuric acid (TCI) solutions is a common surface treatment to improve the adhesion of rubber materials [4–8]. Due to the nonpolar nature and lack of wettability of most of the rubbers (both limiting their bonding with adhesives in the shoe and automotive industries [6, 9]), a surface treatment is required [10–13]. The treatment of vulcanized SBR rubbers with TCI solutions improves the wettability and produces chemical (C–Cl and C=O moieties) and morphological (cracks and roughness) modifications [14, 15] on their surfaces. These modifications justify their increased adhesion to polyurethane adhesive.

Alternatively to the halogenation treatment, in previous papers [16–18] different surface treatments have been proposed to enhance the adhesion properties of vulcanized rubbers; one of them is the application of carboxylic acid solutions [1, 2, 19, 20]. The application of FA (*trans*-1,2-ethylenedicarboxylic acid) solutions provides noticeable increase in the adhesion of vulcanized SBR rubber to polyurethane adhesive. This increase in adhesion has been ascribed to an enhancement in the surface energy of the rubber (formation of C=O and C–OH moieties by surface oxidation) and the formation of a barrier that avoids the migration of antiadherent moieties to the rubber-polyurethane interface [2, 20].

In previous papers, the surface modifications produced by treatment of different SBR rubbers with only TCI or only FA has been extensively studied. However, the treatment with mixtures of TCI and FA has not been considered. Therefore, in this study the surface modifications and adhesion properties of a difficult-to-bond vulcanized SBR rubber were assessed by treatment with only TCI or FA solutions, by treatment with FA solution before or after treatment with TCI solution, and finally by treatment with TCI + FA mixture solution.

The surface modifications produced by halogenation with TCI solutions or by treatment with FA solutions depend on several factors, such as the formulation and nature of the rubber, concentration of the solutions, nature of the solvent, treatment time, etc. [3, 5, 7, 8, 21, 22]. For this reason, in this study mainly solutions containing 3 wt% TCI/ethyl acetate and 0.5 wt% FA/ethanol have been used.

EXPERIMENTAL

Materials

A sulfur-vulcanized SBR rubber (R2) prepared using a molding process (at 150°C for 50 min) after open-mill mixing was used in this study. The formulation and some physical properties of R2 rubber are given in Tables 1 and 2, respectively. The R2 rubber contains precipitated silica as filler and zinc stearate as antioxidant. During the vulcanization process, the zinc oxide reacts with stearic acid, producing more zinc stearate. The R2 rubber formulation also includes a microcrystalline paraffin wax as antiozonant. It has been established that both the microcrystalline paraffin wax and the zinc stearate are responsible for the poor adhesion of the R2 rubber [23].

To determine the adhesion, T-peel tests of R2 rubber treated with 3 wt% TCI/EA before or after treatment with 0.5 wt% FA/EtOH/polyurethane adhesive/leather joints were carried out. The polyurethane adhesive solution was prepared by dissolving 18 wt% Desmocoll 540 pellets (Bayer, Leverkusen, Germany) in methyl ethyl ketone (MEK) in a Cowles laboratory mixer (2000 rpm for 2h). A Brookfield viscosity of 5.8 Pa.s (23°C) was obtained.

TABLE 1 Formulation of Synthetic Vulcanized Styrene-Butadiene Rubber R2

Ingredient	Percentage (phr)
SBR 1502	100
Precipitated silica	42
Sulfur	2.0
Cumarone-indene resin	5.0
Zinc oxide	1.5
Stearic acid	2.4
N-cyclohexyl-2-benzothiazole sulphenamide	2.0
Phenolic antioxidant	0.5
Dibenzothiazyl disulfide	2.5
Microcrystalline paraffin wax	0.8
Hexamethylene tetramine	1.0
Zinc stearate	5.4

Composition in parts per hundred parts of rubber (phr).

TABLE 2 Some Physical Properties of the Styrene-Butadiene Rubber R2 (UNE Standard Procedures 53-510, 53-516, 53-527, 53-130, and 53-526)

Property	Value
Tensile strength	11.4 MPa
Elongation at break	612 %
Tear resistance	14.7 kN/m
Abrasion resistance	201 mm^3
Hardness	72 °ShoreA
Density	1.1 g/cm^3

The leather used to produce the adhesive joints was a chromium-tanned bovine leather, and some of its properties are: Tensile strength = 13 MPa; Elongation-at-break = 60%; Ash content (950°C) $<$ 5 wt%.

Description of the Surface Treatments

The R2 rubber test pieces (150 × 30 × 6 mm) were treated using the following three different procedures.

1. Treatment with only 3 wt% TCI/EA or 0.5 wt% FA/EtOH solution.
2. A solution of 0.5 wt% FA/EtOH before or after chlorination with a solution of 3 wt% TCI/EA. After application of the first solution, 1 h was allowed for solvent evaporation before applying the second solution.
3. Treatment with 3 wt% TCI/EA + 0.5 wt% FA/EtOH (50:50, w:w) or 0.5 wt% TCI/EA + 2 wt% FA/EtOH (50:50, w:w) mixtures (the use of 2 wt% FA/EtOH has been considered instead of 3 wt% FA/EtOH solution, due to the low solubility of fumaric acid in ethanol).

All treatments were applied on the R2 rubber surface using a brush. One hour was allowed prior the application of the polyurethane adhesive or the surface characterization of the rubber.

Experimental Techniques

Contact Angle Measurements

The wettability of the as-received and treated R2 rubber surfaces was evaluated from contact angle measurements using a *Ramé-Hart 100* goniometer (Mountain Lakes, NJ, USA). The R2 rubber test pieces were placed into a hermetic and isothermal (25°C) chamber of the goniometer previously saturated with water vapor for at least 10 min before placing the drop. Drops (4 μl) of twice-distilled and deionized water (test liquid) were placed on the treated R2 rubber surface. The tilting plate method was used to measure the advancing contact angle values and a micrometric syringe *(Hamilton Instruments*, Nevada, USA) provided with a flat-end needle was used. These advancing contact angle values were obtained 15 min after the water drop was placed on the treated R2 rubber surface. At least three drops on two identically treated R2 rubber samples were measured and averaged. The experimental error was ±2 degrees.

Attenuated Total Multiple Reflection Infrared (ATR-IR) Spectroscopy

A *Brucker Vector* 22 (Weissemboug, Germany) spectrometer was used to obtain the IR spectra of the as-received and treated R2 rubber surfaces. The attenuated total multiple reflection technique (ATR) was used to analyze the chemical modifications produced in about 5 μm depth of the R2 rubber surface. A ZnSe crystal was used. 200 scans with a resolution of 4 cm^{-1} were obtained and averaged. The incident angle of the IR radiation was 45°.

The loci of failure of the adhesive joints were assessed by analyzing the ATR-IR spectra of the failed surfaces obtained after T-peel tests.

X-Ray Photoelectron Spectroscopy (XPS)

Chemical modifications produced on the outermost surface (about 5 nm) of the treated R2 rubber were analyzed using a *VG Scientific Microtech Multilab* spectrometer (Surrey, UK) with a Mg-K_α X-ray Source (1253.6 eV). The analyzer operated at 15 keV and 300 watts, and the incident angle was 45°. The analysis was performed on 5×2 mm R2 rubber surfaces at a residual pressure below 5×10^{-8} Torr. For each sample, a survey scan encompassing the region 0–1200 eV was first obtained. High resolution XPS of all photopeaks were obtained 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. Atomic concentration calculations were carried out using a *VGX900-W* system.

Scanning Electron Microscopy (SEM)

The roughness and heterogeneities produced on the treated R2 rubber surfaces were analyzed using a *JEOL JSM-840 SEM* (Peabody, MA, USA). The rubber samples were gold coated before analysis, and the energy of the electron beam was 20 kV.

T-Peel Strength Test

Treated R2 rubber/polyurethane adhesive/leather joints were prepared using the following procedure. One hour after treatment of the R2 rubber, 0.8 ml of polyurethane adhesive solution was applied on the R2 rubber surface. The leather surface was roughened in a *Superlema S.A.* (Zaragoza, Spain) roughening machine operating at 2800 rpm. A P100 aluminium oxide abrasive cloth was used to produce roughening, and about 0.5 mm of leather were removed (until the corium was exposed at the surface). The adhesive solution (0.8 ml) was then applied to the roughened leather surface to fill the pores, and 30 min later additional 0.8 ml of adhesive solution was applied on the leather surface to assure that sufficient adhesive was available to produce the joint. Afterwards, the solvent of the adhesive solutions applied on the R2 rubber and the leather surfaces was allowed to evaporate for 45 min. Then, the dried solid adhesive films were melted at 100°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 (Canton, Massachussetts, USA). A peeling rate of 0.1 m/min was used. Five replicates for each adhesive joint were tested and averaged. The experimental error was less than 1.0 kN/m.

RESULTS AND DISCUSSION

Treatment of R2 Rubber with 0.5 wt% FA/EtOH Solution Before or After Treatment with 3 wt% TCI/EA Solution, and with 3 wt% TCI/EA + 0.5 wt% FA/EtOH Mixture Solution

The water-advancing contact angle values on the as-received and differently treated R2 rubber surface are given in Figure 1. The as-received R2 rubber shows a high contact angle (103 degrees) due to the high concentration of hydrocarbon moieties on its surface (Tables 3a and 3b). According to Table 3a, the as-received R2 rubber shows a low O/C ratio, due to the nonpolar hydrocarbon moieties on its surface. Therefore, the as-received R2 rubber shows a poor wettability. All treatments decrease the advancing contact angle values of R2 rubber, and similar values (87–90 degrees) are obtained by treatment with solutions of 0.5 wt% FA/EtOH or 3 wt% TCI/EA. This decrease in the contact angle values is due to an increase in polarity (Table 3a) and/or surface roughness, and wettability of the treated R2 rubber. The decrease in advancing contact angle values is more marked (70–71 degrees) when the treatment is carried out with 0.5 wt% FA/EtOH applied before or after treatment with 3 wt% TCI/EA,

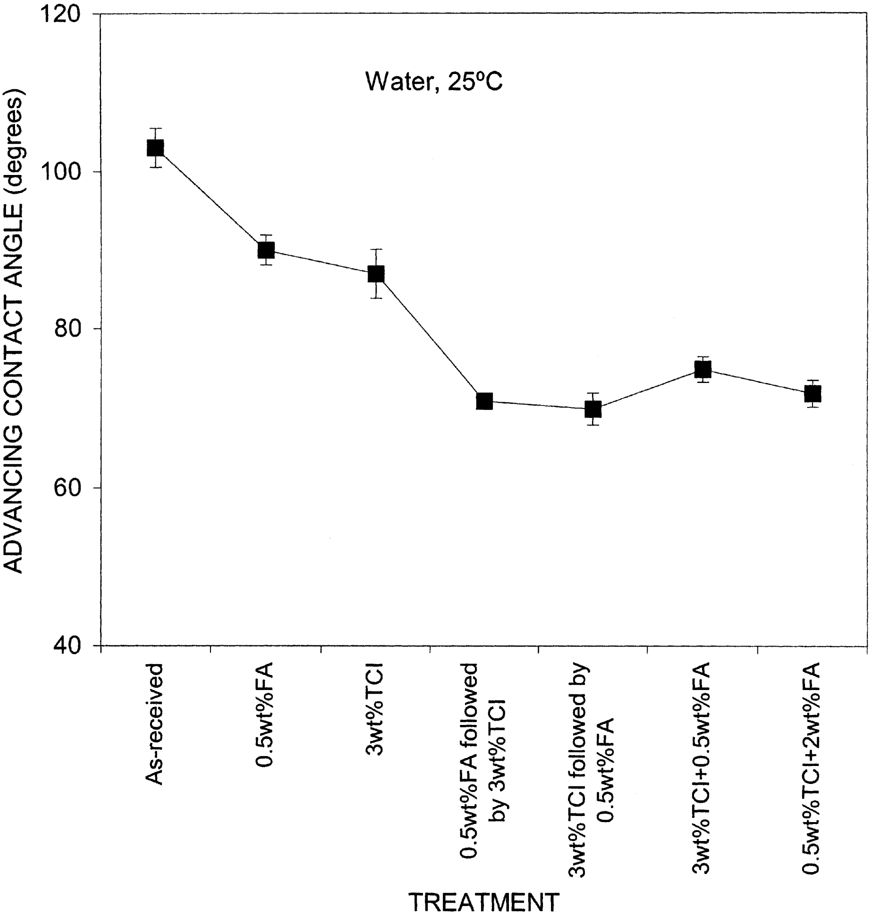


FIGURE 1 Advancing contact angle values (water, 25°C) on the as-received and treated R2 rubber.

indicating improved wettability. Furthermore, the treatment with 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture gives a contact angle value of 75 degrees. Therefore, the treatment with 3 wt% TCI/EA and 0.5 wt% FA/EtOH allows greater wettability of R2 rubber, irrelevant to the sequence of application of the solutions on the rubber.

The ATR-IR spectrum of the as-received R2 rubber (Figure 2) shows the bands due to butadiene and styrene. Bands at 2919 and 2851 cm^{-1} correspond to C–H stretching (CH_2 groups) in the butadiene units. Other butadiene absorption bands are CH_2 in-plane

TABLE 3a Atomic Percentages of Elements on the As-received and Treated R2 Rubber

		Treatment					
Element	As-received (at%)	0.5 wt% FA (at%)	3 wt% TCI (at%)	0.5 wt% FA followed by 3 wt% TCI (at%)	3 wt% TCI followed by 0.5 wt% FA (at%)	3 wt% TCI + 0.5 wt% FA (at%)	0.5 wt% TCI + 2 wt% FA (at%)
C1s	94.9	93.8	78.0	78.2	77.0	78.1	77.4
O1s	3.8	3.9	10.6	10.6	12.9	11.2	11.1
N1s	—	0.2	3.6	3.1	2.6	2.9	2.6
Si2p3	1.1	1.8	2.4	2.1	3.4	3.0	4.4
Zn2p3	0.2	0.1	—	—	—	0.1	0.2
S2p3	—	0.2	0.6	0.6	0.5	0.4	1.4
Cl2p3	—	—	4.8	5.4	3.6	4.3	2.9
O/C	0.04	0.04	0.14	0.14	0.17	0.14	0.14

TABLE 3b Percentage of Species in the As-Received and Treated R2 Rubber

			Treatment					
Species	Binding energy (eV)	As-received (at%)	0.5 wt% FA (at%)	3 wt% TCI (at%)	0.5 wt% FA followed by 3 wt% TCI (at%)	3 wt% TCI followed by 0.5 wt% FA (at%)	3 wt% TCI + 0.5 wt% FA (at%)	0.5 wt% TCI +2 wt% FA (at%)
C–C, C–H	285.0	93.2	93.0	72.2	69.7	76.3	65.6	80.4
C–O, C–Cl	286.5	6.8	7.0	25.2	26.1	20.7	31.5	19.6
C=O	288.0	—	—	0.4	1.9	—	2.1	—
COO^-	290.0	—	—	2.2	2.3	3.0	0.8	—

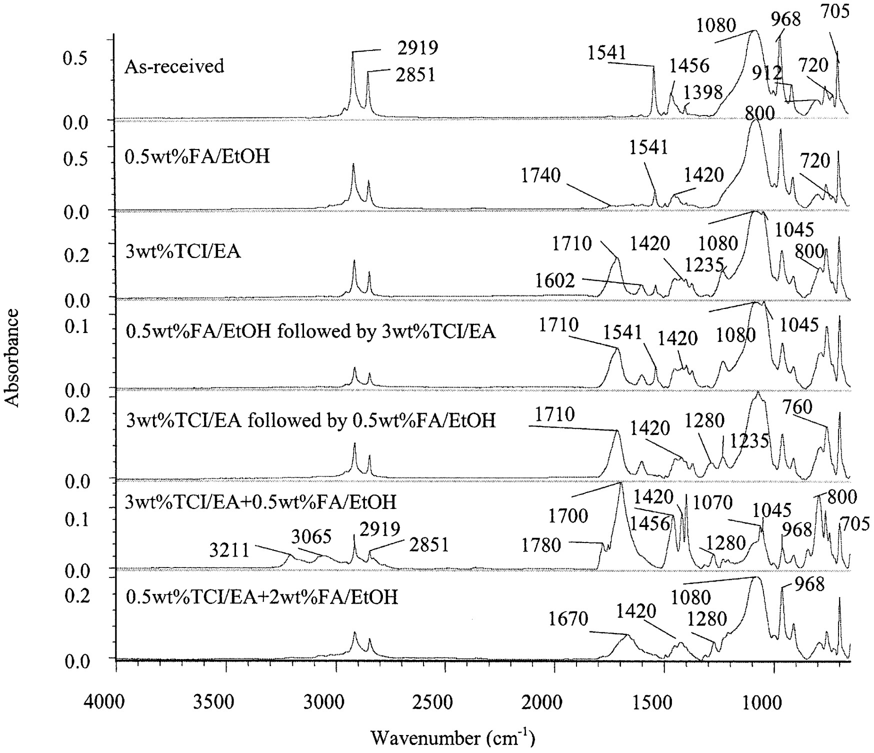
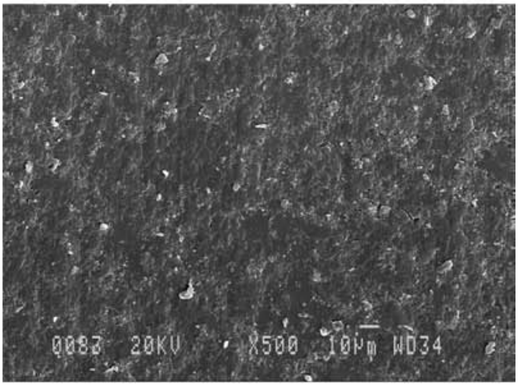


FIGURE 2 ATR-IR spectra of the as-received and treated R2 rubber.

deformation ($1456\,cm^{-1}$), *trans*-1,4-C=C stretching ($968\,cm^{-1}$) and C–H out-of-plane bending in C=CH groups ($800\,cm^{-1}$). Styrene absorption occurs at $705\,cm^{-1}$ and $912\,cm^{-1}$ (C–H out-of-plane deformation) and $1602\,cm^{-1}$ (aromatic C–C). The microcrystalline paraffin wax contributes to the high intensity of the bands at 2919, 2851, 1456, and $720\,cm^{-1}$ (CH_2 rocking) [24]. The band at $1541\,cm^{-1}$ is typical of zinc stearate [23], and the band at $1080\,cm^{-1}$ is due to the silica filler (Si–O stretching). According to XPS (which analyzes about 5 nm of the outermost rubber surface), the as-received R2 rubber surface is mainly composed of carbon (94.9 at%, 285.0 eV) and a small amount of oxygen (3.8 at%, 532.0 eV) and silicon (1.1 at%, 102.0 eV) (Table 3a). Carbon corresponds mainly to C–C and C–H species (Table 3b) likely due to the microcrystalline paraffin wax migrated to the R2 rubber surface, and most of oxygen corresponds to silica filler and a small amount of zinc stearate. Therefore, similar information is obtained for the as-received R2 rubber by using ATR-IR and XPS spectroscopy. Because of the presence of paraffin wax and zinc stearate and the lack of surface roughness (Figure 3), a low adhesion is obtained in the adhesive joint produced with the as-received R2 rubber (Figure 4). The locus of failure of the as-received R2 rubber/PU adhesive/leather joint was assessed by ATR-IR spectroscopy of the failed surfaces. In this study, the surface which visually corresponds to the adhesive surface was called the A surface, and that corresponding to the R2 rubber was called the R surface. Figure 2 shows the ATR-IR spectrum of the as-received R2 rubber, and Figure 5 shows the ATR-IR spectra of the PU adhesive and the leather used to make the joints before bond formation. Figure 5 shows the typical bands of the polyurethane: NH_2 stretching absorption at $3350\,cm^{-1}$, C–H stretching bands of CH_2 groups in the polyurethane (2860, $2939\,cm^{-1}$), C=O stretching due to urethane at $1730\,cm^{-1}$, NH_2 bending absorption at $1602\,cm^{-1}$, N=C=O symmetric stretching absorption at $1531\,cm^{-1}$, and C–O stretching bands at 1168, 1228, and $1267\,cm^{-1}$. On the other hand, the leather used to make the joints shows the bands due to N–H stretching ($3310\,cm^{-1}$), C–H stretching in CH_2 groups (2930, $2853\,cm^{-1}$), C=O stretching ($1650\,cm^{-1}$), N–H in-plane bending and C–N stretching ($1545\,cm^{-1}$), and C–N stretching ($1242\,cm^{-1}$) and C–O stretching ($1030\,cm^{-1}$). Figure 6a shows the ATR-IR spectra of the failed surfaces obtained after the peel test of the as-received R2 rubber/PU adhesive/leather joint. The ATR-IR spectrum of the A surface shows similar bands to that of the PU and additional bands at 2851 and $2919\,cm^{-1}$ (due to CH_2 of the paraffin wax). On the other hand, the ATR-IR spectrum of the R surface shows the same bands as that of the as-received R2 rubber before joint formation (Figure 2), although the bands at 720, 2851, and $2919\,cm^{-1}$ of CH_2 groups are less intense, and the band at $1080\,cm^{-1}$ due to Si-O becomes more intense. Therefore, during joint formation the paraffin wax on the as-received R2 rubber surface is transferred to the adhesive surface, and therefore the failure occurs in a weak boundary layer of paraffin wax on the R2 rubber surface.

The treatment of R2 rubber with 0.5 wt% FA/EtOH creates a new small band at $1420\,cm^{-1}$ (C–O stretching and C–O–H in-plane bending) due to fumaric acid (Figure 2); furthermore, the relative intensity of the CH_2 groups due to the paraffin wax is reduced. On the other hand, zinc stearate is partially removed by the treatment. XPS shows that the treatment of R2 rubber with 0.5 wt% FA/EtOH produces a slight increase in silicon, a reduction in zinc, and the appearance of a small amount of sulfur from N-cyclohexyl-2-benzothiazole sulphenamide and/or dibenzothiazyl disulfide (compounds in the rubber

As-received



0.5 wt% FA/EtOH

3wt% TCI/EA

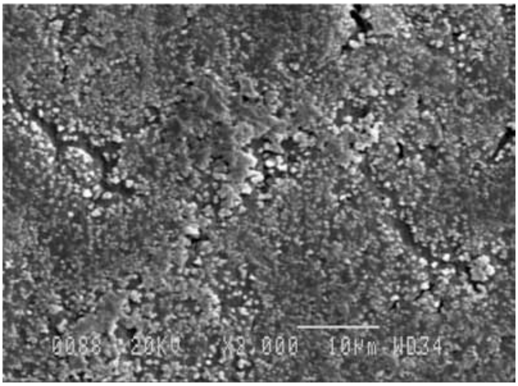
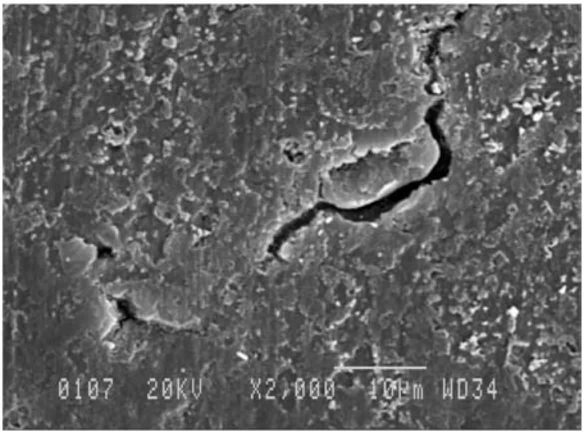


FIGURE 3 SEM micrographs of the as-received and treated R2 rubber. (Continued).

0.5 wt% FA/EtOH followed by 3 wt%TCI/EA



3 wt% TCI/EA followed by 0.5 wt% FA/EtOH

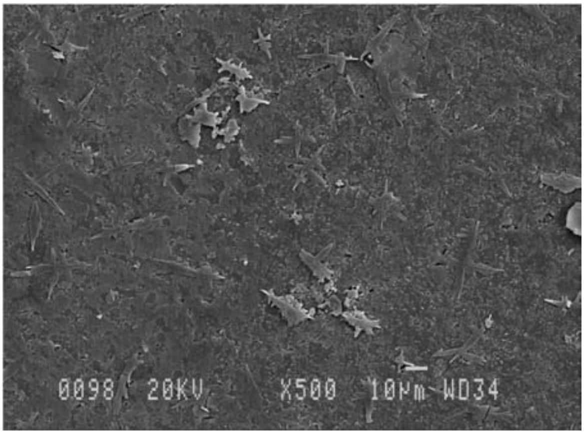
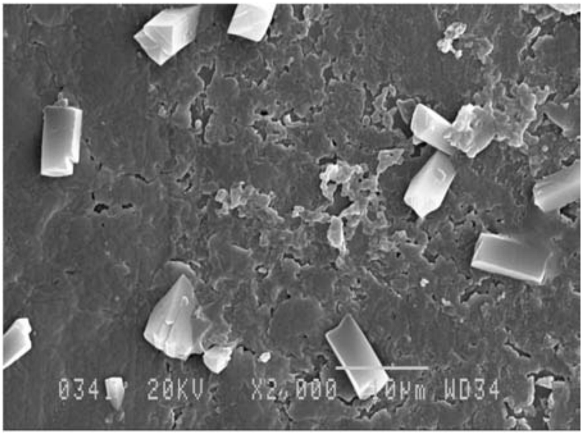


FIGURE 3 Continued.

formulation) (Table 3a). Therefore, the treatment with fumaric acid deposits carboxylic acid moieties on the R2 rubber surface and partially removes the paraffin wax and zinc stearate. The SEM micrograph (Figure 3) shows the presence of unreacted fumaric acid crystals (irregular shapes) on the R2 rubber surface which may act as a contaminant, giving reduced adhesion (Figure 4). The ATR-IR

3 wt% TCI/EA+0.5 wt% FA/EtOH



0.5 wt% TCI/EA + 2 wt% FA/EtOH

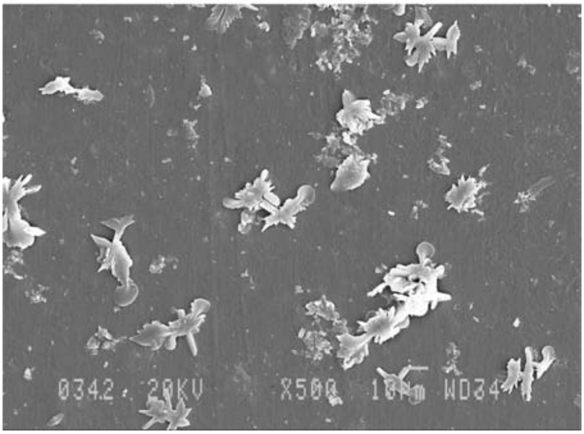


FIGURE 3 Continued.

spectra of the failed A and R surfaces of the 0.5 wt% FA/EtOH-treated R2 rubber/polyurethane adhesive/leather joint are similar to those observed in Figure 6a for the as-received R2 rubber/polyurethane adhesive/leather joint.

The R2 rubber treated with 3 wt% TCI/EA shows the following noticeable surface modifications:

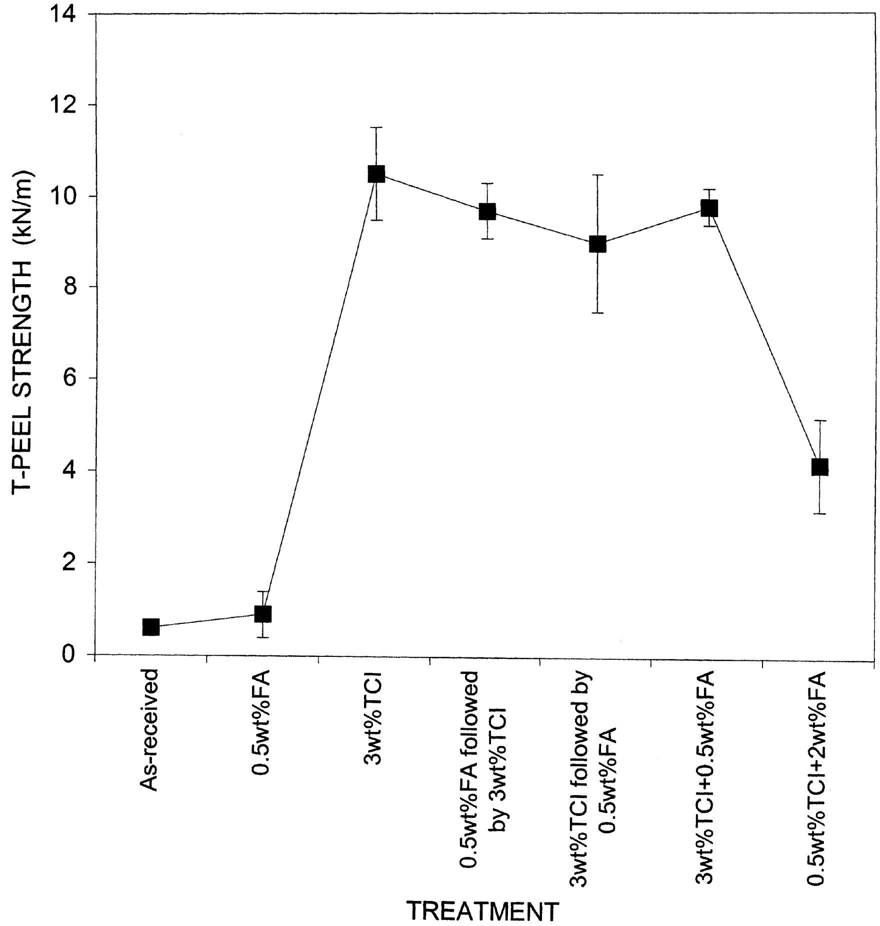


FIGURE 4 T-peel strength values of as-received and treated R2 rubber/polyurethane adhesive/leather joints (72 h after joint formation).

1. The relative intensity of the bands due to paraffin wax (2919, 2851, 1456, and 720 cm^{-1}) decreases (Figure 2), and a noticeable reduction in carbon is produced (Table 3a).
2. Chlorination moieties are produced (Table 3a) that correspond to O=C–Cl stretching (1235 cm^{-1}), CH_2–Cl bending deformation (1420 cm^{-1}), and C–Cl stretching (800 and 760 cm^{-1}). Chlorination is also evidenced by the decrease in the relative intensity of the bands due to C=C stretching (968 and 912 cm^{-1}; see Figure 2).
3. Deposition of unreacted TCI and/or isocyanuric acid (by-product of the reaction of TCI with the R2 rubber), evidenced by the bands at

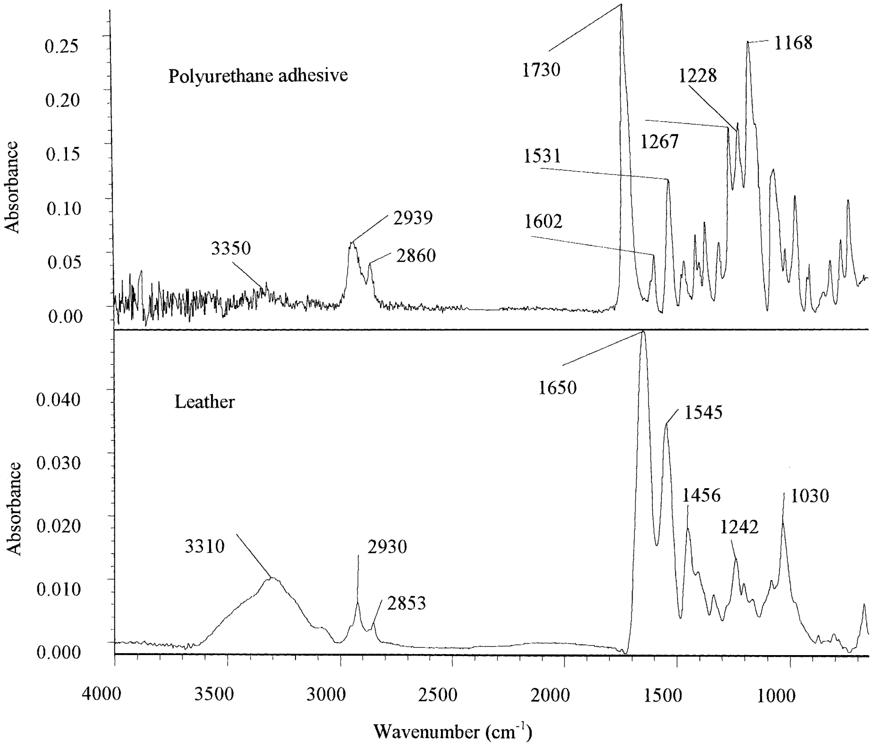
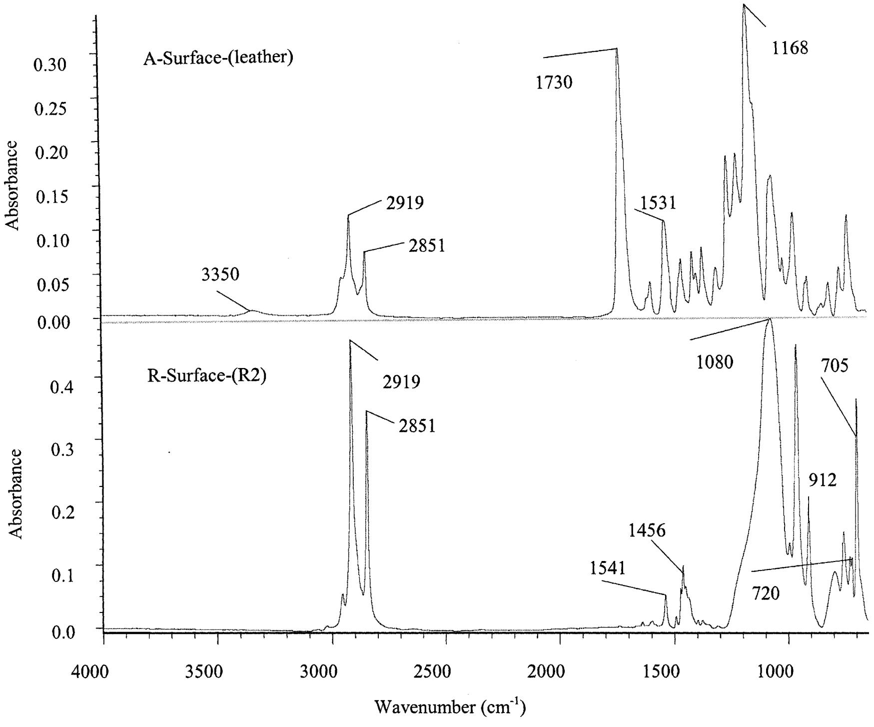


FIGURE 5 ATR-IR spectra of the polyurethane adhesive and the leather used to produce the adhesive joints.

3211 and 3065 cm^{-1} corresponding to N-H stretching of an aromatic ring, the band at 1602 cm^{-1} from NH stretching and N–C=O symmetric bending. In fact, XPS (Table 3b) shows that C–O and C–Cl, and C=O and COO^- groups are created.

4. Surface oxidation is also produced (10.6 at% oxygen, Table 3a), evidenced by the C=O stretching band at 1710 cm^{-1} and the wag vibration in O-CH_2 groups (1420 cm^{-1}).
5. The chlorination of the R2 rubber changes the shape of the band at 1080 cm^{-1} and an increase in silicon concentration is produced (Table 3a), indicating the removal of paraffin wax which allows the presence of sulfur species (Table 3a) from N-cyclohexyl-2-benzothiazole sulphenamide and/or dibenzothiazyl disulfide on the surface. As a consequence, the treatment of R2 rubber with 3 wt% TCI increases the O/C ratio as a result of the oxidation reaction on the R2 rubber surface. Furthermore, this treatment creates



(a)

FIGURE 6 ATR-IR spectra of the failed surfaces obtained after peel test: (a) as-received R2 rubber/polyurethane adhesive/leather joint; (b) 3 wt% TCI/EA-treated R2 rubber/polyurethane adhesive/leather joint; and (c) 0.5 wt% TCI/EA + 2 wt% FA/EtOH-treated R2 rubber/polyurethane adhesive/leather joint. (Continued).

roughness and pits on the R2 rubber surface (Figure 3), and a thin chlorinated layer on the R2 rubber surface seems to be produced.

All these modifications noticeably increase the adhesion in the joint produced with 3 wt% TCI/EA-treated R2 rubber to 10.5 kN/m (Figure 4). The ATR-IR spectrum obtained for the A surface of the 3 wt% TCI/EA treated R2 rubber/polyurethane adhesive/leather joint (Figure 6b) shows the main bands of the polyurethane adhesive (Figure 5—2933, 2861, 1730, 1531, 1168, and 735 cm^{-1}) and bands corresponding to the leather used to make the joints (Figure 5—3310, 1650, and 1456 cm^{-1}). On the other hand, the ATR-IR spectrum of the R surface (Figure 6b) shows the bands of the rubber (2919 and

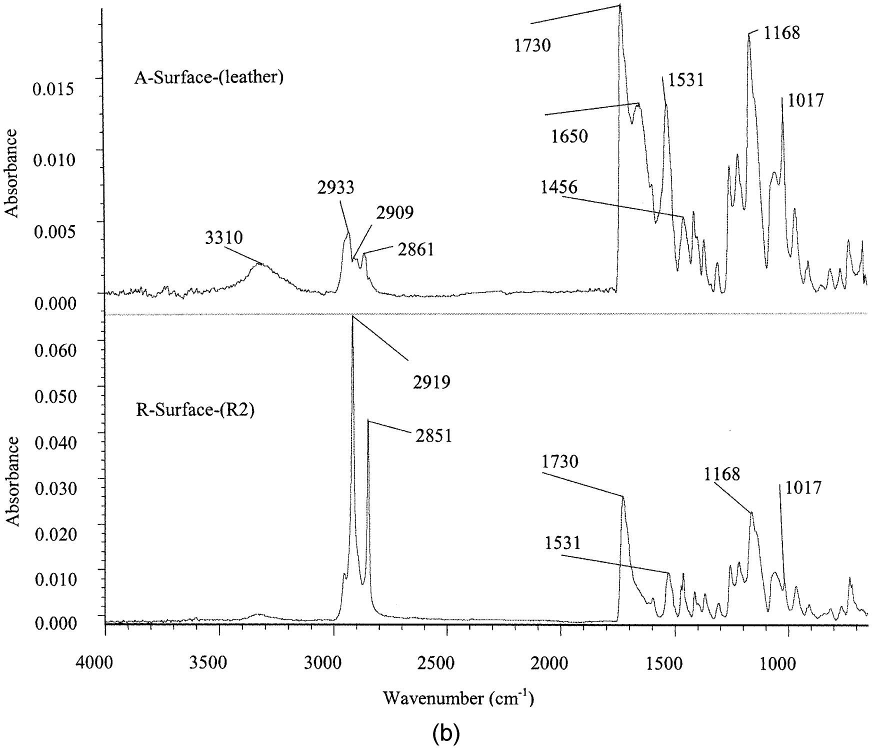


FIGURE 6 Continued.

2851 cm^{-1}) and the polyurethane adhesive (1730, 1531, 1168, and 735 cm^{-1}). Thus, a mixed failure located between the R2 rubber and the adhesive, and the leather and the adhesive, is produced.

If the R2 rubber is treated with 0.5 wt% FA/EtOH solution followed by treatment with 3 wt% TCI/EA solution, the ATR-IR spectrum (Figure 2) and XPS results of the R2-treated rubber are similar to those of the R2 rubber treated with only 3 wt% TCI/EA, although the relative intensity of the C–H stretching (2919 and 2851 cm^{-1}) and C=C stretching (968 and 912 cm^{-1}) bands is lower, and the bands due to C=O stretching and CH_2-Cl bending are somewhat more intense. However, the application of 0.5 wt% FA/EtOH followed by 3 wt% TCI/EA is not so effective in the removal of zinc stearate. Thus, the modifications produced on the R2 rubber surface by the 3 wt% TCI/EA solution are dominant over those of the 0.5 wt% FA/EtOH solution. On the other hand, a few fumaric acid crystals and the

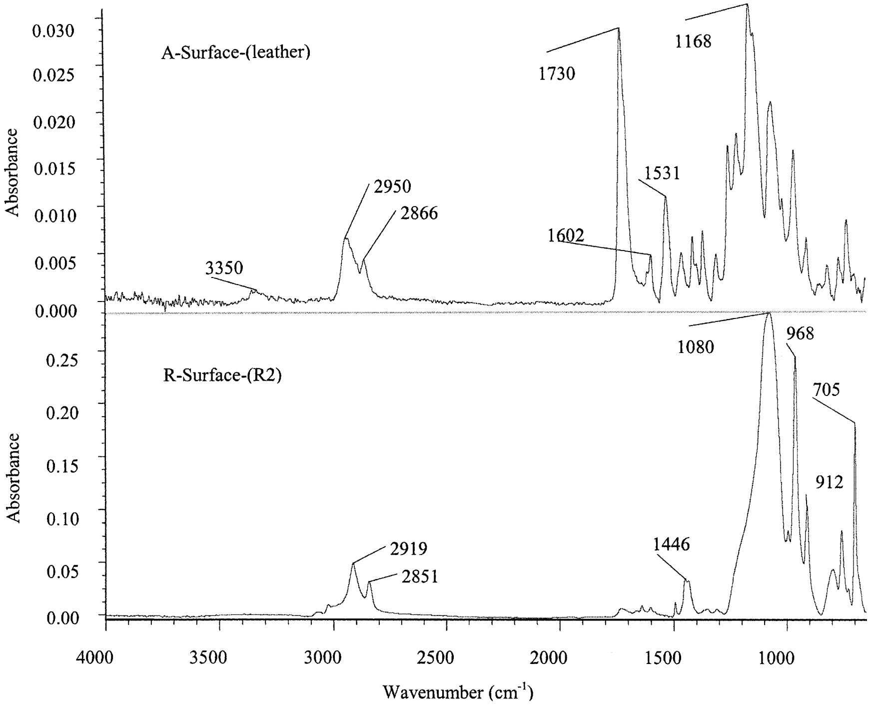


FIGURE 6 Continued.

formation of cracks on the R2 rubber surface are observed (Figure 3). T-peel strength value of the adhesive joint and the locus of failure produced with 0.5 wt% FA/EtOH followed by 3 wt% TCI/EA-treated R2 rubber is quite similar to that obtained for the only 3 wt% TCI/EA-treated R2 rubber (Figure 4).

When the R2 rubber surface is treated with 3 wt% TCI/EA followed by treatment with 0.5 wt% FA/EtOH solution, zinc stearate is completely removed from the R2 rubber surface (Figure 2), and C–O stretching and C–O–H in-plane bending bands due to the FA (1280 cm^{-1}) are also observed. Because the TCI particles are not soluble in ethanol (the solvent used to apply FA) and the deposition of fumaric acid on the R2 rubber surface is likely produced (Figure 3), the degree of chlorination of the R2 rubber is lower than that obtained with only 3 wt% TCI or with 0.5 wt% FA followed by treatment with 3 wt% TCI (Table 3a). High peel strength is obtained for the 3 wt% TCI/EA followed by 0.5 wt% FA/EtOH-treated R2 rubber/

polyurethane adhesive/leather joint (9.0 kN/m—Figure 4), because of the improved wettability, creation of polar moieties, and roughness on the R2 rubber. The locus of failure obtained for this joint is similar to that obtained for the joint produced with the R2 rubber treated with 0.5 wt% FA followed by 3 wt% TCI.

Finally, a mixture of 3 wt% TCI/EA + 0.5 wt% FA/EtOH was prepared before treatment of the R2 rubber surface. The treatment of R2 rubber with the 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture solution produces a different ATR-IR spectrum (Figure 2) than those obtained by treatment with 0.5 wt% FA/EtOH before or after applying 3 wt% TCI/EA solution. Thus, the bands due to chlorination and to fumaric acid—C=O stretching in *trans*-RC=CH–C(=O)H at 1700 cm^{-1} and out-of-phase C–C–O stretching of alcohols at 1070 cm^{-1} [25]—are enhanced. The C–C–O stretching band at 1070 cm^{-1} overlaps with the band of Si–O (1080 cm^{-1}), giving a reduced relative intensity, *i.e.*, a layer of TCI and FA is created on the R2 rubber surface. On the other hand, zinc stearate is completely removed.

The concentrations of O and Cl on the R2 rubber surface treated with 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture solution are similar to those obtained by treatment with 3 wt% TCI/EA and with 0.5 wt% FA/EtOH before or after 3 wt% TCI/EA solutions (Table 3a). The treatment leads to the formation of C–Cl, C–O, C=O, and COO^- bonds (Table 3b). The SEM micrograph (Figure 3) shows typical TCI (prismatic shape) and some fumaric acid crystals on the R2 rubber surface treated with 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture. These crystals are larger than in all other surface treatments due likely to the presence of FA. The T-peel strength of the joint produced with the R2 rubber treated with 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture is similar (9.8 kN/m) to that obtained for all the other chlorination treatments (Figure 4), and similar locus of failure is also obtained.

Therefore, similar peel strength values and loci of failure are obtained in all joints produced with the R2 rubber treated with only TCI, TCI and FA, and TCI + FA mixture, because the modifications due to chlorination are dominant over those produced by treatment with FA.

Modifications Produced on the R2 Rubber Surface Treated with 3 wt% TCI/EA +0.5 wt% FA/EtOH or 0.5 wt% TCI/EA +2 wt% FA/EtOH Mixture Solutions

In the previous section, it has been established that the effects due to chlorination with 3 wt% TCI are dominant over those produced by treatment with both TCI and FA. To confirm this finding, a mixture containing a lesser amount of chlorination agent and a higher concentration of FA was prepared. The effects produced by treatment of R2 rubber with the 0.5 wt% TCI/EA + 2 wt% FA/EtOH (50:50 w:w) mixture solution were compared with those produced by treatment with the 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture solution.

The water-advancing contact angle values obtained on the R2 rubber treated with the two mixtures are similar (70 degrees). However, the ATR-IR spectrum of R2 rubber treated with 0.5 wt% TCI/EA + 2 wt% FA/EtOH mixture (Figure 2) shows the bands due to the as-received R2 rubber and the fumaric acid. Zinc stearate and paraffin wax were removed from the R2 rubber surface. However, no chlorination bands are observed, because a small amount amount of chlorinated agent was used. It has been shown [14, 26] that the treatment of SBR rubbers with small amounts of TCI is restricted to the outermost surface. Considering that the ATR-IR spectroscopy analyzes microns below the surface, the chlorine moieties cannot be distinguished; however, XPS (a more surface-sensitive analysis technique than ATR-IR) showed the presence of chlorine moieties. Table 3a shows the atomic concentration of elements in the 0.5 wt% TCI/EA + 2 wt% FA/EtOH mixture treated R2 rubber surface. Relatively similar concentrations of elements are obtained for the R2 rubber treated with the 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture (similar O/C ratio), except for the lower concentration of chlorine and the higher amounts of Si and S. Table 3b shows the absence of C=O and R–COO$^-$ moieties but the existence of C–Cl and C–O bands. This is in agreement with the reaction of FA with the R2 rubber surface and the lower degree of chlorination obtained by treatment with 0.5 wt% TCI/EA. On the other hand, the SEM micrographs (Figure 3) of the R2 rubber treated with 0.5 wt% TCI/EA + 2 wt% FA/EtOH mixture show fumaric acid crystals and a lack of roughness as compared with the treatment with 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture. Thus, a higher degree of modification is produced on the R2 rubber surface treated with the 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture due to the higher concentration of the chlorination solution. As a consequence of the lower degree of surface modifications produced on the R2 rubber surface treated with 0.5 wt% TCI/EA + 2 wt% FA/EtOH mixture solution, the T-peel strength obtained is only 4.2 kN/m, a lower value than that obtained in the joint produced with 3 wt% TCI/EA + 0.5 wt% FA/EtOH mixture (9.8 kN/m).

Figure 6c shows the ATR-IR spectra of the failed surfaces (A and R surfaces) of the 0.5 wt% TCI/EA + 2 wt% FA/EtOH mixture treated R2 rubber/polyurethane adhesive/leather joint. The ATR-IR spectrum of the A surface shows the bands of the polyurethane adhesive (3350, 2950, 2866, 1730, 1531, and 1168 cm^{-1}) and that of the R surface shows the bands of the as-received R2 rubber, except for the absence of the bands due to zinc stearate and paraffin wax. This indicates that an adhesion failure has been produced.

CONCLUSIONS

The treatment of the R2 rubber surface with only 0.5 wt% FA/EtOH solution is not as effective as the chlorination treatments. The treatment with only 3 wt% TCI/EA greatly improves the adhesion of the R2 rubber surface because of the creation of polar moieties and roughness and the removal of antiadherent moieties (paraffin wax and zinc stearate).

The application of 0.5 wt% FA/EtOH before or after treatment with 3 wt% TCI/EA mainly shows the dominant effects of the chlorination on the R2 rubber surface. If a mixture containing 3 wt% TCI/EA + 0.5 wt% FA/EtOH is applied on the R2 rubber surface, the adhesion properties are not further improved. The treatment with a mixture containing less chlorination agent and higher concentration of fumaric acid (0.5 wt% TCI/EA + 2 wt% FA/EtOH) does not greatly enhance the adhesion properties of the R2 rubber.

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