

# Surface modifications of a vulcanized rubber using corona discharge and ultraviolet radiation treatments

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Two different surface treatments have been applied to a synthetic vulcanized styrene-butadiene rubber (R1): corona discharge and UV treatment. Corona discharge treatment has been carried out on R1 rubber by varying the electrode-sample distance (2–4 mm), the duration (1 to 11 sec) and several parameters in the treatment of R1 rubber with UV treatment (lamp-sample distance between 1 and 5 cm, the duration between 30 sec and 5 min). The effects on both treatments on the surface of R1 were analyzed using contact angle measurements, ATR-IR spectroscopy, Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). A noticeable decrease in contact angles was observed on the R1 rubber by applying both treatments, although the modifications produced on the rubber surface were different. Corona discharge mainly affected the morphology of the R1 rubber surface whereas UV treatment mainly modified its chemistry. The migration of zinc stearate was only produced by UV treatment but not with corona discharge. Therefore, the UV treatment of R1 rubber was more aggressive, facilitating the migration of moieties from the bulk to the surface and producing oxygen moieties. © 2001 Kluwer Academic Publishers

## 1. Introduction

The gas phase treatment of a vulcanized styrene-butadiene rubber has been investigated in this study. One of the major applications of this material is the use as sole material to be bonded to the leather shoes upper material by means of an adhesive joint. Polyurethane adhesives are usually employed to produce adequate bonding [1]. Because the vulcanized styrene-butadiene (SBR) rubbers have low surface energy, a surface treatment is necessary in order to increase that surface energy and produce a suitable adhesive joint [2].

Different surface treatments have been used to improve the surface properties of rubber materials, although chemical treatments based on solutions of different halogenation agents are the most commonly used [3–9]. In previous papers [10, 11] the effects of these treatments have been studied; a decrease in the contact angles (good wettability and high surface energy), morphological and chemical modifications are produced, and an increase in the adhesive properties as well.

Trichloroisocyanuric acid (TCI) is the most common halogenation agent for SBR materials. Although

effective, its use shows some limitations: (i) it is difficult to guarantee a given level of active chlorine in the halogenation solution, (ii) if an excess of the halogenation solution is applied, cracks and weak surface layers can be produced (negative effects in adhesion and mechanical properties), (iii) to obtain complete effectiveness, relatively long reaction times are required, (iv) halogenation with TCI implies the use of organic solvents, which may be dangerous, and there is the risk of chlorine evolution during manipulation [4, 8].

Therefore, halogenation is not an environmentally friendly treatment, so alternative treatments have to be found. In this paper, corona discharge and ultraviolet (UV) treatments were employed to modify the surface of a SBR material. Neither treatments require high pressure, and the degree of surface modification can be controlled by varying the treatment time [12–14].

Corona discharge treatment was invented over a hundred years ago [15]. In the 1960's corona discharge was first used commercially to modify the surface of different polymeric materials such as polypropylene, polystyrene and polyethylene-terephthalate [16], and

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other polymers as well [17–19]. Stannett and Meats [20] and Kelen and Dick [21] concluded that the formation of relatively stable free radicals can be responsible for the higher adhesion of polymers as a result of the corona treatment. Ieda *et al.* [22] investigated the changes produced on the surface of polyethylene after the corona discharge treatment using mixtures of oxygen and nitrogen. Similar studies were carried out using polyolefins [23]. Since 1982, extensive work has been done to investigate the modifications produced on the morphology and surface chemistry of different polymers [24, 25]. UV treatment has been used to clean contaminants and increase the surface energy of polyethylene (PE), polyetherketone (PEEK), polyethyleneterephthalate (PET) and polystyrene (PS) surfaces [26–33]. SBR rubbers contain C–H and C–C bonds. After UV exposition, oxygen moieties can be created which may be useful to improve adhesion properties and wettability of rubbers. Studies of UV degradation (at wavelength >350 nm) of rubber followed with XPS and Auger Microscopy [34–37] conclude that oxygen was incorporated into the structure of the rubber to form carbonyl and carboxyl groups. Also, the additives of the rubber could absorb the radiation to act as free radical initiators.

Although a great number of publications using corona discharge as a surface treatment for polymers can be found in the literature to our knowledge, only one study [38] describes the effects produced on vulcanized natural (NR), SBR and nitrile (NBR) rubbers. Despite the modifications produced on the surfaces, poor bonding was obtained after the corona discharge treatment. Furthermore, no previous studies have been published on the use of UV treatment as surface treatment of rubber. Therefore, the aim of this study is the comparison of the effects produced on the surface of a vulcanized SBR rubber treated with corona discharge and UV treatment.

## 2. Experimental

### 2.1. Materials

The composition of the vulcanized styrene-butadiene rubber used in this study (R1) is given in Table I. The R1 rubber contains silica and carbon black as fillers and also zinc stearate can be formed during

TABLE I Formulation of R1 rubber

Component	Amount (phr) <sup>a</sup>
SBR 1502	65
SBR 1904	35
Carbon black (N-330)	23
Precipitated silica	25
Sulphur	1.8
Cumarone-indene resin (85°C)	3.5
Zinc oxide	3.8
Stearic acid	0.8
<i>N</i> -cyclohexyl-2-benzothiazole sulphenamide	1.1
Tetramethyl tiuram disulphide	0.2
Polyethylene glycol (Mw = 4000)	1.1
Phenolic antioxidant	0.8

<sup>a</sup>phr = parts per one hundred parts of rubber.

vulcanization by reaction of zinc oxide and stearic acid. Some physical properties of R1 rubber are: tensile strength = 18.0 MPa; elongation at break = 397%; abrasion resistance = 157 mm<sup>3</sup>. Standardized tests were used to obtain those values [39].

## 2.2. Apparatus for surface treatment

### 2.2.1. Corona discharge unit

The corona discharge treatment was carried out in a TANTEC H9 equipment (Lunderskov, Denmark). A hook-shaped stainless steel electrode was used. The system was provided with an electronic speed controller and the sample was placed over a nylon non-conductive platform.

The dimensions of the samples were 150 mm length, 30 mm width and 3 mm thick. The corona discharge was produced for different time of treatment (1 to 11 seconds). This is the time during which all the sample was passing under the electrode, receiving the discharge from the beginning to the end of the test piece. As the length of the sample is 150 mm, the time of treatment of 1 and 11 sec corresponds to speed of treatment of 900 and 80 cm/min, respectively.

In some samples, several consecutive treatments were applied to the rubber to produce a more aggressive treatment. Furthermore, the distance between the electrode and the sample was varied between 2 and 4 mm.

### 2.2.2. UV treatment unit

The UV radiation source was a low-pressure vapour grid mercury lamp, manufactured by American Ultraviolet (USA). The lamp works at the wavelength of 253.7 nm which provided a radiation intensity of 10 mW/cm<sup>2</sup> taken at a distance of 2 inches from the lamp. Photodecomposition of ozone into atomic and molecular oxygen occurs due to the absorption of ozone by the radiation. The UV lamp was placed inside a UV protective polycarbonate box (Fig. 1). The box has an extraction unit to avoid high concentration of ozone during the treatment, and the heating of the lamp was also avoided. The sample was placed in a polycarbonate plate which distance from the lamp may be varied. The distance between the UV source and the rubber sample was varied between 1 and 5 cm. The duration of the treatment was also studied (10 sec, 30 sec, 1 min and 5 min).

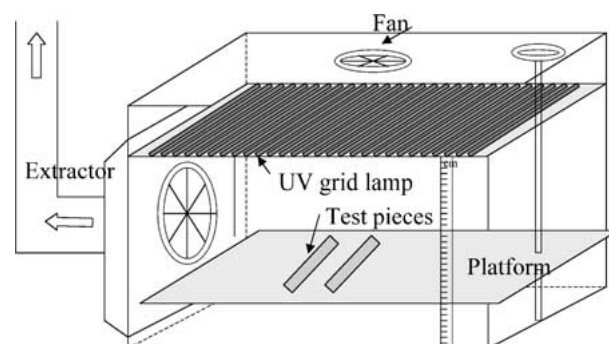


Figure 1 Scheme of the UV treatment unit.

## 2.3. Surface characterization techniques

### 2.3.1. Contact angle measurements

The R1 rubber treated with corona discharge or UV treatment was placed into a hermetic, isothermal (25°C) and saturated chamber of a Rame Hart 100 goniometer. Drops (4  $\mu\text{l}$ ) of ethylene glycol as test liquid were placed on the surface of the rubber. The immediate contact angle values (just after drop was placed on the treated rubber surface) on both sides of the drop were measured. The experimental error was  $\pm 2$  degrees.

### 2.3.2. ATR-IR spectroscopy

The attenuated transmission reflectance (ATR) technique was used to determine the chemical modifications produced on the most external 5  $\mu\text{m}$  rubber surface after treatment was carried out. A Nicolet 205 FTIR spectrophotometer was used to obtain the ATR-IR spectra of the as-received rubber and corona discharge and UV treated samples. A Germanium crystal (absorption 690–4000  $\text{cm}^{-1}$ ) was used. The signal-to-noise ratio was 0.04% (at 2000  $\text{cm}^{-1}$ ); the incident angle was 45°, and 200 scans per experiment were carried out.

### 2.3.3. Scanning electron microscopy (SEM)

The morphological modifications produced on the rubber surfaces were analyzed using a JEOL JSM-840 SEM microscope, provided with a Mamiya 6  $\times$  7 camera. Samples were coated with Au before the analysis.

### 2.3.4. X-Ray photoelectronic spectroscopy (XPS)

Untreated and treated rubbers were analyzed using XPS (VG SCIENTIFIC ESCALAB MK II) with Al  $K_{\alpha}$  radiation. The spectrometer was interfaced to a VGS 5000-S data system based on a DEC PDP 11/73 computer for data acquisition and analysis. Samples were placed onto stubs with double-sided tape. The analyses were carried out at a take-off angle of 45°. The spectrometer was operated in the fixed analyser transmission mode at pass energies of 100 eV or 20 eV.

Survey spectra were recorded in the range of 0–1200 eV binding energy together with high resolution spectra of the core levels on interest. Quantitative surface analysis and curve-fitting were carried out using the manufacturer's standard software. The binding energies were referenced to the value for the hydrocarbon species at 285.0 eV.

### 2.3.5. Atomic force microscopy (AFM)

In this study we used a Nanoscope III AFM system (Digital Instruments Inc. USA) equipped with a Tapping AFM (TM AFM). Samples were glued to steel disks and this structure was placed on a top of piezoscanner. In the TM AFM mode silicon cantilevers (purchased from Digital Instruments Inc.) were employed. The typical apex radius of a tip on the cantilever is nominally 15 nm. The microfabricated cantilever is rectangular-shaped and has a total length of 100  $\mu\text{m}$  and a spring constant of 44 N/m. The TM AFM was operated in air and the images were stored as either 256  $\times$  256 or 512  $\times$  512 point pixel arrays.

All data processing for the TM AFM was conducted using the Nanoscope III software.

## 3. Results and discussion

### 3.1. Corona discharge treatment

Three experimental variables have been considered: the distance between the rubber sample and the electrode, the duration of the treatment and the number of consecutive treatments on the same sample.

#### 3.1.1. Sample-electrode distance

Two different sample-electrode distances were used: 2 mm and 4 mm (the minimum distance at which corona discharge was not evident at the rubber surface). Corona discharge treatment was carried out for 1 and 11 sec (speeds of 900 and 80 cm/min, respectively).

The contact angles values were obtained immediately after treatment with rubber-electrode distances of 2 and 4 mm. Table II shows the values obtained using ethylene glycol as liquid test. The immediate contact angle value of as received R1 (treatment time = 0 sec) is 80 degrees and is noticeably decreased after the treatment was carried out. Lower contact angle values (improved wettability) were obtained for a rubber-electrode distance of about 2 mm. The variation in contact angle is more pronounced by increasing the duration of the corona discharge. A rubber-electrode distance of 2 mm was selected.

#### 3.1.2. Duration of the treatment

Rubber R1 was treated using corona discharge for different times between 1 and 11 seconds. Contact angle values obtained on the R1 rubber surface after the treatment are given in Fig. 2. The contact angles decreased after the treatment at least in 20 degrees (treatment for 11 sec shows a contact angle of 53 degrees),

TABLE II Immediate contact angle (ethyleneglycol, 25°C) on R1 rubber surface treated with corona discharge

Treatment time (s)	Contact angle (degrees)	
	$d = 2$ mm	$d = 4$ mm
0	80	80
1	59	67
11	53	56

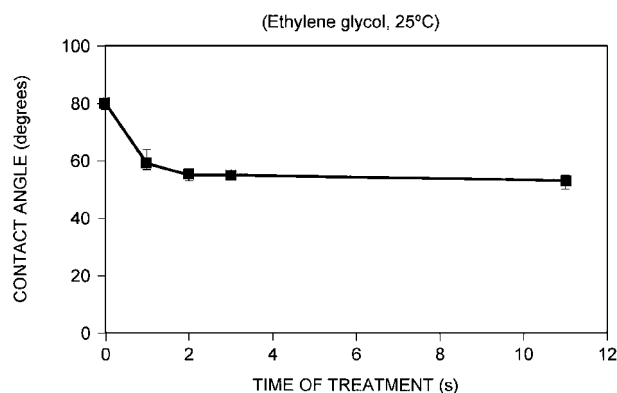


Figure 2 Contact angle values (ethylene glycol, 25°C) of as-received and corona discharge treated R1 rubber as a function of the duration of the treatment.

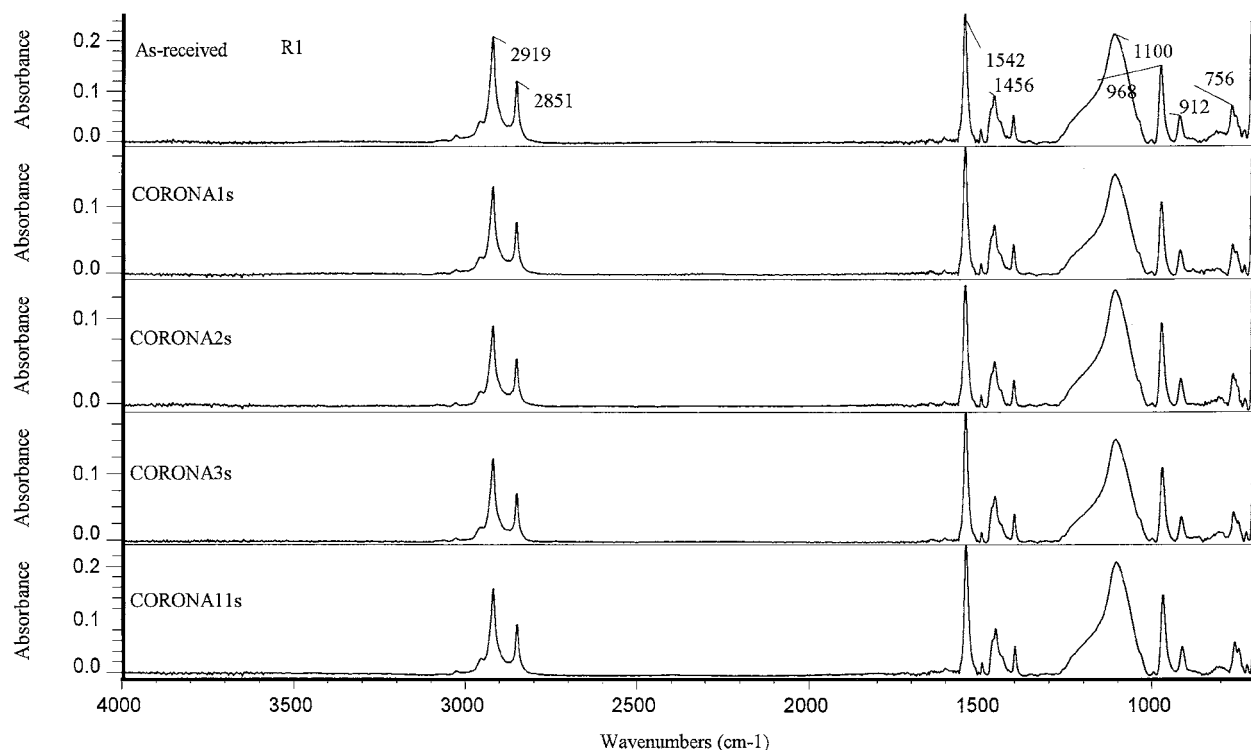


Figure 3 ATR-IR spectra of as-received R1 and corona discharge treated R1 rubber for 1 to 11 seconds.

and the increase in the duration of the treatment produces a slight decrease in values (i.e. improved wettability).

The decrease in contact angle values obtained after corona discharge treatment can be ascribed to modifications in the surface chemistry. Fig. 3 shows the ATR-IR spectra of the as-received and corona discharge treated R1 rubber. The ATR-IR spectrum of the as-received R1 rubber shows bands at 2851 and 2919  $\text{cm}^{-1}$  attributed to  $\text{CH}_2$  and  $\text{CH}_3$  groups; a strong band at 1542  $\text{cm}^{-1}$  from zinc stearate (antiadherent compound which is responsible of the poor adhesion of this rubber) [9, 10] also appears. Furthermore, there are bands at 1456  $\text{cm}^{-1}$ , scissoring vibration of  $=\text{CH}_2$  (butadiene), the band at 1100  $\text{cm}^{-1}$  due to Si-O (filler), 968 and 912  $\text{cm}^{-1}$  bands due to C-H bonds in the butadiene and the band at 756  $\text{cm}^{-1}$  due to C=C bonds (styrene). The treatment of R1 rubber with corona discharge produces similar ATR-IR spectra to that for the as received R1 rubber. The only difference is the small decrease in the intensity of bands at 2851 and 2919  $\text{cm}^{-1}$  due to the removal of  $\text{CH}_2$  moieties from the rubber surface. Therefore, the modifications produced on the R1 rubber surface by

corona discharge must be produced on the most external surface.

ATR-IR spectroscopy analyses some 5  $\mu\text{m}$  into the sample and therefore XPS was used. This technique analyses only 5 nm deep into the rubber. The XPS data of Table III and Fig. 4a show as expected that carbon is

TABLE III Composition (at.%) of as-received and corona discharge treated R1 rubber for different duration of treatment

Element	Time of treatment (s)		
	0	1	11
C	85.4	78.7	76.6
O	10.8	14.3	16.7
N	–	0.6	0.6
Si	0.9	4.5	4.1
Zn	2.9	1.9	2.0
C/O	7.9	5.5	4.6

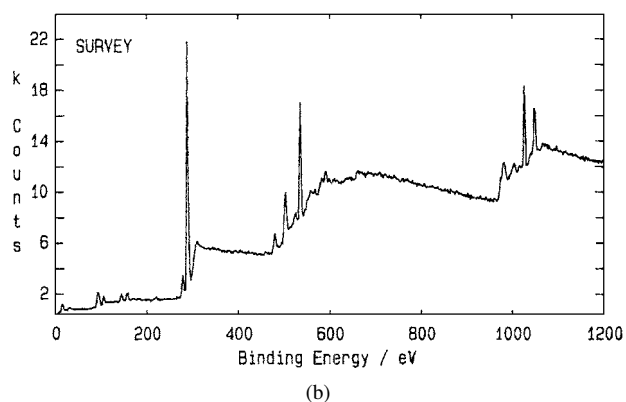
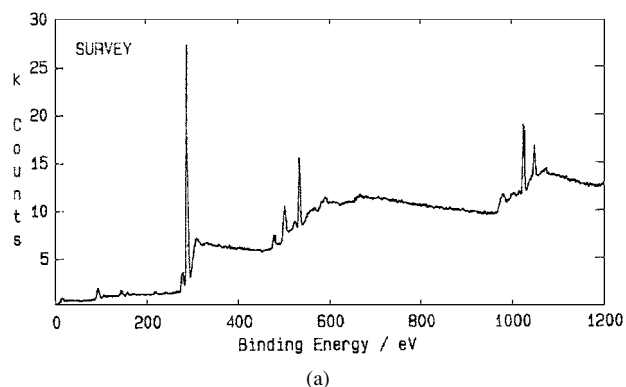


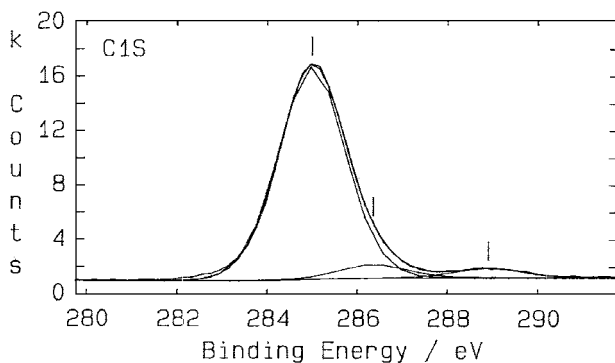
Figure 4 (a) Survey spectra of as-received R1 rubber. (b) Survey spectra of corona discharge treated R1 rubber for 11 seconds.

the main element on the as received R1 rubber; oxygen is also relevant. The C/O ratio is 7.9. There is a low amount of Si and Zn on the R1 surface and sulfur and nitrogen are not present. Those elements were added to the rubber formulation in important amounts but they are not present on the surface, confirming the migration of low molecular species composed by C, O and Zn, i.e. zinc stearate.

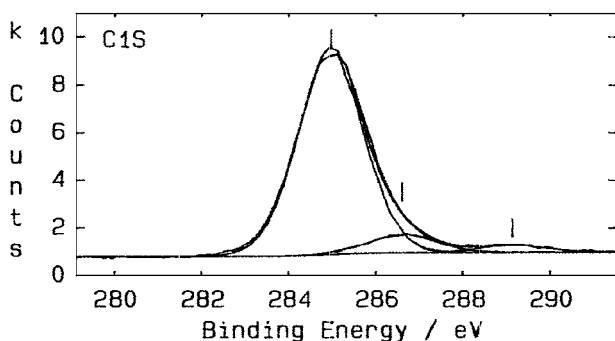
Corona discharge treatment for 11 seconds produces a decrease in the amount of C and an increase in O, Si and N; the amount of Zn is small. As a consequence, the C/O ratio decreases to 4.6 as shown in Fig. 4b. Therefore, the treatment with corona discharge removes zinc stearate from the as-received R1 rubber and increases the amount of silica at the surface, i.e. the low molecular weight moieties are partially removed from the surface. The decrease in the ratio C/O is more important when

TABLE IV Percentages of species obtained from C1s curve fitting of as-received and corona discharge treated R1 rubber

Species	Percentage of species (%)		
	As-received	1 s	11 s
C—C, C—H	90	92	89
C—O	6	6	8
COO <sup>-</sup>	4	2	3



(a)

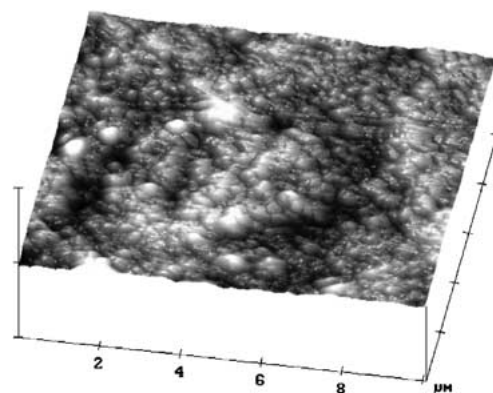


(b)

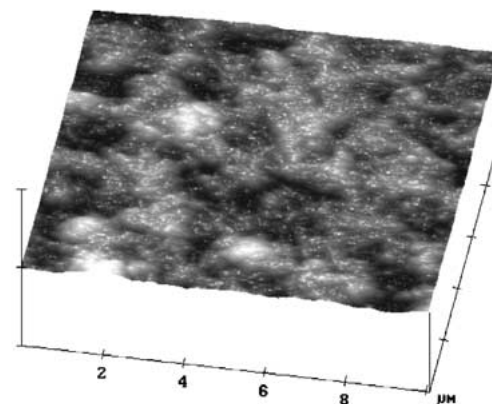
Figure 5 (a) C1s curve-fitting of as-received. (b) C1s curve-fitting of corona discharge treated R1 rubber for 11 seconds.

the duration of the treatment increases. That decrease can be ascribed to two different effects: (i) incorporation of oxygen on the surface of the rubber due to the treatment (which will be in agreement with the decrease observed in contact angles), and (ii) the oxygen is associated to Si as SiO<sub>2</sub> (in agreement with the Si 2p band at 102 eV, Fig. 4b).

For as-received R1 rubber the 0.9 at.% Si corresponds to 1.8 at.% oxygen as SiO<sub>2</sub>. If there is a total oxygen concentration of 10.8 at.%, only 9 at.% can be associated to C. Using the same argument, the amount of oxygen-carbon species in the R1 rubber treated with corona discharge for 1 and 11 sec is 7 and 11 at.%, respectively. Therefore, according to these calculations the increase in oxygen concentration after corona discharge is associated to the presence of SiO<sub>2</sub> on the rubber surface, but no oxygen incorporation due to oxidation is produced. Those results agree with the data shown in Table IV where the percentage of different carbon-oxygen species obtained from the C1s curve fitting is 10, 8 and 11% for the as-received and the corona discharge treatment for 1 and 11 sec treatment, respectively. The C1s curve fitting (Fig. 5) of the as-received R1 rubber shows C—C and C—H species at 285.0 eV and two types of oxidized carbon moieties at 286.6 eV (6 area%) due to C—O and 289.0 eV (4 area%) due to carboxylate groups [40]. The analysis of the area (%) from the C1s curve fitting (Table IV) for the R1



a) As-received R1



b) R1 Corona Discharge - 11seconds

Figure 6 (a) AFM images of as-received R1 rubber. (b) AFM images of corona discharge treated R1 rubber for 11 seconds.

rubber treated with corona discharge produces a slight increase in C–O moieties (286.5 eV) and a slight decrease in C=O species (288.9 eV). This is in agreement with the decrease in Zn (Table III) and is due to the formation of zinc stearate. The increase in the duration of the treatment slightly enhances the effects due to the treatment with corona discharge.

The surface treatment also may produce a modification of the morphology of the rubber. AFM was used to study the variation in the microroughness of the rubber after corona discharge treatment. The AFM image of as-received R1 shows the presence of SiO<sub>2</sub> particles spread on the polymer matrix surface (Fig. 6a and b). After 11 sec of treatment with corona discharge, an increase in roughness and a greater amount and large size SiO<sub>2</sub> particles is produced. Despite the removal of zinc stearate due to the treatment and the presence of SiO<sub>2</sub> particles, these inorganic particles seem to be partially covered by an organic layer of polymer.

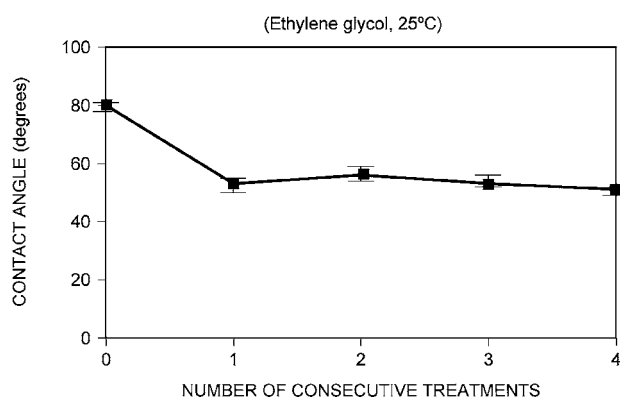


Figure 7 Contact angle values (ethylene glycol, 25°C) of as-received and corona discharge treated R1 rubber using 1 to 4 consecutive treatments (11 seconds for each treatment).

Unlike other surface treatments for rubber where chemical modifications are mainly produced [10, 11], the treatment with corona discharge mainly modifies the topography of the R1 rubber. Furthermore, the treatment with corona discharge is somewhat more effective when is carried out for 11 seconds.

### 3.1.3. The effect of several consecutive corona discharge treatments

The corona discharge treatment of R1 rubber does not produce the complete removal of zinc stearate. Therefore, the effectiveness of the treatment was tried to be improved by carrying out several treatments (1 to 4) on the same rubber. The duration of the treatment was always 11 sec.

The corona discharge treatment produced a noticeable decrease in contact angle values (Fig. 7) and this slightly decreases by increasing the number of consecutive treatments (48 degrees for 4 treatments). This decrease in contact angles may be ascribed to more extensive modification of the chemistry and/or morphology of rubber.

The ATR-IR spectra (Fig. 8) show how the number of consecutive treatments leads to more intense bands due to oxygen species (bands at 1600–1700 cm<sup>-1</sup>, probably CH<sub>2</sub>=CH–COR or CH<sub>2</sub>=CH–O–CO) [41]. Furthermore, the degree of removal of CH<sub>2</sub> and CH<sub>3</sub> groups is more effective, and the band due to zinc stearate (1542 cm<sup>-1</sup>) shows a more marked decrease in respect to the Si–O band (1100 cm<sup>-1</sup>).

The XPS analysis of R1 surface treated for 1 and 4 consecutive treatment shows the chemical composition given in Table V.

When the corona discharge treatment is carried out 4 consecutive times a somewhat lower C/O ratio than when only 1 treatment is produced (Table V). For 4

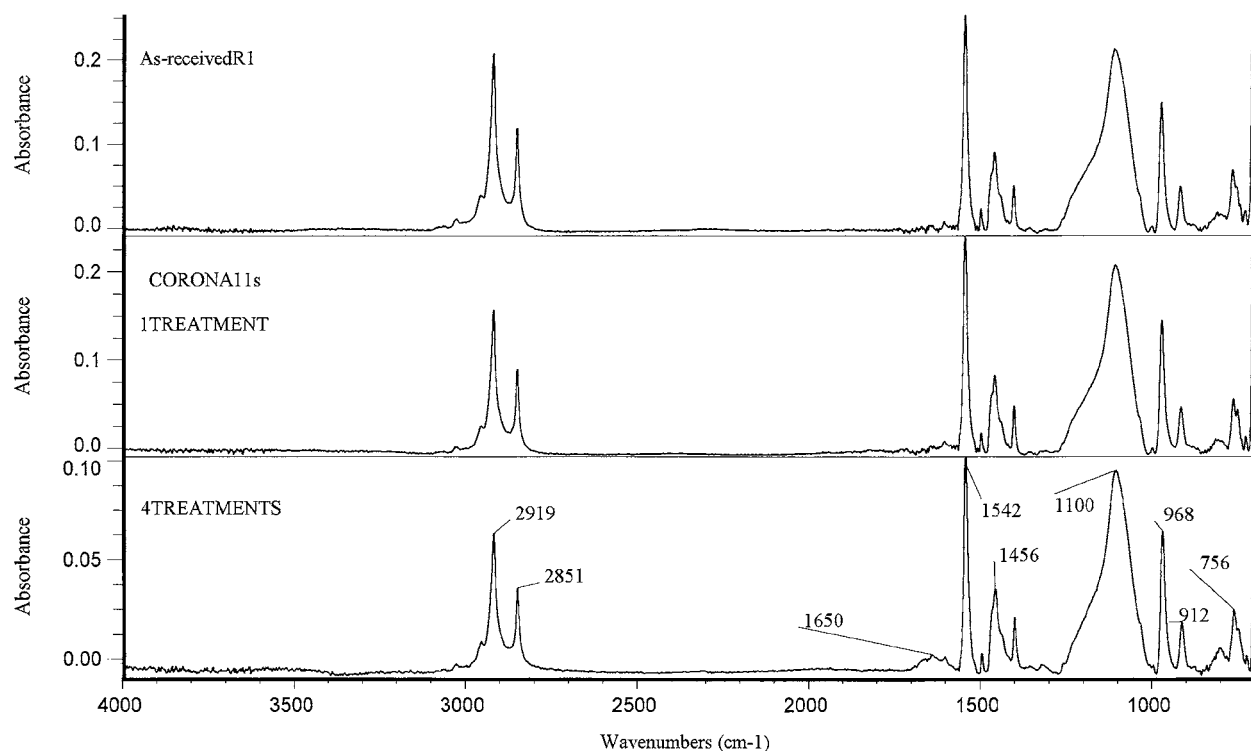


Figure 8 ATR-IR spectra of untreated and corona discharge treated R1 rubber with 1 and 4 consecutive treatments (11 sec each treatment).

TABLE V Composition (at.%) of as-received and corona discharge treated R1 rubber with 1 and 4 consecutive treatments (11 sec for each treatment)

Element	Number of consecutive treatments		
	0	1	4
C	85.4	76.6	74.3
O	10.8	16.7	18.7
N	–	0.6	–
Si	0.9	4.1	5.0
Zn	2.9	2.0	2.0
C/O	7.9	4.6	4.0

TABLE VI Percentages of species obtained from C1s curve fitting of as-received and corona discharge treated R1 rubber with 1 and 4 consecutive treatments (11 sec each treatment)

Species	Percentage of species (%)		
	As-received	1 Treatment	4 Treatments
C–C, C–H	90	89	86
C–O	6	8	11
COO <sup>-</sup>	4	3	3

treatments, the amount of oxygen associated to Si is 10 at.%, so, 8.7 at.% oxygen is bonded to C, resulting in 12 at.% of oxygenated carbon. Therefore, there is not a great increase in the degree of the oxidation, mainly in the form of C–O moieties (286.5 eV) (Table VI). Furthermore, the amount of silica on the R1 surface increases with the number of treatments.

The SEM micrographs of untreated and corona discharge treated R1 rubber with 1 and 4 consecutive treatments are presented in Fig. 9. The increase in the number of consecutive treatments produces a somewhat more marked removal of material from the rubber surface, resulting a less rough surface.

### 3.2. UV treatment

The influence of the distance between UV source and the rubber surface and the effect of the duration of the UV treatment was considered in this study.

#### 3.2.1. Distance between the UV source and the rubber

To analyze the influence of the distance between the UV source and the rubber, a treatment for 2 min was selected, and the distance was varied between 1 and 5 cm.

A noticeable decrease in contact angle (Fig. 10) is produced when the R1 rubber is treated with UV treatment; the increase in the distance between the UV-source and the sample gradually produced a less marked decrease, i.e. the improved wettability due to the treatment is higher when the rubber is near the UV source. An increase in contact angle produced on the rubber surface is always observed after UV treatment.

The ATR-IR spectra (Fig. 11) of R1 rubber treated for 2 min at different distance from the UV source show

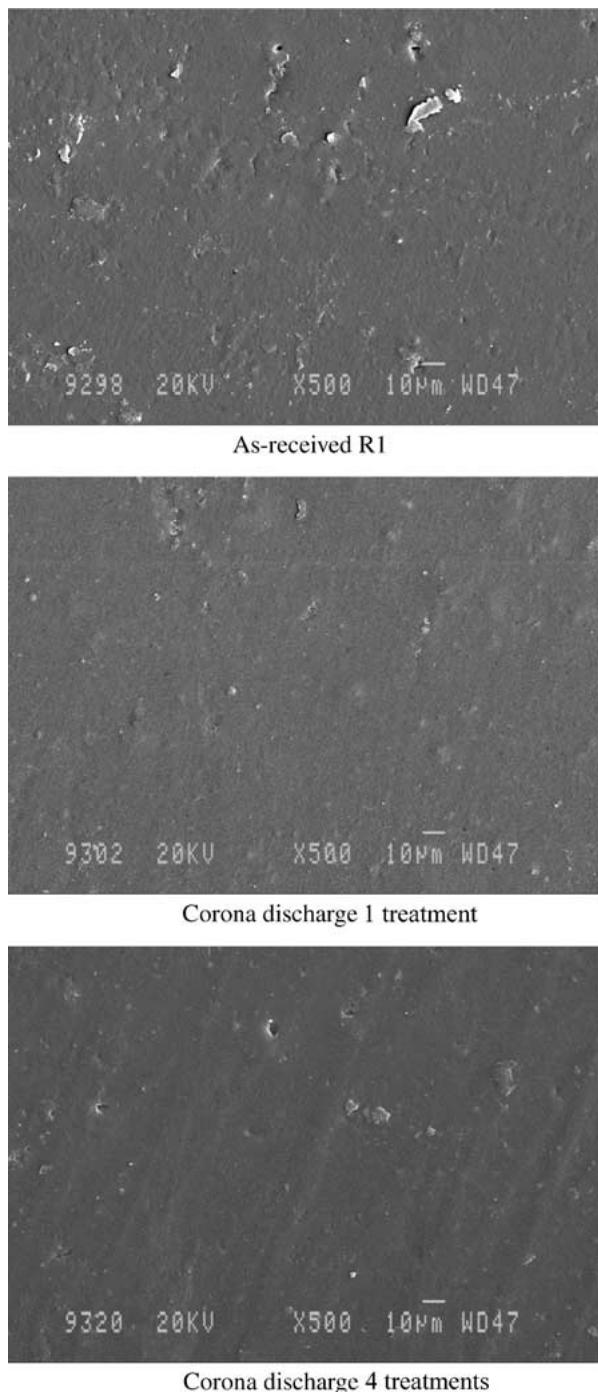


Figure 9 SEM micrographs of as-received and corona discharge R1 rubber with 1 and 4 consecutive treatments (11 sec each treatment).

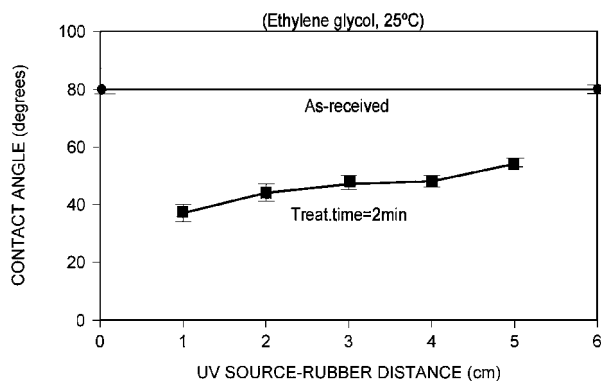


Figure 10 Contact angle values (ethylene glycol, 25°C) on the R1 rubber surface treated with UV at different distances between the lamp and the sample.

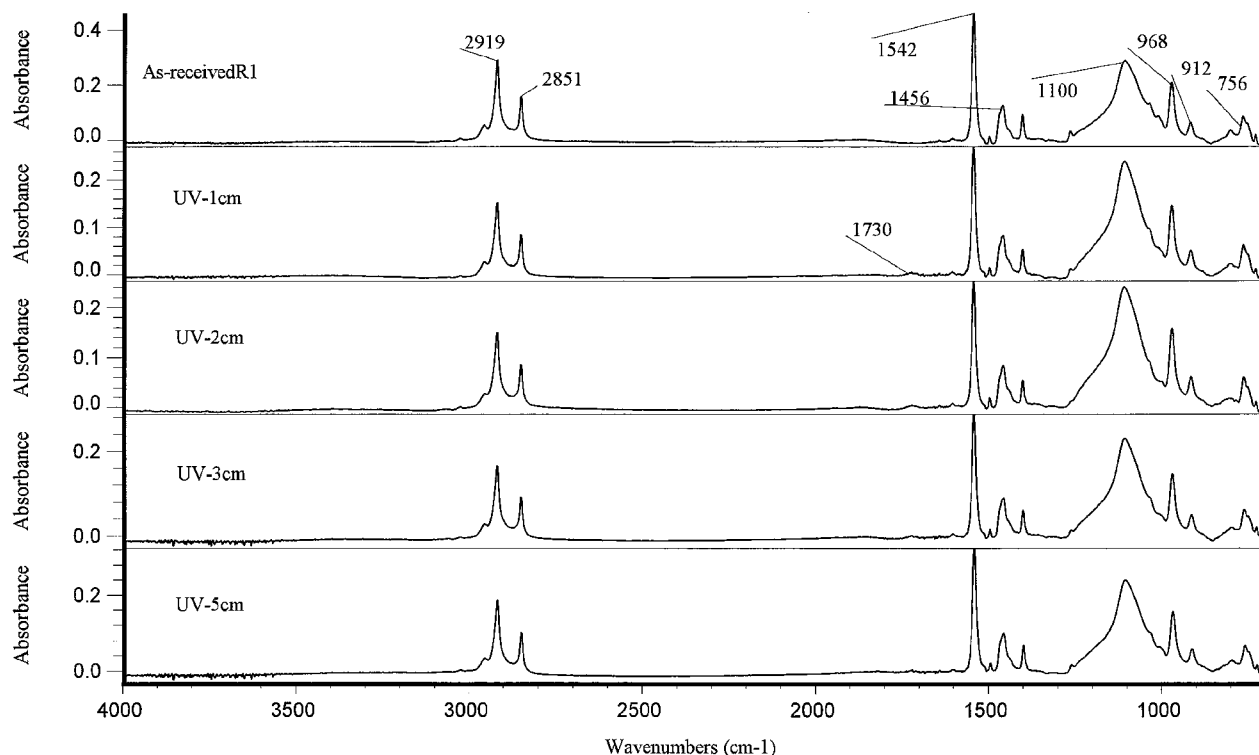


Figure 11 ATR-IR spectra of R1 rubber treated with UV for 2 min at different UV lamp-rubber distance.

a small band at  $1730\text{ cm}^{-1}$  due to carbonyl groups on the surface of the treated rubber. The intensity of this band is high when the distance between UV source and the rubber is shorter, indicating a higher effectiveness of the treatment. Furthermore, as a consequence of the UV treatment the intensity of the Si–O band ( $1100\text{ cm}^{-1}$ ) increases, and that of the  $\text{CH}_2$  and  $\text{CH}_3$  groups ( $2851, 2919\text{ cm}^{-1}$ ) decreases. Therefore, zinc stearate ( $1542\text{ cm}^{-1}$ ) is partially removed from the rubber. This can be more clearly noticed in Table VII where the Si–O band to ( $\text{CH}_2, \text{CH}_3$ ) band at  $2919\text{ cm}^{-1}$  ratio increased after UV treatment and is increased as the UV lamp-sample distance decreases. Furthermore, the Si–O to zinc stearate band shows the partial removal of zinc stearate from the R1 surface after UV treatment.

The analysis of the untreated and UV treated rubber using SEM (Fig. 12) show how the UV treatment produces a more homogeneous R1 surface. When the distance is shorter the treatment is more aggressive and several white rounded particles appear on the R1 surface. EDX analysis of those particles indicates that corresponds to silica (filler in the rubber).

TABLE VII Bands ratio ( $\text{cm}^{-1}$ ) in the ATR-IR spectra of Fig. 11

UV source-sample distance (cm)	Si–O/( $\text{CH}_2, \text{CH}_3$ )	Si–O/Zn stearate
As-received	1	0.6
1	1.5	0.9
2	1.5	0.9
3	1.4	0.8
5	1.2	0.7

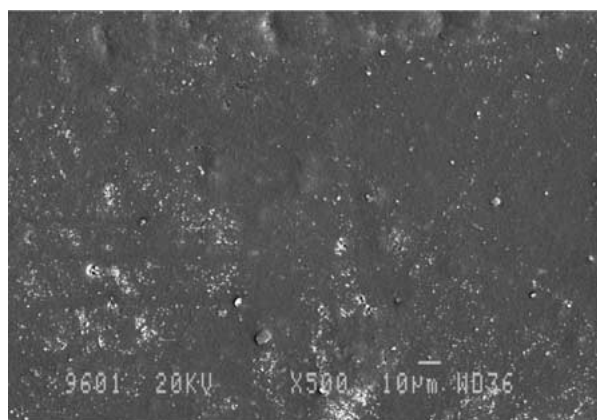
### 3.2.2. Duration of treatment

The distance between UV source and R1 rubber was set to 2 cm, and the UV treatment was varied between 10 sec and 5 min. The contact angle value of as-received R1 rubber (80 degrees) was decreased to 68 and 56 degrees after 30 sec and 1 min UV treatment, respectively (Fig. 13). The increase in the duration of the treatment produces a more marked decrease in the contact angle up to 3 min treatment; for higher times the contact angle values were not modified (40 degrees).

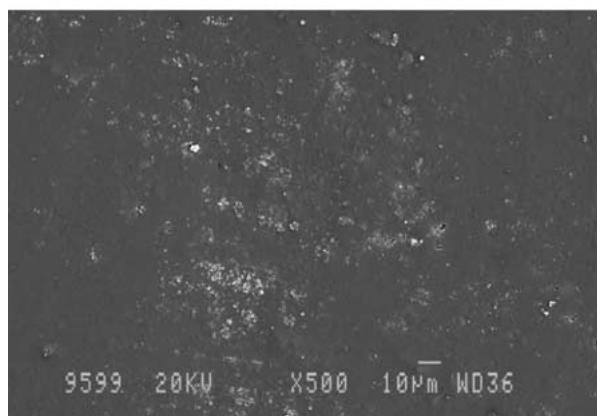
The creation of oxidized moieties on the surface becomes noticeable when the R1 rubber was treated with UV at least for 2 min. Fig. 14 shows the ATR-IR spectra of the R1 rubber treated with UV for different times. The band at  $1730\text{ cm}^{-1}$  (due to carbonyl groups) increases its intensity and width as the duration of treatment increases. At the same time a band at  $1600\text{--}1650\text{ cm}^{-1}$  appears for high duration of the treatment, probably due to alkenes conjugated near to carbonyl groups [44]. Furthermore, the increase in the duration of the UV treatment leads to an increase in the relative intensity of the Si–O band ( $1100\text{ cm}^{-1}$ ) with respect to those for  $\text{CH}_2$  and  $\text{CH}_3$  groups ( $2851, 2919\text{ cm}^{-1}$ ). Therefore, the increase in the duration of the treatment produces the partial removal of zinc stearate and also produces oxidation of the surface. Those effects are more marked than when the treatment is produced with corona discharge.

XPS analysis of R1 rubber treated with UV during 30 sec, 2 and 5 min are given in Table VIII. The C/O ratio obtained for UV treated R1 rubber is always lower than for the as-received rubber, indicating an increase in the presence of oxygen and a removal

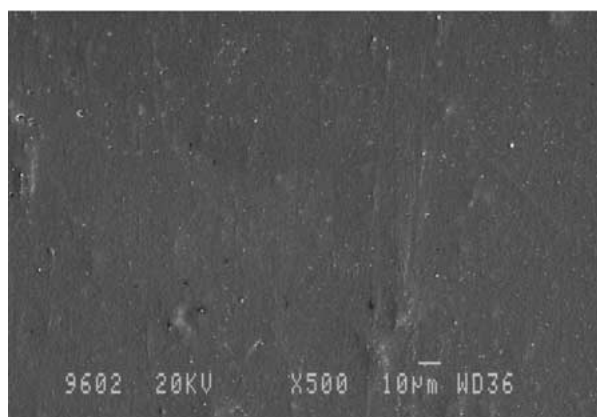




UV treatment 1 cm



2 cm



5 cm

Figure 12 SEM micrographs of R1 rubber treated with UV at different UV lamp-rubber distance.

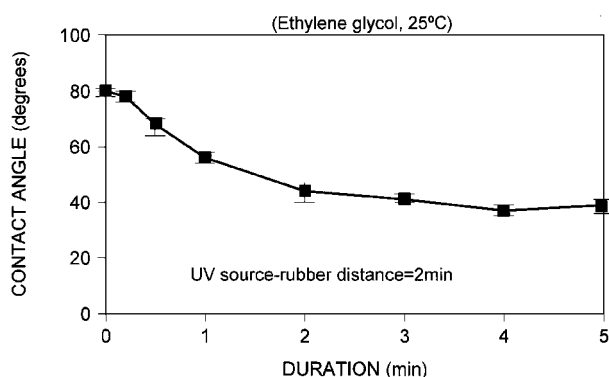


Figure 13 Contact angle values (ethylene glycol, 25°C) on R1 rubber surface treated with UV at different time.

TABLE VIII Composition (at.%) of as-received and UV treated R1 rubber for different time

Element	Duration of UV treatment			
	As-received	30 sec	2 min	5 min
C	85.4	80.4	76.7	71.8
O	10.8	14.1	17.2	19.7
N	–	–	0.9	1.5
Si	0.9	2.8	2.0	2.0
Zn	2.9	2.7	3.2	5.0
C/O	7.9	5.7	4.5	3.6

TABLE IX Percentages of species obtained from C1s curve fitting of as-received and UV treated R1 rubber for different time

Species	Percentage of species (%)			
	As-received	30 sec	2 min	5 min
C–C, C–H	90	88	87	87
C–O	6	5	6	6
C=O	–	–	1	1
COO <sup>–</sup>	4	7	5	7

of carbon moieties when R1 is treated with UV. The amount of oxygen increases as the duration of treatment increases. Although in the UV treated rubber an increase in the silica at.% was observed, it was not so important than for the corona discharge treated R1 rubber. The UV treatment produces an increase in the zinc at.% from 2.9 (as-received) till 5.0 at.% (UV- 5 min) (Table VIII). The presence of zinc and oxygen on the surface can be associated to zinc stearate, and UV treatment favours the migration of zinc stearate to the rubber surface. In fact, Table IX shows an increase in the percentage of C=O and COO<sup>–</sup> groups. By using corona discharge similar ratios were obtained but the removal of zinc stearate was produced. On the other hand, nitrogen appears on the rubber surface after UV treatment, but whereas the treatment with corona discharge showed a stabilization in the amount of nitrogen when the duration was increased, after UV treatment the amount of nitrogen continues increasing with the duration (0.9 at.% at 2 min and 1.5 at.% at 5 min).

The SEM micrographs (Fig. 15) show that the increase in the duration of the UV treatment up to 2 min favours the formation of silica particles on the surface. The amount of these particles is increased in respect to the rubber treated for 30 sec. However, when the surface was treated in UV for 5 min, the amount of particles decreases. Furthermore, the increase in the duration of the UV treatment produces some degree of swelling on the R1 rubber surface.

AFM images (Fig. 16) after UV treatment for 30 sec and 5 min show more clearly the presence of SiO<sub>2</sub> particles in respect to the as received R1 rubber (Fig. 4), but there are no important differences for the treatment between 30 sec and 5 min. Therefore, the UV treatment of R1 rubber does not produce a so heterogeneous surface than the corona discharge does, but greater chemical modifications are produced using UV treatment.

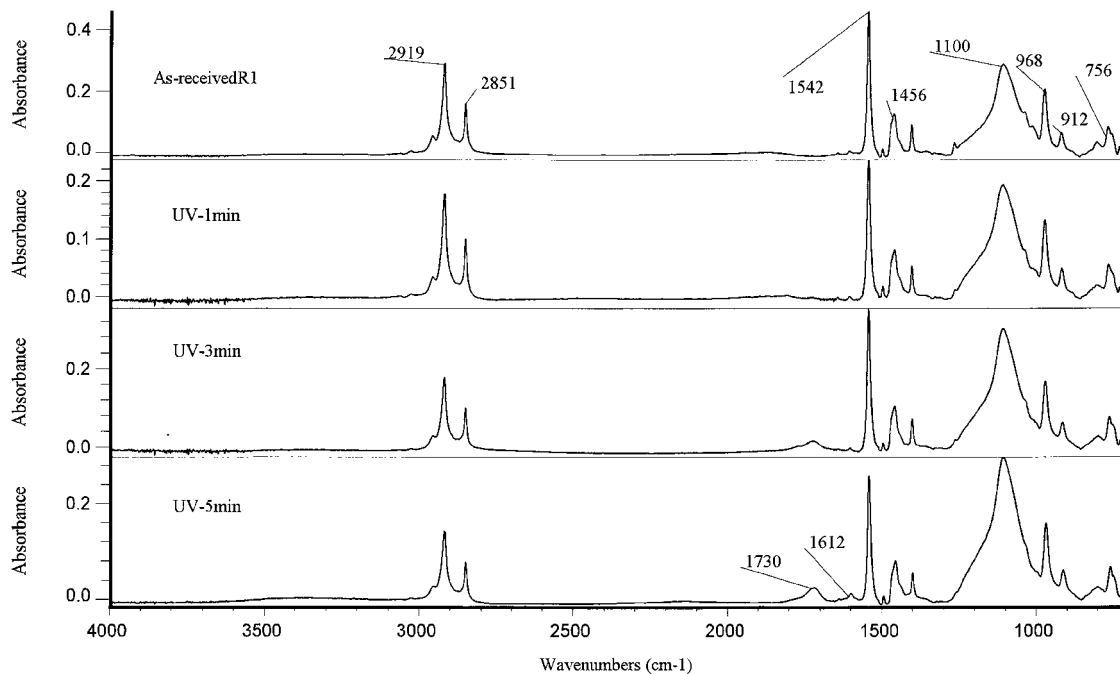
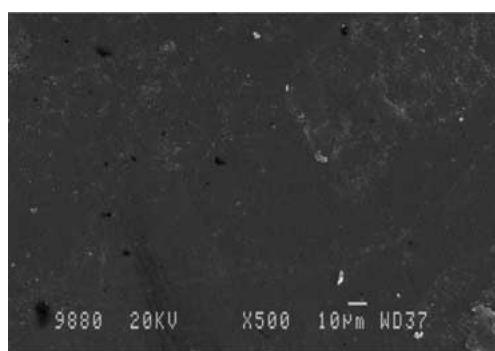
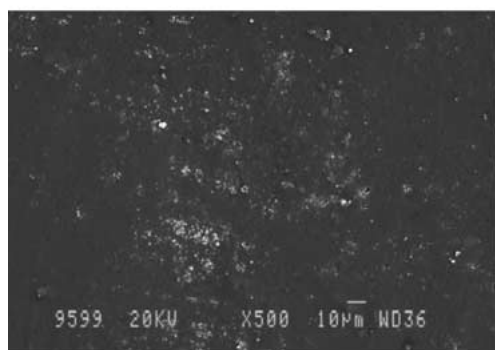


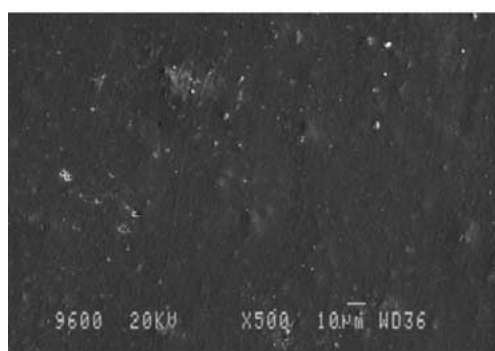
Figure 14 ATR-IR spectra of R1 rubber treated with UV at different time.



UV treatment 30 seg

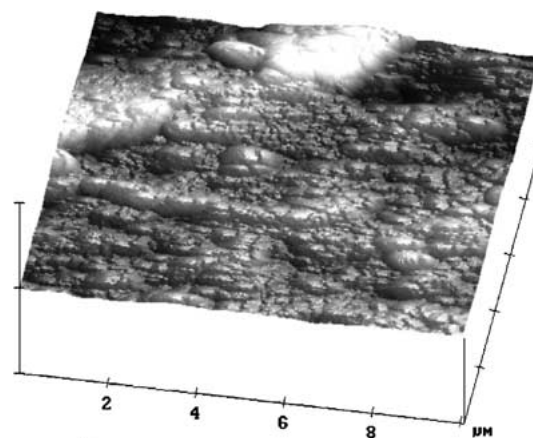


2 min

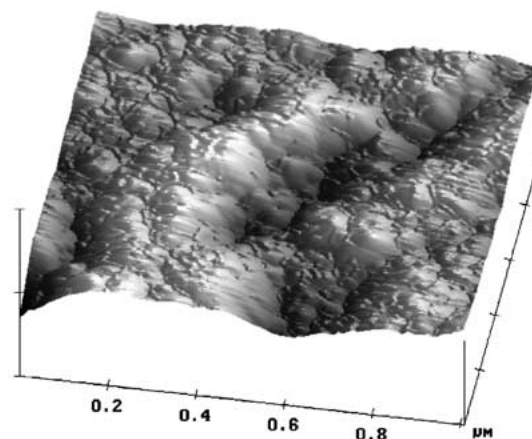


5 min

Figure 15 SEM micrographs of R1 rubber treated with UV at different time.



a) R1 UV treatment—30 sec



b) R1 UV treatment—5 min

Figure 16 (a) AFM images of R1 rubber treated with UV for 30 sec. (b) AFM images of R1 rubber treated with UV for 5 min.

#### 4. Conclusions

Both treatments produce a noticeable decrease in the amount of carbon (C–C and C–H bonds) on the R1 rubber surface, accompanied by an increase in the amount of oxygen very similar for the two treatments. The

presence of oxygen, however, is a result of different mechanisms for the two treatments. Corona discharge shows an increase in oxygen because the surface is eroded exposing SiO<sub>2</sub> particles. UV treatment produces a similar effect, but not to the same extent, zinc stearate also migrates to the surface (zinc and oxygen concentration increases in UV treated R1 rubber). Furthermore, the corona discharge increases the concentration of SiO<sub>2</sub> particles near the surface. Although, as evident from the AFM images, these particles are covered with a very thin layer of polymeric material. This thin layer can explain the decrease in contact angle values. However, this is not associated with an increase in the amount of C–O species. UV treatment modifies the R1 surface in a different way. As a consequence of the treatment (and more noticeable as the duration increases), the most external layer of hydrocarbon species was removed and the incorporation of oxygen leading to the creation of polar groups (responsible for the decrease in contact angle values); furthermore, the migration of zinc stearate to the surface was produced. This migration of zinc stearate was not produced in the R1 rubber treated with corona discharge. This can be explained considering that the R1 rubber contains high degree of crosslinked chains of polymer, thus a substantial input of energy is required to bring about the migration of zinc stearate from the bulk to the surface. Corona discharge does not provide enough energy, in an accesible form, whilst UV irradiation does.

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