

Addition of ozone in the UV radiation treatment of a synthetic styrene-butadiene-styrene (SBS) rubber

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Abstract

The effect of exposure to different ozone concentrations, in conjunction with UV radiation, on the surface modification and adhesion properties of a block synthetic styrene-butadiene-styrene (S6) rubber was studied. The treatment time varied between 10 s and 30 min. Three different surface treatments were investigated: ozone only (O₃), UV radiation in the presence of air, and UV radiation in the presence of externally generated, supplemental ozone (UV/O₃). The surface modified S6 rubber was characterized using contact angle measurements (ethylene glycol, 25 °C), Fourier transform infrared spectroscopy using an attenuated total reflection attachment (ATR-IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). T-peel tests of surface modified S6 rubber/polyurethane (PU) adhesive/leather joints were carried out to quantify the changes in the adhesion properties.

The O₃, UV and UV/O₃ treatment of S6 rubber improved wettability, created oxygen-containing moieties at the surface, and resulted in ablation of the surface (removal of a thin rubber layer from the treated S6 rubber surface). Different surface modifications were produced using each treatment and these modifications were enhanced with increasing treatment time. Whereas the UV and UV/O₃ treatments created C=O and COO⁻ moieties on the S6 rubber surface, the O₃ treatment produced a lower degree of oxidation (predominantly O–H moieties). For short treatment time, O–H and C–O moieties were dominant, and the increase in the length of treatment lead to more oxidized moieties (C=O, COO⁻). Lower degree of oxidation was obtained with O₃ treatment as compared to that obtained with UV and UV/O₃ treatments.

Adhesion was highly improved after UV and UV/O₃ treatments of S6 rubber, more markedly with increasing treatment time. A moderate increase in peel strength of the joints produced with O₃-treated S6 rubber was produced and an adhesion/cohesive failure in a thin rubber layer was observed irrespective of treatment time. On increasing the treatment time with UV and UV/O₃, the adhesive joints showed different loci of failure: adhesion + cohesive failure in a thin rubber layer for the S6 rubber treated for 2 min with UV or UV/O₃, and cohesive failure in the S6 rubber treated for 30 min with UV or UV/O₃ treatments.

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1. Introduction

Thermoplastic rubbers styrene-butadiene-styrene (SBS) are block copolymers of soft, elastic butadiene and hard, tough styrene, which do not require vulcani-

zation to provide dimensional stability. These thermoplastic rubbers are widely used in the manufacture of footwear, adhesives manufacturing, molded or extruded goods and as modifiers for asphalt and other resins. Because of the non-polar nature of SBS rubbers, poor adhesion is found when used with polyurethane adhesives in footwear industry, and surface modification of the SBS is required to produce suitable joints [1,2].

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Several surface treatments for thermoplastic rubbers have been proposed in the literature including various chemical (halogenation, cyclization—treatment with sulphuric acid) and physical (corona discharge, low pressure plasma) treatments [3–5]. In this study, UV radiation (184.9 and 253.7 nm) in the presence of air or supplemental ozone is proposed as a surface treatment to improve the adhesion of a difficult-to-bond thermoplastic styrene-butadiene-styrene rubber.

The surface modifications produced by UV treatment of several polymers have been studied previously [6]. Bolland [7] and Keller [8] established the mechanisms of the oxidative attack of UV radiation on low molecular weight hydrocarbons similar to rubber; the generation of free radicals on the polymer surface was recognized as the key parameter of the oxidative degradation.

UV radiation (wavelength = 185 nm) removes contaminants from many surfaces by reacting with atmospheric oxygen to form atomic oxygen and ozone, both strong oxidizers. Ozone absorbs the 254 nm UV radiation and dissociates into molecular oxygen and atomic oxygen. The type and degree of rubber surface modifications depend on the ozone concentration [9]. Some authors have demonstrated that ozone can generate peroxy radicals, unstable species that decompose to form hydro-peroxide, carbonyl and carboxyl functionalities, these groups being responsible for the increased wettability of treated polymer and rubber surfaces [10–12]. The number of peroxy groups that are created depends on the ozone concentration and the exposure time of the rubber to ozone, among other factors [13,14].

Treatment with ozone in the absence of UV light has been used previously to increase the adhesion of polypropylene, polyethylene, polyurethane and polyethylene terephthalate [13,15–16]. Double bonds in the polymeric chains are susceptible to oxidation and ozone attack through an ionic mechanism [17].

Several papers in the literature have shown that the combined treatment of UV radiation with ozone (additional to the ozone generated by the UV radiation) produces more effective and faster oxidation of polypropylene, polyethylene terephthalate and polyethylene surfaces than either ozone only or UV treatment. Different reaction mechanisms are implied for each treatment [18–25].

Previous studies [26,27] showed that the extent of the rubber surface modifications produced by UV treatment depended on the treatment time and the concentration of the ozone produced in situ by the UV radiation. In this study, additional ozone was supplied by means of an ozone generator during UV treatment of a styrene-butadiene-styrene (S6) rubber surface, and the surface modifications produced with ozone only (O₃), UV radiation, or UV/O₃ as a function of treatment time have been investigated.

2. Experimental

2.1. Materials

An oil extended (45 phr non-staining paraffinic oil) thermoplastic block styrene-butadiene-styrene (S6) rubber containing 32 wt% styrene was used in this study. Some properties of the S6 rubber are given in Table 1.

To determine the adhesion properties, surface treated-S6 rubber/polyurethane adhesive/leather joints were prepared. Table 2 shows some of the properties of the chromium-tanned bovine leather used to produce the adhesive joints. The polyurethane adhesive solution was prepared by dissolving 18 wt% polyurethane pellets (Desmocoll 540, Bayer, Leverkusen, Germany) and 2 wt% fumed silica (Aerosil 200, Degussa, Hanau, Germany) in an acetone/toluene (80:20, w:w) mixture. To facilitate the dispersion of the fumed silica in the polyurethane and avoid further settling, the adhesive solution was prepared in two consecutive steps: (i) The fumed silica was mixed with a small amount of the solvent mixture at 2500 rpm for 15 min in a laboratory mixer to facilitate the dispersion; (ii) The polyurethane pellets were added to the solvent-fumed silica mixture, simultaneously adding all of the solvent; the mixture was stirred in the laboratory mixer at 2000 rpm for 2 h, 30 min until an homogeneous solution was obtained. The viscosity of the solution was 4.4 Pa.s at 25 s⁻¹ as measured by a rotational rheometer (Rheolab MC 100 Physica).

Table 1
Some properties of the styrene-butadiene-styrene (S6) rubber

Property	Value
Ash content	0.3 wt%
Density	0.94 g/cm ³
Modulus 300%	1.9 MPa
Tensile strength	12 MPa
Elongation-at-break	1100%
Abrasion resistance	100 mm ³
Shore a hardness	43
Thickness	5 mm

Table 2
Some properties of the chromium-tanned bovine leather used to prepare the adhesive joints

Property	Value
Tensile strength	13 MPa
Elongation-at-break	60%
Ash content, 950 °C	< 5 wt%
Thickness	2 mm

2.2. Experimental techniques

2.2.1. UV radiation reactor

The UV radiation treatment was carried out in a barrel-type reactor equipped with an O-ring seal able door at one end and O-ring seal able gas inlets at the other. Gases can be introduced into the reactor through appropriate inlets and a thermocouple can be inserted to monitor the temperature inside the reactor. The interior of the reactor was equipped with a medium pressure mercury vapor grid lamp (BHK Inc.). The lamp was made of pure, clear fused silica, able to transmit the two strong lines at 184.9 and 253.7 nm. The intensity of the UV radiation was 12–15 mW/cm² at a distance of 2.54 cm. The gas supplied to the interior of the reactor was extra-dry compressed air (dew point = -65 °C), at a flow rate of 1000 sccm (standard cubic centimeters per minute) measured using a MKS mass-flow controller.

To carry out the UV radiation treatment in the presence of supplemental ozone (UV/O₃), extra-dry air was introduced into an ozone generator. The ozone produced was fed into the UV reactor (Fig. 1). The treatment consisting of ozone only (O₃) was carried out by introducing the supplemental ozone into the reactor while the UV lamp was off.

2.2.2. Contact angle measurements

The wettability of the as-received and surface-treated S6 rubber was evaluated from contact angle measurements using a Ramé-Hart 100 goniometer. Drops (4 μl) of ethylene glycol were placed on the treated S6 rubber surfaces using a micrometric syringe (Gilmont Instrument). Advancing and receding contact angles (increasing–decreasing drop size procedure) were measured. At least three measurements on each of two identically treated samples were taken and averaged. The experimental error was ±2 degrees.

2.2.3. ATR-IR spectroscopy

A Bruker IFS-55 FTIR spectrometer was used to analyze the chemical modifications produced in the top 0.5–1 μm of the treated S6 rubber surfaces. A *Spectra-Tech Baseline* attenuated total reflectance (ATR) attach-

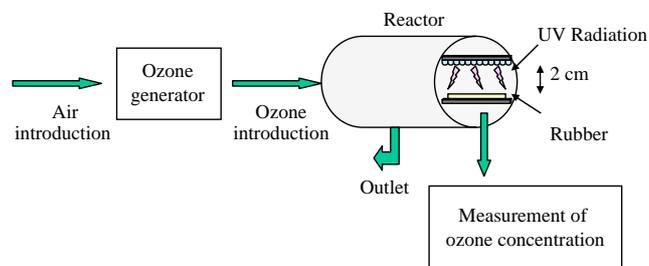


Fig. 1. Scheme of the UV reactor provided with an external supplemental ozone generator.

ment equipped with a minigrip pressure device and a germanium ATR crystal were used.

To assess the locus of failure of the joints, the failed surfaces obtained after T-peel test were characterized by ATR-IR spectroscopy using a Nicolet FTIR 205 spectrometer. 200 scans were obtained and averaged with a resolution of 4 cm⁻¹.

2.2.4. X-ray photoelectron spectroscopy (XPS)

Elemental compositional changes and oxidation state changes at the outermost 5–10 nm of the treated S6 rubber surfaces were monitored using XPS. A Surface Science SSX-100 ESCA spectrometer with an Al-K α X-ray source (1486.6 eV) was used. Prior to analysis, samples were exposed to a vacuum in the introduction chamber until the pressure was lower than 2.10⁻⁶ Torr. To avoid sample charging the flood gun/screen technique was used. XPS survey spectra were collected in the range of binding energies between 0 and 1200 eV, using a spot size of 600 μm and a pass energy of 150 eV. High-resolution C1s spectra were obtained over a 20 eV range. The binding energies were corrected using a peak position of 285.0 eV for the main hydrocarbon peak.

2.2.5. Scanning electron microscopy (SEM)

The morphological modifications produced on the treated S6 rubber surfaces were analyzed using a JEOL JSM-840 SEM system. The rubber samples were gold-coated prior to analysis and an electron beam energy of 20 kV was used.

2.2.6. T-peel strength

S6 rubber pieces of 100 × 30 × 5 mm³ and leather pieces of 100 × 30 × 2 mm³ were used to produce the adhesive joints. Treated S6 rubber/PU adhesive/leather joints were prepared to quantify the adhesive strength. Immediately after treatment of S6 rubber, 0.8 ml of adhesive solution was applied. The leather surface was roughened, to expose the corium, using a Superlema S.A. (Zaragoza, Spain) instrument operating at 2800 rpm. A P100 aluminum oxide abrasive cloth was used to produce roughening, and about 0.5 mm leather were removed. Adhesive solution (0.8 ml) was applied to the roughened leather surface and 30 min later, an additional 0.8 ml of adhesive was applied to assure adequate penetration of the adhesive into the leather pores. Once the adhesive solution was applied, the solvent was allowed to evaporate for 45 min. The dried solid adhesive films 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. A peel rate of 0.1 m/min was used. Five replicates of each treatment time were tested and the peel strength values were averaged. The error was less than 0.7 kNm⁻¹.

3. Results and discussion

Ozone concentration in the UV reactor for each treatment (UV, O₃ and UV/O₃ treatments) was monitored with a Resonance Ltd. UV TRANS2 model ozone device mounted at the exit of the reactor. Fig. 2 shows an increase in ozone concentration in the reactor with increasing treatment time. The UV irradiation of the oxygen in air at 185 nm leads to the formation of ozone while exposure of ozone to UV light at 254 nm leads to its photodecomposition to atomic oxygen and molecular oxygen. The overall quantum yield of ozone, taking into account both the formation and decomposition reactions is 0.5 meaning that it takes two photons of light to generate one ozone molecule. The UV irradiation in the presence of flowing air means that there is a constant source of oxygen for ozone generation and, in turn, ozone is available for decomposition in the presence of the 254 nm light. This results in a mixture of ozone, atomic oxygen and various other excited oxygen species being present in the reactor.

The ozone concentration for the ozone only and UV/O₃ treatments should be similar at the entrance to the reactor as the same ozone generator and flow rate are used for these two experiments. Measurement of the ozone concentration at the exit of the reactor for the UV/O₃ conditions shows that the ozone concentration is less than half that of the ozone only conditions, indicating that significant photodecomposition has occurred. The photodecomposition of the ozone leads to the formation of atomic oxygen O(1D). The decrease in the ozone concentration in the presence of UV light should be approximately equal to the increase in the atomic oxygen, a very active oxygen species. The UV treatment in air shows less ozone than the ozone only conditions because the sole source of ozone is that generated by the UV light.

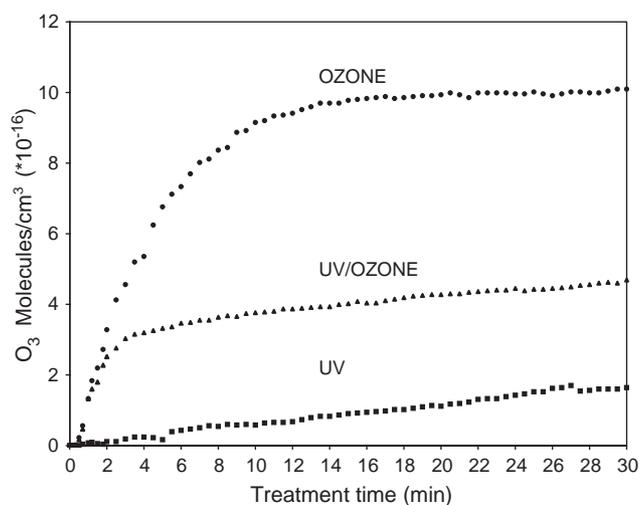


Fig. 2. Ozone concentration in the reactor produced by O₃, UV and UV/O₃ treatments as a function of the length of treatment.

The influence of the treatment conditions on the surface wettability was assessed from the advancing contact angle measurements made on S6 rubber treated for 10 s to 30 min (Fig. 3). Ten seconds of O₃, UV or UV/O₃ treatment produces a considerable and relatively similar decrease in advancing contact angle values, although significant differences among the different surface treatments were found for longer treatment times. While O₃ treatment improved the wettability after 10 s of treatment, a plateau was reached at that short treatment time, with increasing treatment time showing only a slight improvement in wettability. Complete wettability is achieved only with 10 min of UV treatment. Furthermore, the combined UV/O₃ treatment reduces the time to achieve complete wettability to 3 min. These results indicate the presence of functional groups at the surface of the S6 rubber which are susceptible to immediate reaction with very small quantities of ozone in the reactor. These functional groups are likely the double carbon bonds which are known to be present at the surface and susceptible to attack by ozone. The mechanisms of reaction for longer treatment times will vary with the treatment conditions as there are different, more oxidized active species.

The chemical modifications of the S6 rubber produced by each treatment were assessed by ATR-IR and XPS spectroscopy. XPS provides information with respect to changes in the elemental composition of the surface and the oxidation state of the carbon in the top 5–10 nm while the ATR-IR spectroscopy provides information regarding changes in the bonding in the top 0.5–1 μm. The ATR-IR spectrum of the as-received S6 rubber (Fig. 4a) shows the bands attributable to butadiene and styrene. Bands at 2919 and 2851 cm⁻¹ correspond to C–H stretching (CH₂ group) from butadiene. Other butadiene absorption bands are CH₂ in-plane

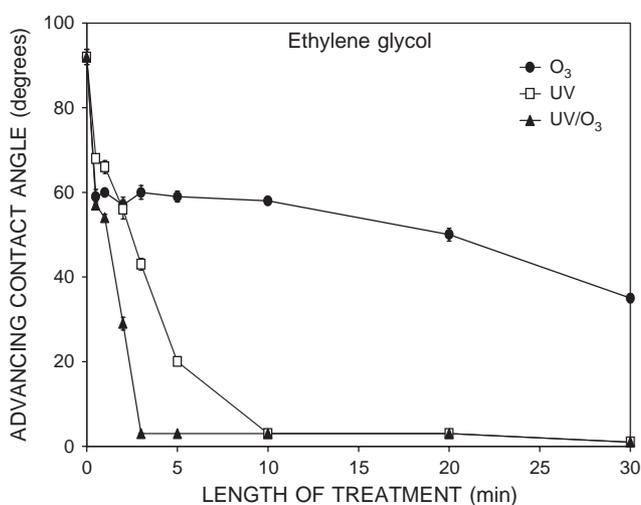


Fig. 3. Advancing contact angles of S6 rubber treated with O₃, UV and UV/O₃ for different length of treatment.

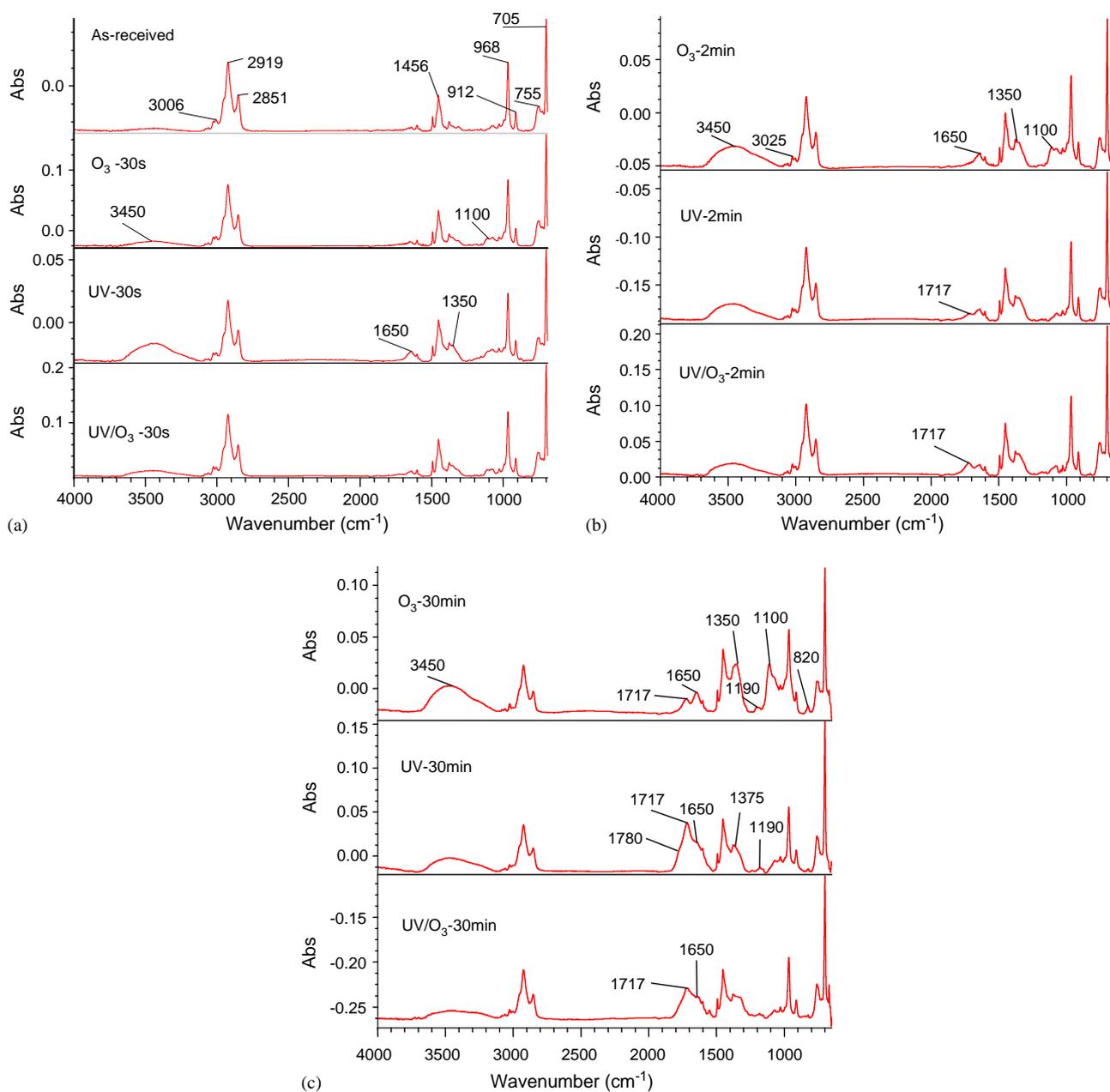


Fig. 4. ATR-IR spectra of S6 rubber treated with O₃, UV or UV/O₃ for: (a) 30 s; (b) 2 min and (c) 30 min.

deformation (1456 cm⁻¹), CH₂ wagging motion (1380 cm⁻¹), C=C stretching in CH=CH₂ groups at 1650 cm⁻¹, C-H out of plane bending in *trans*-1,4-C=C (968 cm⁻¹), and a small band at 3006 cm⁻¹ (=CH stretching). Styrene absorption occurs at 705, 753 and 912 cm⁻¹ (C-H out-of-plane deformation) and 1602 cm⁻¹ (aromatic C-C stretching). The ATR-IR spectrum of S6 rubber treated with O₃ for 30 s shows some oxidation in the presence of absorption bands of low relative intensity at 3450 and 1100 cm⁻¹ likely arising from the O-H stretch and CCO out-of-phase stretch of an alcohol. The ATR-IR spectrum of the UV/

O₃ treated S6 rubber is similar to that of O₃ treated for short treatment times.

Significant oxidation of the S6 rubber is produced by UV treatment for 30 s, and thus considerably more intense absorption bands ascribed to O-H stretching (3450 cm⁻¹) and in-plane and out-of-plane bending motions in O-H deformation (1350 cm⁻¹) is observed [28] (Fig. 4a). In addition to the formation of alcohol functionalities at the surface, there also exists the possibility of some adsorbed water being present at the surface as we observe an increase in a band near 1650 cm⁻¹ which, in conjunction with the absorbance at

3450 cm^{-1} , could be evidence of the presence of water at the surface. As the purpose of the treatment is to make the surface more water wettable, this would not be an unexpected occurrence. There is also the possibility that there is a contribution from a band attributable to the C=C stretch in vinyl alkenes within the broad absorbance at 1650 cm^{-1} . This functional group would arise as a result of a chain scission process by the abstraction of a hydrogen atom (Scheme 1) [17].

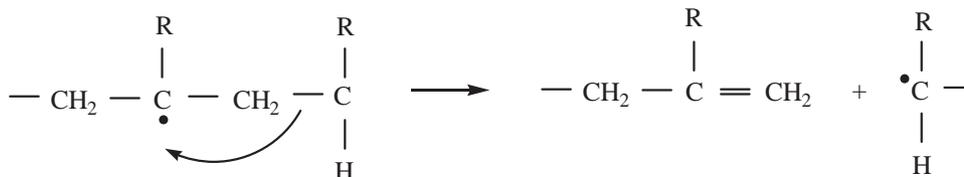
Increasing the treatment time enhances the oxidation of the S6 rubber surface for all treatments, although for each set of conditions, different surface modifications were obtained. After 2 min of treatment, the ATR-IR spectrum of O_3 -treated S6 rubber (Fig. 4b) shows more intense OH (3450 cm^{-1}) and C–C–O absorption bands (1100 cm^{-1}), indicating that the formation of alcohol groups is dominant. However, the treatment of S6 rubber with UV or UV/ O_3 for 2 min also generates C=O moieties (absorption band at 1717 cm^{-1}). The differences in the treatments become more marked after 30 min of exposure (Fig. 4c). 30 min of O_3 treatment favors the creation of more intense OH (3450, 1350 cm^{-1}) and C–C–O moieties (1100 cm^{-1}), and this extensive treatment time also allows the generation of C=O moieties at the surface (1717 cm^{-1}). The presence of a broad absorbance near 1717 cm^{-1} after oxidation of a hydrocarbon-based polymer is indicative of oxidative degradation of the surface. The broad peak at 1717 cm^{-1} is generally assigned to a number of carbonyl functional groups including ketones and carboxylic acids. The carboxylic acid groups form as a result of chain scission. The formation of aldehyde groups is not probable, based on the lack of the typical C–H aldehyde band in the 2870–2695 cm^{-1} region. Also, a band at 820 cm^{-1} is observed which may arise from the =CH out-of-plane bending mode of a C=C–C=O group.

Although the formation of a band typical of oxidative degradation (1717 cm^{-1}) is detected on the O_3 treated sample after 30 min, this band is much stronger in the spectra of the samples treated for the same time using UV and UV/ O_3 treatments, indicating that the presence of the UV radiation has a profound effect on the formation of C=O groups on the S6 rubber surface and therefore on its oxidative degradation. The band centered at 1717 cm^{-1} can be curve fit with a number of peaks representative of C=O containing groups. The formation of ester groups could explain the increase in

the intensity of the bands at 1190 cm^{-1} ascribed to the C–O–C stretch seen in esters, and the peak at 1375 cm^{-1} could arise from the formation of $\text{CH}_3\text{C}=\text{O}$ groups in esters or methyl ketones. In addition to the oxidative degradation of the polymer, the increase in treatment time results in a decrease of the C–H stretching absorption (2919, 2851 cm^{-1}) of S6 rubber, which suggests that an ablation is produced by the extended treatment. The theory of ablation of the surface is supported by both the XPS and SEM data.

In general, the treatment of the sample surface for 30 s using any one of the three stated sets of conditions results in a more wettable surface as evidenced by the similar decreases in the advancing contact angles. For the samples treated for 2 min with O_3 , UV or UV/ O_3 treatments, the mechanism of alcohol formation appears to be dominant with the increased intensities of the bands at 3450 and 1350 cm^{-1} . After 2 min of UV or UV/ O_3 treatments, more highly oxidized groups are formed (C=O moieties, 1717 cm^{-1}) which are not seen after 2 min of O_3 treatment. The 30 min O_3 treatment continues with the formation of alcohol moieties (dominant) and, at this point, some C=O moieties are now seen. On treatment for 30 min with either UV or UV/ O_3 , the formation of C=O moieties, possibly arising from ketones, carboxylic acids and/or esters, is dominant on the S6 rubber surface. The relative intensities of the bands attributed to alcohol moieties (3450, 1350, 1100 cm^{-1}) decreases, likely because of their further oxidation to carbonyl-containing functional groups.

The elemental composition of the outermost surface of the S6 rubber treated with O_3 , UV and UV/ O_3 was also analyzed using XPS (Table 3a). All treatments result in oxidation of the S6 rubber surface and, in general, increasing the treatment time increases the oxygen content and decreases the carbon content on the S6 rubber surface, i.e. an increase in the O/C ratio results. Treatment with UV/ O_3 for 2 min results in more oxygen at the surface in comparison to that obtained with O_3 and UV treatments (Table 3a). Oxidation produces C–O (binding energy = 286.3 eV), C=O (binding energy = 287.6 eV), and COO^- moieties (binding energy = 289.4 eV) (Table 3b and Fig. 5a). O_3 treatment for 2 min or less creates only C–O moieties on the S6 rubber surface, which is in agreement with the ATR-IR spectroscopy data. Treatment with O_3 for



Scheme 1.

Table 3a

Atomic percentages (at%) of elements on the as-received and O₃, UV and UV/O₃ treated S6 rubber(a) O₃ treatment

Element	Binding energy (eV)	As-received (at%)	Length of treatment in O ₃		
			0.5 min (at%)	2 min (at%)	30 min (at%)
C1s	285	93.6	94.4	86.9	86.7
O1s	532.2	4.3	4.8	10.2	11.9
Si2p3	102	2.1	0.8	3	1.3
O/C	—	0.04	0.05	0.12	0.14

(b) UV treatment

Element	Binding energy (eV)	Length of treatment in UV		
		0.5 min (at%)	2 min (at%)	30 min (at%)
C1s	285	89.3	89.4	83.4
O1s	532.2	7.6	9	14.1
N1s	401	—	—	1.7
Si2p3	102	3.1	1.6	0.8
O/C	—	0.09	0.1	0.17

(c) UV/O₃ treatment

Element	Binding energy (eV)	Length of treatment in UV/O ₃		
		0.5 min (at%)	2 min (at%)	30 min (at%)
C1s	285	90.9	83.3	86.2
O1s	532.2	8.2	12.4	12
N1s	401	—	2.3	1.8
Si2p3	102	0.9	2	—
O/C	—	0.09	0.15	0.14

30 min creates some C=O moieties on the S6 rubber surface, but no COO- moieties are detected. UV/O₃ treatment for 30 min is effective in producing a considerable degree of oxidation, but UV radiation in the presence of air effectively oxidizes the S6 rubber surface without additional ozone being supplied.

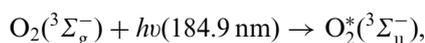
XPS analysis shows also the presence of silicon on the S6 rubber surface. Considering that this element is not present in the rubber formulation, it is likely a contaminant, probably as processing aid. The silicon levels decrease on extended exposure to UV light, likely because of physical changes at the rubber surface. Small amounts of nitrogen are incorporated into the S6 rubber surface treated with UV and UV/O₃, likely due to anchoring of nitrogen moieties from the air on extended treatment.

To explain the chemical modifications on the S6 rubber surface produced by treatment with ozone and UV radiation, it has to be considered that ozone may react with the double carbon bonds of butadiene to form ozonides as intermediate moieties that evolve to carbonyl and carboxylic groups (Scheme 2) [29].

Rabek et al. [24] suggested that ozone may also react with the unsaturated chain of butadiene by hydrogen abstraction, leading to radical formation, which can form hydroxyl groups. This is in agreement with the creation of bands at 3450 and 1100 cm⁻¹ arising from the formation of alcohol functional groups (Figs. 4a and b). Further oxidation of the hydroxyl groups may occur, producing ketones, esters and/or carboxylic acid groups (band at 1717 cm⁻¹ arising from the C=O stretch-Fig. 4c).

The ozone formation and destruction as a consequence of the UV or UV/O₃ treatment has been extensively studied [9,30-31], and different reactive gaseous species able to react with the S6 rubber surface have been recognized.

Ozone is produced via a sequence of reactions. Molecular oxygen absorbs 184.9 nm UV light to form excited-stated molecular oxygen



which can dissociate to form two ground-state oxygen atoms.

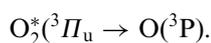


Table 3b

Percentages of species (at%) obtained from C1s curve fitting on the as-received and O₃, UV and UV/O₃ treated S6 rubber(a) O₃ treatment

Species	Binding energy (eV)	As-received (at%)	Length of treatment in O ₃		
			0.5 min (at%)	2 min (at%)	30 min (at%)
C–H, C–C	285	96.5	98.6	90.2	89.1
C–O	286.3	3.5	1.4	9.8	5
C=O	287.6	—	—	—	5.9

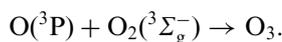
(b) UV treatment

Species	Binding energy (eV)	Length of treatment in UV		
		0.5 min (at%)	2 min (at%)	30 min (at%)
C–H, C–C	285	83.8	87.8	82.2
C–O	286.3	16.2	9.9	8.6
C=O	287.6	—	2.3	3.2
COO [−]	289.4	—	—	5.9

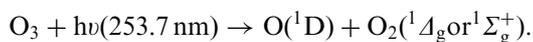
(c) UV/O₃ treatment

Species	Binding energy (eV)	Length of treatment in UV/O ₃		
		0.5 min (at%)	2 min (at%)	30 min (at%)
C–H, C–C	285	90.3	92	82.8
C–O	286.3	9.7	7	10.9
C=O	287.6	—	0.5	2.8
COO [−]	289.4	—	0.5	3.5

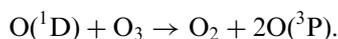
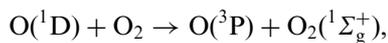
The O(³P) atoms then can react with molecular oxygen to form ozone



Photolysis of ozone occurs on exposure to 253.7 nm UV light to form atomic and molecular oxygen



O(¹D) is a very reactive form of atomic oxygen and therefore is short-lived. It reacts with gaseous species present, such as molecular oxygen and ozone.



Any water vapor present may also react with O(¹D) to produce hydroxyl radicals



Reactive gaseous species produced by reaction of UV with ozone, such as atomic oxygen and molecular oxygen, subsequently may react with the S6 rubber surface. Atomic oxygen is present in O(³P) and O(¹D)

forms, both of which are strong oxidizing agents that may react with the rubber surface in different ways. The O(³P) will abstract hydrogen atoms from carbon atoms of the polymer chain, producing radical carbon sites able to form hydroxyl groups [22,32]. Molecular oxygen also may react with a carbon radical, forming a peroxy group, which then may abstract a hydrogen atom from a neighboring carbon to form a hydroperoxide unit. Further oxidation of hydroxyl, peroxy and hydroperoxide groups may occur, producing ketone, ester and/or carboxylic acid groups. On the other hand, O(¹D) can react with the polymer chain via an insertion reaction into C–H bonds to form hydroxyl groups or into C–C bonds to form ether groups [32]. Further oxidation of hydroxyl and ether groups may occur.

All of these reactions are consistent with the chemical moieties observed on the S6 rubber surface, as different oxidation bands are observed in the ATR-IR and XPS spectra of the UV and UV/O₃ treated S6 rubber (1717 cm^{−1} due to C=O stretch in ketones, esters and or carboxylic acid functionalities, Figs. 4a–c, and C–O, C=O and COO[−] groups at binding energies of 286.3, 287.6 and 289.4 eV, respectively-Table 3b and Fig. 5). The formation of these oxidized groups is enhanced by

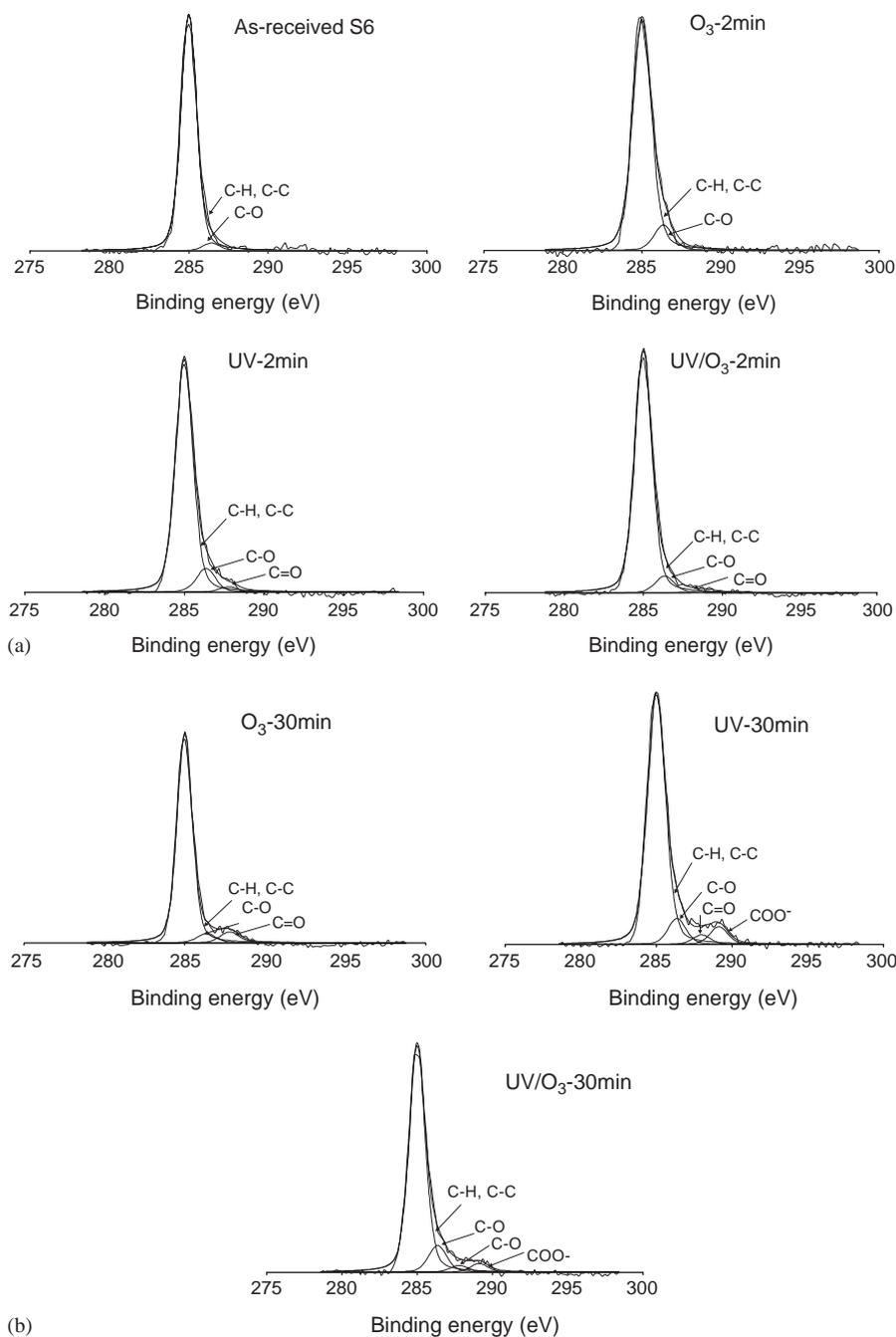
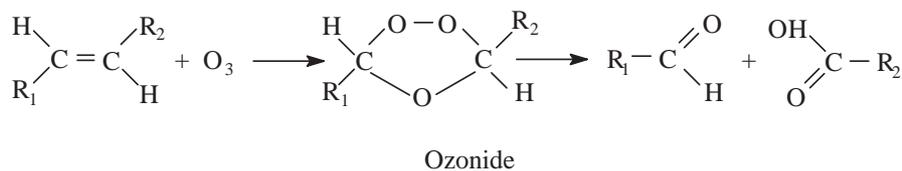


Fig. 5. Curve fitting of C1s peak (XPS) of as-received and S6 rubber treated with O₃, UV and UV/O₃ for: (a) 2 min and (b) 30 min.



Scheme 2.

the presence of UV light with the ozone and with extended treatment times. A lesser degree of oxidation is found when the S6 rubber is treated with ozone alone.

These findings are consistent with the effects produced by UV/O₃ treatment of polypropylene [24] and polyethylene terephthalate [18].

The morphology of the S6 rubber is also differently affected for each treatment. A SEM micrograph of the as-received S6 rubber (Fig. 6) shows a fairly smooth flat surface with some small round white silica particles seen which were detected by both EDX and XPS (Table 3a). The silica particles become much more difficult to detect on the S6 rubber surface after extended treatment with UV/O₃ or O₃ as observed in the SEM micrographs presented in Fig. 6. This difficulty is likely related to ablation of the outermost rubber surface as the surface would become rougher and more labile. Treatment of the rubber with UV or UV/O₃ for 2 min produces some roughness and, for longer treatment times, ablation of the S6 rubber surface is produced. Consistently, UV/O₃ treatment creates a greater degree of roughness on the S6 rubber surface than does treatment with only O₃ (Fig. 6).

The influence of the surface modifications of treated S6 rubber on its adhesion properties was evaluated by T-peel tests of treated S6 rubber/PU adhesive/leather joints. The joints prepared with the as-received S6 rubber show a lack of adhesion (0.5 kN/m) (Fig. 7), which is in agreement with the high advancing contact angle value (Fig. 3) and the dominant non-polar nature of the S6 rubber surface (Fig. 4 and Table 3a). T-peel

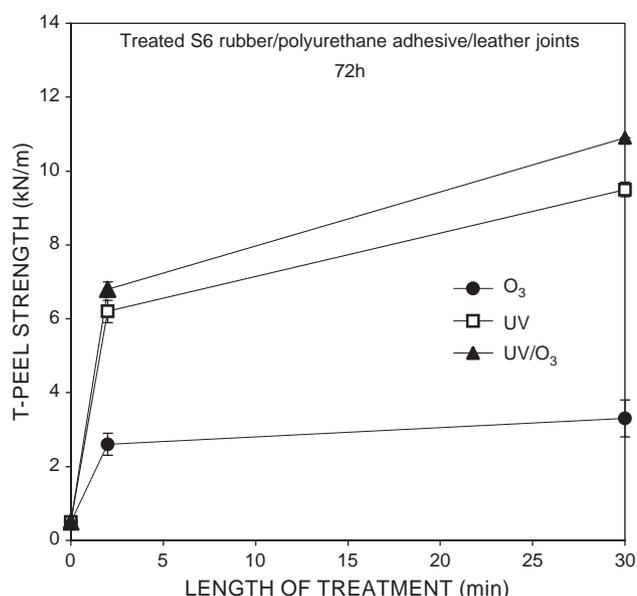


Fig. 7. T-peel strength values of O₃, UV and UV/O₃-treated S6 rubber/polyurethane adhesive/leather joints. Values obtained 72 h after joint formation.

strength values increase moderately for the 2 and 30 min O₃-treated S6 rubber/PU adhesive/leather joints, whereas treatment for only 2 min with UV or UV/O₃ leads to greater adhesive strength. Longer treatment times produce an increase in peel strength values, as expected from the improved wettability (Fig. 3), the chemical oxidation (Fig. 4 and Table 3a), and the increase in roughness/ablation (Fig. 6) seen in the S6 rubber treated with UV or UV/O₃.

Different peel strength values and loci of failure are observed in the joints produced with the O₃, UV and UV/O₃ treated S6 rubber. The locus of failure of the joints was assessed by ATR-IR spectroscopy of the failed surfaces obtained after T-peel test. The failed surface, which visually corresponds to the adhesive surface, has been named A surface, and the one that visually corresponds to the rubber has been called R surface. Fig. 8 shows the ATR-IR spectrum of the polyurethane adhesive film before joint formation. Typical absorption bands can be used to distinguish the polyurethane from the S6 rubber: N–H stretching absorption at 3350 cm⁻¹, C–H stretching bands of CH₂ and CH₃ groups in the polyurethane (2866, 2933 cm⁻¹), C=O stretching in the urethane at 1730 cm⁻¹, N–H bending absorption at 1602 cm⁻¹, N–C=O symmetric stretching absorption at 1531 cm⁻¹, and C–O stretching bands at 1229 and 1178 cm⁻¹.

Fig. 9a shows the ATR-IR spectra of the failed surfaces obtained after the peel test of the as-received S6 rubber/polyurethane (PU) adhesive/leather joint. The ATR-IR spectrum of the R surface is similar to that of the as-received S6 rubber. However, the ATR-IR spectrum of the A surface shows typical PU absorptions

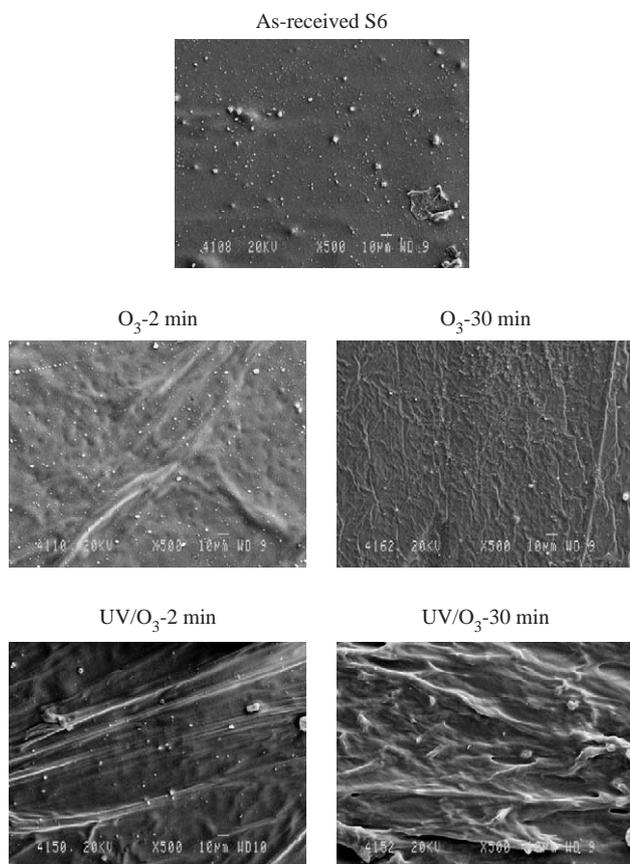


Fig. 6. SEM micrographs of the as-received and S6 rubber treated O₃ or UV/O₃ for 2 and 30 min.

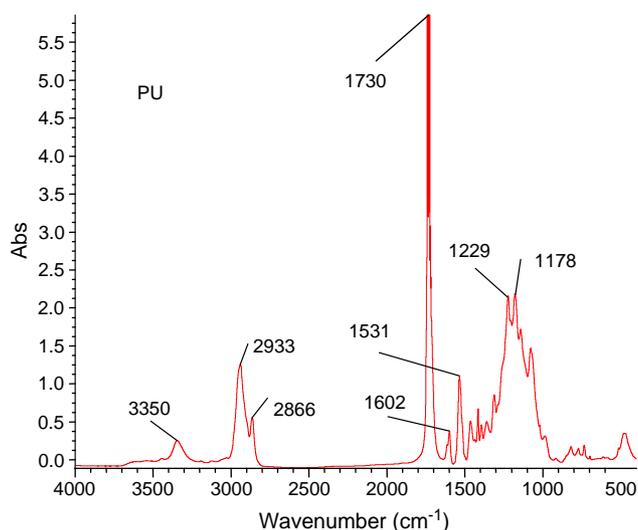


Fig. 8. ATR-IR spectrum of the polyurethane adhesive film.

(2933, 2866, 1730, 1531, 1228 and 1178 cm^{-1}) together with a contribution from the S6 rubber absorption at 968 cm^{-1} ; this suggests that a mixed failure mode is produced (adhesion + cohesive failure in a thin rubber surface layer). A similar locus of failure is observed for the 2 and 30 min O_3 -treated S6 rubber/polyurethane adhesive/leather joints. The ATR-IR spectra of the failed surfaces corresponding to the 2 min UV treated S6 rubber/polyurethane adhesive/leather joint (Fig. 9b) are similar to those for the O_3 -treated sample, in that the failed R-surface does not show oxidation bands. This could be ascribed to a crosslinking between the polyurethane adhesive and the oxidized S6 rubber surface during joint formation, resulting in a cohesion failure in a thin oxidized rubber layer that is transferred to the A surface during the peel test. This phenomenon would explain our inability to detect the oxidation at the surface of the rubber as the remaining oxidized material is likely too thin a layer to be detected by ATR-IR spectroscopy.

Recent studies [22] show that low molecular weight oxidized chain scission products can be formed by extended oxidation. This oxidized material is not bonded to the surface of the polymer and may be water soluble. Other studies [33] suggest that this low molecular weight oxidized material actually may enhance adhesion of polymers to adhesives. In fact, although no bands due to oxidation can be observed in the ATR-IR spectrum of the R surface in Fig. 9b, the peel strength is 6 times higher as compared to that obtained for the as-received S6 rubber/polyurethane adhesive/leather joint, indicating a greater interaction between the treated rubber and the adhesive. The XPS analysis of the treated surface of the rubber before application of the adhesive shows enhanced oxidation which likely plays a significant role in the increased peel

strength. Moreover, the extended UV treatment for 30 min (Fig. 9c) reveals a cohesion failure in a thicker rubber layer, which suggest that the increase of the length of treatment in UV produces a thicker oxidized rubber layer that is crosslinked to the PU adhesive during joint formation, producing higher peel strength value (Fig. 7).

The locus of failure of the 2 min-UV/ O_3 treated S6 rubber/polyurethane rubber/leather joint (Fig. 9d) is different from that obtained for the joints produced with S6 rubber treated with O_3 or UV radiation treatment for similar length of treatment. The ATR-IR spectrum of the A surface (Fig. 9d) shows bands from the PU adhesive (1730, 1531 and 1178 cm^{-1}), but also absorption bands from the S6 rubber (2919, 2851 and 1456 cm^{-1}), which show a higher relative intensity than for the similar joints prepared with 2 min- O_3 or UV S6 rubber. The ATR-IR spectrum of the R surface shows bands similar to the as-received S6 rubber, indicating that a mixed failure mode (adhesion + cohesive failure in a thin rubber layer—deeper than for the joints prepared with 2 min- O_3 or UV treated S6 rubber) has been produced. However, the locus of failure obtained for the 30 min-UV/ O_3 -treated S6 rubber/polyurethane rubber/leather joint (Fig. 9e) is similar to that obtained for the joint produced with the UV treated S6 rubber for the same length of treatment. This fact may indicate that the locus of failure is more cohesive in the rubber when the UV/ O_3 treatment is carried out on the S6 rubber surface and mainly for longer lengths of treatment.

4. Conclusions

The O_3 , UV and UV/ O_3 treatments improve the wettability of S6 rubber, modify its surface chemistry (oxidation) and create roughness. Increasing the treatment time enhances the degree of surface modification on the S6 rubber surface, and complete wettability is achieved on UV or UV/ O_3 treatment for more than 5 min. The modifications produced by UV and UV/ O_3 treatments are not restricted to the outermost S6 rubber surface. Instead, a relatively thick surface layer is modified, resulting in chain scission and the creation of low molecular weight oxidized material on the surface of the S6 rubber.

The O_3 treatment modifies the S6 rubber surface to a lesser degree than does the UV or UV/ O_3 treatments. Exposure to the active oxygen species formed in the presence of the UV radiation is mainly responsible for the chain scission and the formation of oxidized moieties on the S6 rubber surface. In absence of UV radiation, a considerably longer O_3 treatment is necessary to achieve moderate oxidation. Finally, the additional ozone incorporated during UV radiation treatment enhances

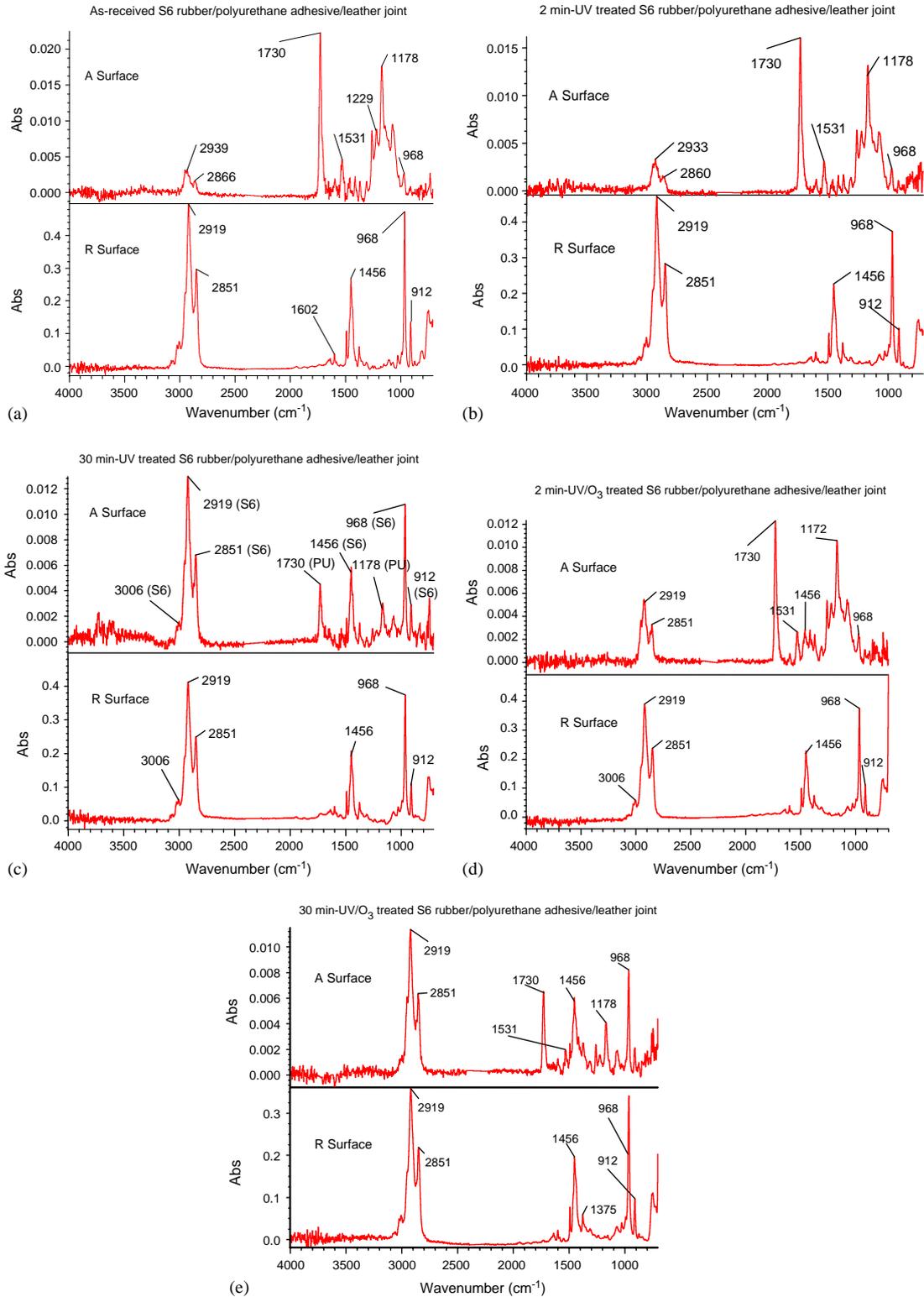


Fig. 9. ATR-IR spectra of the failed surfaces obtained after peel test. (a) As-received S6 rubber/polyurethane adhesive/leather joint; (b) 2 min-UV treated S6 rubber/polyurethane adhesive/leather joint; (c) 30 min-UV treated S6 rubber/polyurethane adhesive/leather joint; (d) 2 min-UV/O₃ treated S6 rubber/polyurethane adhesive/leather joint; (e) 30 min-UV/O₃ treated S6 rubber/polyurethane adhesive/leather joint.

the effects of UV only treatment on the S6 rubber surface and improved adhesive strength is obtained.

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