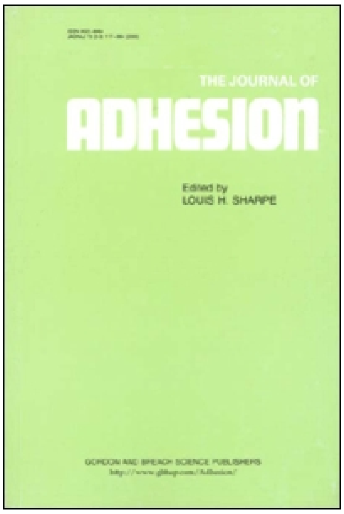

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Surface Analysis of Debonded Chlorinated Vulcanized Styrene-Butadiene Rubber Joints*

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A synthetic vulcanized styrene-butadiene rubber (R) was treated with a halogenation agent (TCI = trichloroisocyanuric acid) to produce improved adhesion (*i.e.* high T-peel strength) in joints prepared with a one-component, solvent-based polyester urethane adhesive. Several amounts (0.5 to 7 wt%) of TCI solutions in ethyl acetate were applied to the rubber surface and, after T-peel tests were carried out, the surfaces of the debonded chlorinated rubber pieces were analyzed with XPS, ATR-infra-red (ATR-IR) spectroscopy, Scanning Electron Microscopy (SEM) coupled with EDX analysis, and contact angle measurements. The T-peel strength of unchlorinated rubber (0 wt% TCI) joints was small due to the migration of low molecular species (mainly microcrystalline wax) to the rubber surface during the cure of the adhesive, creating a weak layer in which the failure was produced. Chlorination with amounts of TCI up to 2 wt% produced a noticeable increase in T-peel strength, but treatment with higher amounts of TCI resulted in a decrease in joint strength. Although chlorination with TCI created chlorinated hydrocarbon groups and C—O moieties on the rubber surface, the surface in contact with the adhesive was additionally degraded and, consequently, the locus of failure of the joints varied in a manner which depended on the amount of TCI applied to the surface. Treatment with amounts of TCI up to 2 wt% did not greatly degrade the rubber surface and the mode of failure of the joint was mainly interfacial. Chlorination at higher TCI concentration produced a weak chlorinated surface layer which

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was mechanically weak, facilitating the failure in this layer during the T-peel test. The thickness of the chlorinated layer created on the treated rubber is about 5 μm, and the thickness seemed to be independent of the amount of TCI applied to the rubber surface.

Keywords: Surface treatment; halogenation; trichloroisocyanuric acid; styrene-butadiene rubber; T-peel strength; XPS; ATR-IR spectroscopy; contact angle measurements; SEM; EDX analysis; surface mapping

1. INTRODUCTION

The joining of vulcanized rubber to several materials generally requires a surface treatment [1]. Among the different kinds of surface treatments proposed for vulcanized rubber [2–5], halogenation is the most common and effective [6–9]. Although several chlorination agents for vulcanized rubber have been proposed [10–14], TCI is the most widely used [15–24]. Although the effects produced on rubber surfaces by chlorination with TCI have been studied, several aspects need to be clarified. In previous studies [20–24], it has been stated that the chlorination of synthetic vulcanized styrene-butadiene rubbers affects the surface chemistry and the mechanical properties of the rubber. The relative effectiveness of chlorination is affected by the nature and compounding of the rubber, the way in which the chlorination is carried out, the experimental conditions (time of chlorination, the solvent used to apply the chlorination agent, etc.), and the concentration of chlorination agent used. In this study, the concentration of chlorination agent applied to the surface of a synthetic vulcanized styrene-butadiene rubber has been considered.

Most of the studies [15–26] dealing with chlorination of synthetic rubber materials have been carried out by characterizing the surface before the formation of the adhesive bond. Such studies do not consider the effects of the viscoelastic properties of the rubber and adhesive materials during the adhesion test which will affect the measured joint strength. In general, it is difficult to analyze the surface of debonded rubber test specimens due to the presence of heterogeneities and because, very often, the locus of failure of the joints is cohesive in the rubber. In this study, rubber compounding was selected to avoid cohesive failure in the rubber during the adhesion test and, therefore, the characterization of the debonded rubber test samples was facilitated.

On the other hand, precise surface analysis of the debonded chlorinated rubber materials requires the use of several experimental techniques. Some of the most common surface analysis techniques used for investigating the nature of the modifications produced by chlorination with TCI have been IR spectroscopy, contact angle measurements, SEM and, more recently, XPS [19, 23, 25, 26]. Considering that the chlorination agent penetrates into the rubber bulk to an extent which needs a more precise determination [23, 24], in this study the debonded rubber materials were analyzed by combining all of these surface analysis techniques.

2. EXPERIMENTAL

Materials

A sulfur-vulcanized synthetic styrene-butadiene rubber (R) was used in this study. The formulation of rubber is given in Table I. This rubber contains silica as filler and relatively important amounts of oil and plasticizer (zinc stearate, stearic acid, microcrystalline wax) to prevent cohesive failure during the adhesion test. Some properties of the rubber were obtained using standardized procedures: °Shore A hardness = 72; Density (20°C) = 1.1 g cm^{-3}; Tensile strength at break = 11.4 MPa; Maximum elongation at break = 612%; Tear resistance = 14.7 kN m^{-1}.

TABLE I Formulation of synthetic vulcanized styrene-butadiene rubber (R)

Compound	*Composition (phr)*
SBR 1502	100
Precipitated silica	42.0
Sulfur	2.0
Cumarone-indene resin (85°C)	5.0
Zinc oxide	1.5
Stearic acid	2.4
N-Cyclohexyl-2-benzothiazole sulphenamide	2.0
Phenolic antioxidant	0.5
Dibenzothiazyl disulphide	2.5
Microcrystalline paraffin wax	0.8
Hexamethylene tetramine	1.0
Zinc stearate	5.4

The rubber was immersed in ethyl acetate for 20 seconds, dried at RT in air for 30 min and then wiped with a tissue saturated with the solution of the chlorination agent (0.5–7 wt% trichloroisocyanuric acid – TCI – in ethyl acetate). The chlorination reaction was carried out for one hour. The chlorination may deposit unreacted solid TCI crystallites and residues of the reaction of TCI with rubber (mainly cyanuric and/or isocyanuric acid), so a postchlorination treatment has been recommended [15]. In this study, the postchlorination treatment was carried out by immersing the treated rubber in an aqueous solution containing 25 wt% ethanol for 30 seconds. The specimen was then placed at RT in the open air for one hour to permit evaporation of the alcohol and water.

To determine the T-peel strength, a one-component thermoplastic polyester-urethane adhesive (*Desmocoll 510*) manufactured by Bayer (Leverkusen, Germany) was used. This polyester-urethane has a high crystallization rate and short open time. The adhesive was prepared by dissolving 18 wt% polyurethane in 2-butanone in a laboratory mixer (400 rpm, 2 hours), a Brookfield viscosity of 3.8 Pa.s (23°C) being obtained.

The adhesive joints were prepared by applying approximately 150 mg of adhesive to each of the identically-treated rubber surfaces. After allowing the solvent to evaporate for 30 minutes, the dry adhesive films were quickly melted at 80°C under IR radiation, putting them into contact immediately under a pressure of 0.8 MPa. The adhesive joints were conditioned for 72 hours at 23°C and 50% relative humidity before undergoing the T-peel test.

Experimental Techniques

T-peel strength measurements: The strength of the adhesive joints was determined using a T-peel test (European Standard: PREN 1391) in an *Adamel L'Homargy DY 32* test instrument, with a peel rate of 0.1 m/min. Five experimental determinations for each analyzed experimental variable were obtained, the experimental error obtained being less than 10%.

The characterization of the treated rubber surfaces was carried out on the failed samples obtained after carrying out the T-peel test. In general, both sides of debonded joints were characterized, taking care to analyze similar regions in the two rubber samples (*i.e.* the two surface regions which were originally in intimate contact before bonding).

X-ray Photoelectron Spectroscopy (XPS): XPS was used to determine the modifications produced in the outermost (50–100 Å) rubber-treated surface. XPS analysis was performed using a *Perkin-Elmer PHI 5400* spectrometer with a Mg K_α achromatic X-ray source (1253.6 eV), operating at 15 keV and 400 watts with an emission current of 30 mA. Pressure inside the analysis chamber of the instrument was kept below 5×10^{-7} torr (6.6×10^{-5} Pa) during the course of the analysis. Rectangular sample pieces (10 mm × 20 mm) were used, although the dimensions of the analyzed areas on the samples were 1 mm × 3 mm. For each sample, a survey scan encompassing the region of 0–1100 eV was first taken. Multiplex scanning of all observed photopeaks (carbon, oxygen, chlorine, zinc, nitrogen, sulfur, silicon) in the survey scan was then carried out. Binding energies of all photopeaks were referenced to the C 1s photopeak position for C—C and C—H species at 285 eV. Atomic concentration calculations and curve fitting were carried out on an Apollo 3500 computer, using PHI software version 4.0. In general, two spots of the same sample were measured. Multi-component carbon 1s photopeaks were curve fitted using photopeaks of Gaussian peak shape with a full-width-at-half maximum (FWHM) of 1.6 ± 0.1 eV. The C 1s binding energy values were selected to correspond to carbon–carbon, carbon–hydrogen, carbon–chlorine and carbon–oxygen-containing functional groups [27].

Contact angle measurements: The surface-treated rubber pieces were introduced into the thermostated chamber at 25°C of a *Ramé Hart 100* goniometer. The chamber was previously saturated with the vapour of the test liquid for at least 10 minutes before placing a liquid drop on the surface of the rubber. The contact angles on the surface-treated rubbers were measured on 4 μl drops of ethylene glycol; the time required to reach the equilibrium was 15 minutes. The experimental error was ±2 degrees.

Fourier Transform InfraRed Spectroscopy (FTIR): The IR spectra of rubber treated with different amounts (0.5–7 wt%) of TCI in ethyl acetate were obtained using a *Nicolet FTIR 205* spectrophotometer. To avoid deep penetration of the IR radiation into the sample, the attenuated total multiple reflection method was employed (ATR-IR), a thallium bromoiodide KRS-5 crystal being used. More details on this technique were presented earlier [21–25].

SEM: The failed rubber treated samples were cut perpendicularly to the surface to determine the depth of the chlorination treatment. The cut was clean (especially at the outermost surface) and was analyzed in an *ISI SX 400* SEM instrument coupled with an EDX system (*Noran 5402*) having a micro Z series detector. With this detector it is possible to detect X-rays from elements of atomic number as low as 5 (boron). The rubber samples were gold-coated (15 seconds, gold sputtered in an argon plasma) to provide good contrast in the SEM micrographs without noticeably altering the qualitative chemical analysis of the rubber samples. Chemical composition of treated rubber samples was assessed by mapping the surface profile of the sample and analyzing simultaneously the relative concentration of chlorine, carbon, silicon and nitrogen.

3. RESULTS AND DISCUSSION

Figure 1 shows the variation of T-peel strength of chlorinated R/polyurethane adhesive joints as a function of chlorination solution concentration. Chlorination of rubber with small amounts of TCI (*i.e.* 0.5 wt%) produces a noticeable increase in joint strength. The increase in the amount of chlorination agent up to 2 wt% produced a further increase in T-peel strength, whereas a 7 wt% TCI produces a sudden decrease in joint strength. All adhesive joints show, by visual inspection, 100% interfacial failure. According to Figure 1, two experimental results require an explanation: *i*) the noticeable increase in T-peel strength of chlorinated R/polyurethane adhesive when a small amount of TCI (up to 2 wt%) is applied to the rubber surface; *ii*) the lack of adhesion produced on R surfaces chlorinated with high amount of TCI. The decrease in peel strength for 7 wt% TCI treated rubber can be ascribed to the formation of a weak boundary layer [24]. To understand the experimental findings, several surface analysis techniques (XPS, contact angle measurements, SEM-EDX, IR-ATR spectroscopy) were used to characterize the two failed rubber surfaces. In the discussion which follows, side 1 corresponds to the debonded

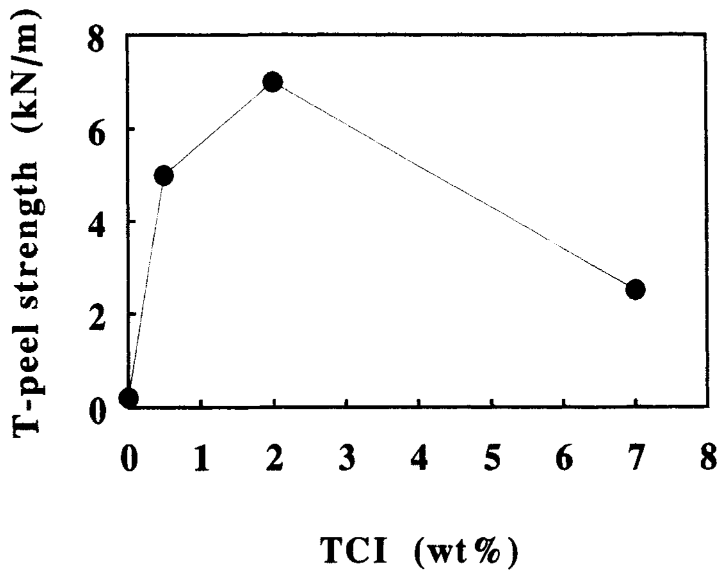

FIGURE 1 Variation of T-peel strength of chlorinated rubber/polyurethane adhesive joints as a function of TCI percentage. 100% interfacial failure (visually inspected) was always obtained.

sample without adhesive, whereas side 2 corresponds to the debonded sample containing the adhesive film (this distinction is based on visual analysis).

Unchlorinated R Rubber

XPS was used to characterize the surface chemistry of untreated (*i.e.* as-received) and unchlorinated (0 wt% TCI) rubber samples. The chemical compositions of the untreated rubber and the cured polyurethane adhesive film are given in Table II. The untreated R rubber contains carbon as hydrocarbon as the main chemical component, and zinc and sulfur are not detected (<0.2 atomic%) on the outermost surface. The chemical composition of the cured polyurethane adhesive shows higher amounts of oxygen and silicon (probably corresponding to silica as a filler in the adhesive), and a small amount of nitrogen (corresponding to a small amount of urethane groups – *i.e.* hard segments – in the elastomeric adhesive). The chemical composition of the unchlorinated (0 wt% TCI) rubber before bonding is given

TABLE II Atomic concentration (%) of the untreated R and polyurethane adhesive

Element	*Untreated R*	*Polyurethane adhesive*
C	98.9	73.1
O	0.6	20.4
Si	0.2	5.8
N	0.3	0.7

in Table III, which shows that the treatment with solvents increases the amount of silica on the surface. The surface composition of the two failed unchlorinated rubber samples (0 wt% TCI, *i.e.* only treated with solvents and after bonding) is included in Table IV. The two sides of the debonded unchlorinated R samples show relatively similar atomic compositions which correspond closely to that for the untreated R surface (Tab. II). However, the higher amount of oxygen and the presence of nitrogen on side 2 of the debonded sample provides an indication of traces of adhesive on the surface. Therefore, these evidences indicate a mixed locus of failure in the joint which

TABLE III Atomic concentration (%) of the surface chlorinated rubber with TCI (before bonding)

Element	*0 wt% TCI*	*2 wt% TCI*	*7 wt% TCI*
C	95.7	92.7	91.5
O	2.8	4.3	4.6
Si	1.5	1.0	0.7
N	–	1.0	1.9
Cl	–	0.8	0.9
S	–	0.2	0.4

TABLE IV Atomic concentration (%) of the surface of debonded joints of rubber chlorinated with TCI

Element	*0 wt% TCI*		*0.5 wt% TCI*		*2 wt% TCI*		*7 wt% TCI*	
	Side 1	*Side 2*	*Side 1*	*Side 2*	*Side 1*	*Side 2*	*Side 1*	*Side 2*
C	97.7	93.5	93.5	93.8	89.8	93.9	79.7	82.5
O	1.7	4.5	3.9	3.8	6.0	4.2	14.0	12.4
Si	0.6	0.4	1.2	1.1	1.7	0.7	0.2	0.1
N	–	0.4	0.5	0.7	1.1	0.5	3.1	2.5
Cl	–	–	0.4	0.2	1.2	0.4	2.2	2.0
S	–	0.5	0.2	0.2	0.2	0.3	0.5	0.4
Zn	–	0.6	0.3	0.2	–	0.2	0.3	0.2

may correspond to interfacial and to a rupture in the weak layer created by migration of low-molecular species to the rubber surface.

Considering that the contact angles for the untreated rubber (83°) and the cured polyurethane adhesive film (62°) are quite different, the measurement of the contact angle of the failed rubber samples may provide an indication of the locus of failure of the joints. According to Table V, the treatment with solvents (*i.e.* 0 wt% TCI) does not change the surface properties of rubber (contact angle = 78°), but the contact angles of the two sides of the debonded unchlorinated (0 wt% TCI) rubber joint are higher than in the untreated and unchlorinated rubber before bonding, and similar between them (88° and 93°). This indicates the migration of rubber components to the surface during adhesive curing creating a weak layer in which the failure is produced.

Figure 2 shows the ATR-IR spectra of the untreated (*i.e.* as received) rubber and the polyurethane adhesive, whereas in Figure 3 the

TABLE V Contact angle (ethylene glycol, 25°C) on surfaces of debonded joints of R rubber chlorinated with different amounts of TCI

Rubber side	*Raw materials*	*0 wt% TCI*	*0.5 wt% TCI*	*2 wt% TCI*	*7 wt% TCI*
Before bonding	–	78	–	58	57
side 1	83 (rubber)	88	91	77	60
side 2	62 (adhesive)	93	81	61	62

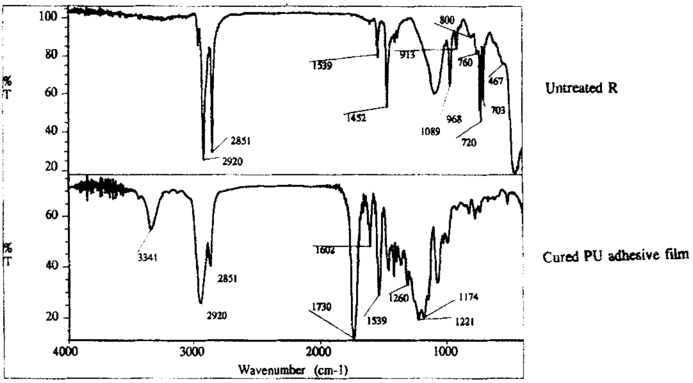

FIGURE 2 ATR-IR spectra of the original rubber and the cured polyurethane adhesive.

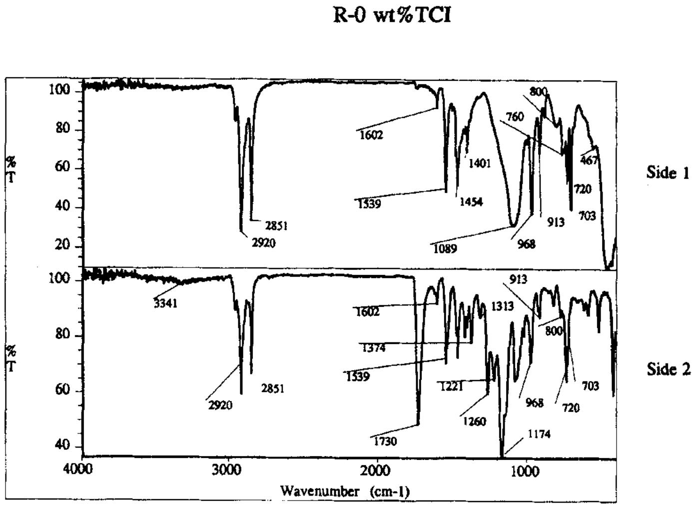

FIGURE 3 ATR-IR spectra of the two sides of the debonded unchlorinated (0 wt% TCI) rubber joint.

corresponding spectra for the two failed unchlorinated (0 wt% TCI) R rubber surfaces are presented. The ATR-IR spectra of the untreated R rubber and side 1 of the 0 wt% TCI debonded sample show some characteristic bands of styrene-butadiene: C—H out-of-plane bending of the styrene group (703, 760 cm^{-1}), C—H of vinyl and *trans* butadiene groups (913, 968 cm^{-1}), CH_2 scissoring (1452 cm^{-1}) and CH_2 stretching of butadiene (2851, 2920 cm^{-1}). Furthermore, the ATR-IR spectra of the original and 0 wt% TCI treated R show zinc stearate (carboxylate band at 1539 cm^{-1}), a paraffin (720 cm^{-1}), and silica (800 cm^{-1}, and the broad characteristic band at 1089 cm^{-1}). Both the zinc stearate and the paraffin substantially contribute to the CH_2 bands at 1452, 2851 and 2920 cm^{-1}. On the other hand, the ATR-IR spectrum of the polyurethane adhesive (Fig. 2) shows typical N—H (1539, 3341 cm^{-1}) and C = 0 (1730 cm^{-1}) bands of the urethane group, and a broad band in the region 1100–1230 cm^{-1} due to silica. The ATR-IR spectrum of side 2 of the debonded unchlorinated R specimen (Fig. 3) shows most of the typical bands of the adhesive and, in addition shows characteristic C—H bands (720, 913, 968 cm^{-1}) of microcrystalline wax, a rubber component which migrates to the surface during the cure of the adhesive. Furthermore, the IR spectrum of the failed side 2 does not show evidence of a silica peak. These results confirm that the locus of failure of the 0 wt% TCI treated rubber joint is mixed (interfacial plus failure in the weak layer created by migration to the surface of microcrystalline wax).

Chlorination of R with Small Amounts of TCI (up to 2 wt% TCI)

Surface analysis of the 2 wt% TCI chlorinated rubber specimen before bonding is given in Table III. Chlorination of rubber with 2 wt% TCI introduces C—Cl and C—O moieties on the surface, providing a polarity which is responsible for the decrease in contact angle (Tab. V) from 78° (0 wt% TCI) to 58° (2 wt% TCI).

Surface analysis results for the side 1 failure surfaces are presented in Table IV. A general observation is that the surface chemistry for failed chlorinated samples is unlike that for the failed unchlorinated specimen. Relative to the results for untreated samples, the atomic concentration of C is reduced, whereas an increase of oxygen and silicon content is produced (relative to 0 wt% TCI samples). Halogenation introduces chlorine (Cl 2p, BE = 199.9 eV) and nitrogen (N 1s, BE = 400.4 eV) functionalities on the surface of side 1 (Tab. IV). The binding energy of chlorinated R corresponds to organic C—Cl moieties on the surface. The amount of carbon–chlorine species (0.4–1.2 atomic%) on the surface is similar to that in the chlorinated samples before bonding. On the other hand, the N content (0.5–1.1 atomic%) corresponds to isocyanuric acid ($C_3O_3N_3H_3$) remaining on the surface. The amount of oxygen on the surface of the side 1 sample is 3.9–6.0 atomic%, and corresponds to about 0.5–1.1 atomic% of isocyanuric acid, 2.4–3.4 atomic% silica (*i.e.* twice the atomic concentration of silicon), and about 1–1.5 atomic% of carbon–oxygen species. The nature of these carbon–oxygen species may correspond to single C—O moieties (according to the curve fitting of the C 1s photopeaks – Fig. 4). On the other hand, the atomic composition of the side 2 of the failed R chlorinated joints with 0.5 and 2 wt% TCI (Tab. IV) are quite coincident between them and almost identical to that of 0 wt% TCI and 2 wt% TCI (before bonding), except for a slightly higher amount of nitrogen and traces of chlorine in the chlorinated samples.

A comparison between the chemical composition of sides 1 and 2 (Tab. IV) indicates differences in the locus of failure for the joints of

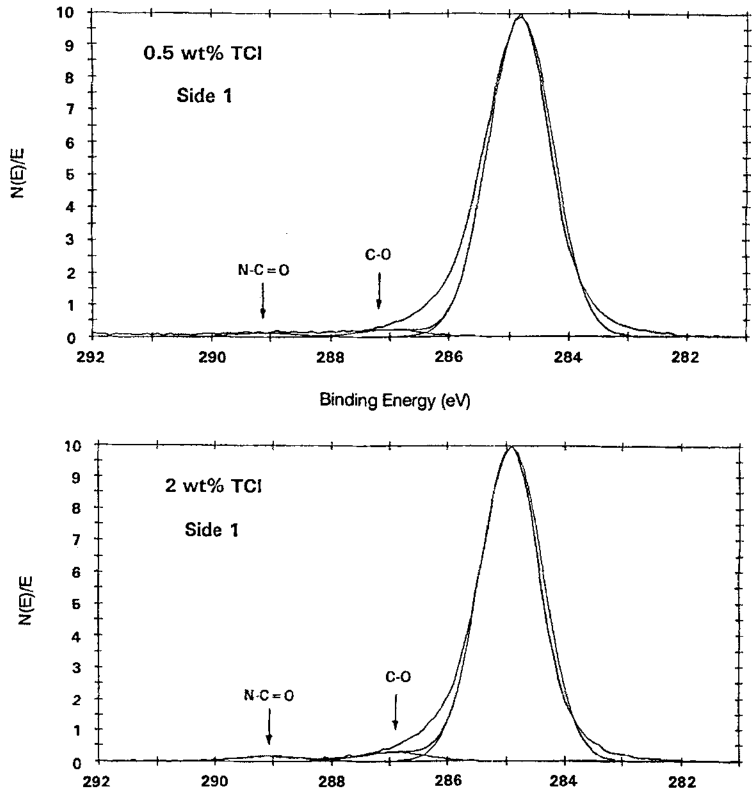

FIGURE 4 Curve fitting of C 1s photopeaks of the side 1 failed rubber surface; samples chlorinated with 0.5 and 2 wt% TCI.

chlorinated R with 0.5 and 2 wt% TCI. The two failed R surfaces treated with 0.5 wt% TCI have similar atomic compositions. For surfaces treated with 2 wt% TCI, a lower percent C and higher atomic% O, Si, N and Cl were found for side 1 relative to the corresponding composition for side 2. The contact angle measurements (Tab. V) also show high and not very different values for the two failed R samples treated with 0.5 wt% TCI, whereas the contact angles obtained for the failure surfaces treated with 2 wt% TCI are different: side 1 has a lower contact angle (77°) than the 0 wt% TCI sample, but higher than the specimen treated with 2 wt% TCI before bonding; the contact angle of side 2 may correspond to the chlorinated rubber (it is similar to the contact angle of R treated with 2 wt% TCI before bonding) and/or to the polyurethane adhesive. These differences can be correlated with the different mode of failure for R treated with 0.5 and 2 wt%. The presence of C—Cl and C—O moieties on the failed side 1 of 0.5 wt% TCI treated R may be related to the increase in T-peel strength show in Figure 1. Furthermore, the treatment with 2 wt% TCI produces a further increase in T-peel strength (Fig. 1) due to a higher concentration of C—Cl and C—O species.

The treatment of R with 0.5 wt% results in a relatively similar locus of failure in the joint compared with unchlorinated R joints. The ATR-IR spectrum of side 1 of the debonded joint (Fig. 5) show evidence of chlorinated hydrocarbon groups (weak band at 1237 cm^{-1}) in the butadiene, and C=O (1730 cm^{-1}) groups created on the surface which may correspond to isocyanuric acid and surface oxidized carbon–oxygen species. Furthermore, the relative intensity of CH_2 bands (2851, 2920 cm^{-1}) is decreased because there is less microscrystalline wax on the surface. The ATR-IR spectrum of side 2 of the failed joint (Fig. 5) show bands typical of urethane groups (1121, 1174,

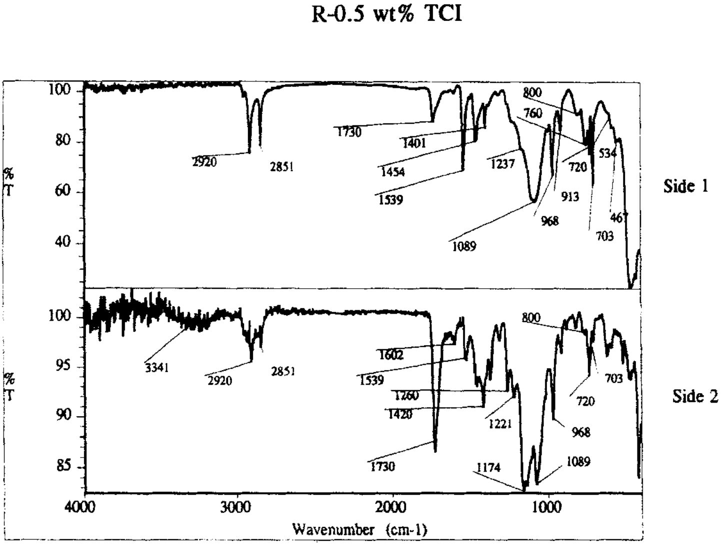

FIGURE 5 ATR-IR spectra of the two sides of the 0.5 wt% TCI treated rubber debonded joint.

1260, 3341 cm^{-1}) and the Si—O band (800, 1089 cm^{-1}) existing in the ATR-IR spectrum of original R rubber (Fig. 2). Therefore, the improved T-peel strength in joints produced with R treated with 0.5 wt% TCI is due to the presence of polar species on the surface, and the locus of failure corresponds to a mixture of interfacial and cohesive failure in the chlorinated layer which is close to the interface. Additional evidence of this mode of failure is given in Figure 6, where the SEM micrograph of the surface profile of the failed side 1 of 0.5 wt% TCI treated R shows evidence of a chlorinated surface layer of about 5 μm thickness. Elemental mapping of the surface profile shows mainly chlorine on the outermost surface, and small amounts of nitrogen and relatively small concentrations of carbon and silicon.

The treatment of R with 2 wt% TCI produces a further increase in T-peel strength (Fig. 1) which corresponds to a great degree of chlorination of the side 1 of the failed joint, which is clearly evidenced by the noticeable decrease in intensity of methylene group (2851, 2920 cm^{-1}) in the ATR-IR spectrum of Figure 7. The ATR-IR spectrum of side 2 of the debonded joint (Fig. 7) corresponds to the adhesive (bands at 1174, 1730 cm^{-1}), indicating an interfacial mode of failure (in good agreement with contact angle measurements). Figure 8, which shows the SEM micrograph of side 1 of the failed 2 wt% TCI R joint, indicates that the chemical composition of the most external 5 μm of the surface corresponds to chlorine and no evidence of adhesive can be seen at the surface. The surface profile shows a thinner chlorinated layer with respect to that of the R treated with 0.5 wt% TCI (Fig. 6), indicating that a cohesive failure in the chlorinated layer can be produced (with respect to the 0.5 wt% TCI one).

Chlorination with 7 wt% TCI

According to Table III, a relatively similar atomic composition is obtained in the rubber treated with 2 and 7 wt% TCI before bonding, although the N content is higher when the amount of TCI applied to the rubber surface increases. The chlorine content in the 7 wt% treated specimen before bonding is smaller than expected considering the amount of chlorination agent applied, probably due to a poor reactivity of the halogenation agent with the surface which may

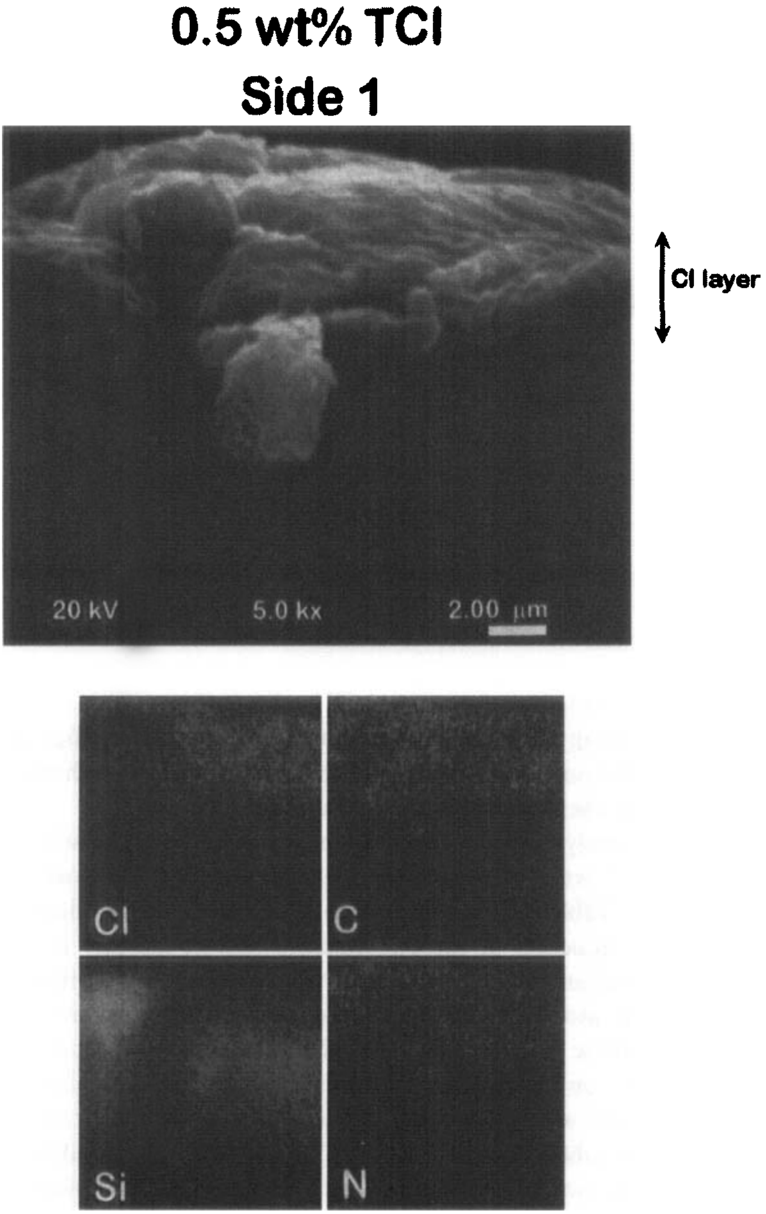

FIGURE 6 SEM micrograph and surface mapping (× 5000) of side 1 of rubber chlorinated with 0.5 wt% TCI joint.

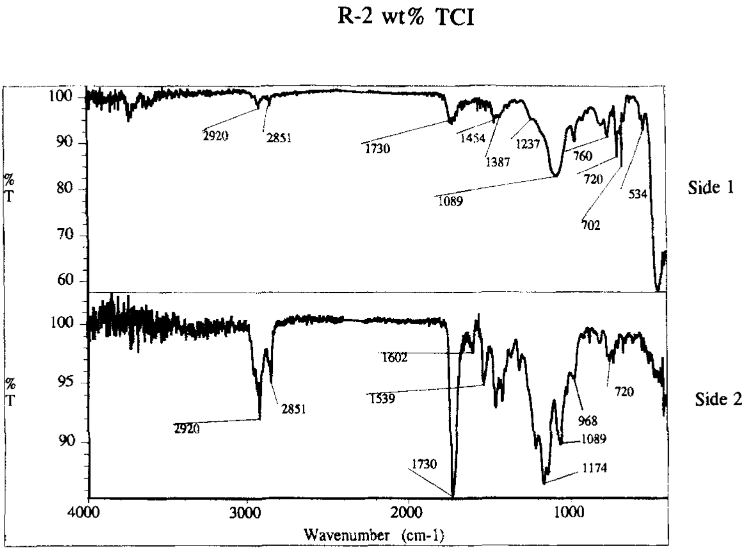
R-2 wt% TCI

FIGURE 7 ATR-IR spectra of the two sides of the 2 wt% TCI treated rubber debonded joint.

facilitate the formation of unreacted TCI solid residues which should be removed using the postchlorination treatment. However, after the T-peel test, the surface analysis of the debonded test samples shows a quite different chemical composition (Tab. IV).

The XPS analysis of the two sides of the joint produced with R treated with 7 wt% TCI indicates a similar chemical composition. According to Table IV, the chlorination with 7 wt% TCI produces a pronounced reduction of carbon atomic% but an increase in the atomic concentration of nitrogen (relative to the 2 wt% TCI treated samples). The atomic percentages of oxygen and chlorine are also higher than those in 2 wt% TCI treated R. The increase of the nitrogen atomic% on the surface is consistent with high amounts of isocyanuric acid which may constitute a weak boundary layer in the chlorinated R rubber surface (7 wt% TCI). The similar chemical composition of the two failed rubber sides of the joint (Tab. IV) presumably indicates that the failure of the joint occurs in the chlorinated layer. Further, the contact angle measurements (Tab. V) confirm the failure in the chlorinated layer, because the contact angles measured

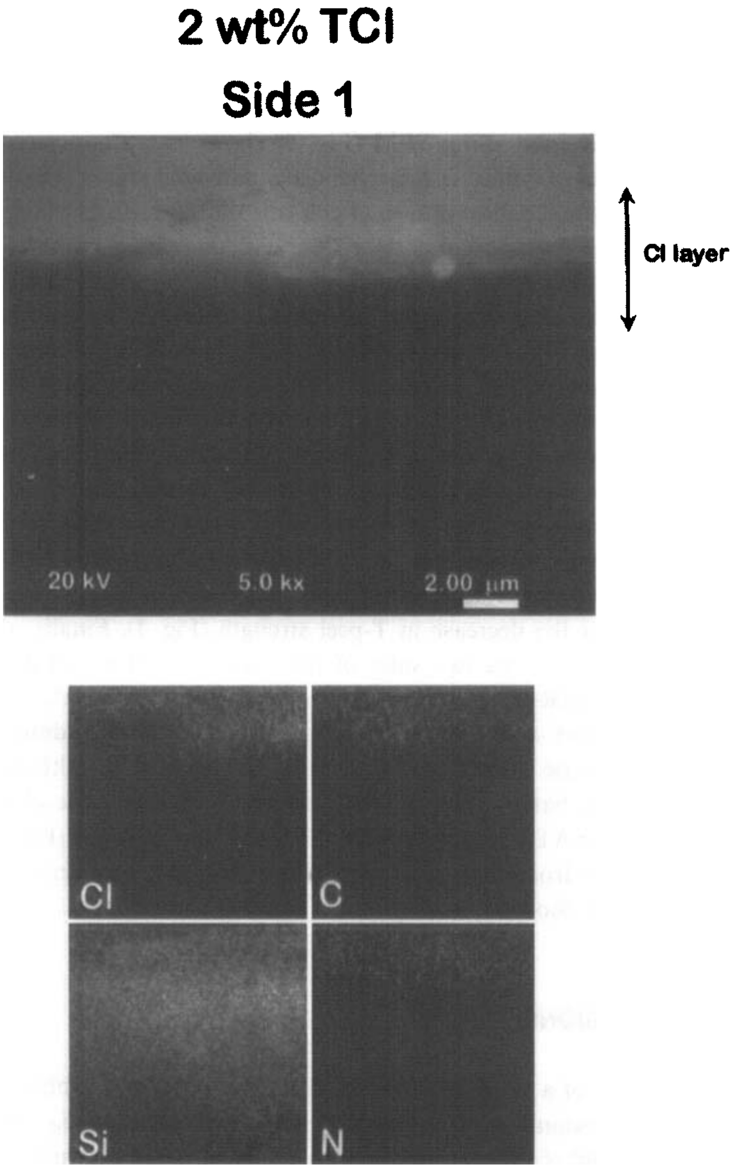

FIGURE 8 SEM micrograph and surface mapping (× 5000) of side 1 of rubber chlorinated with 2 wt% TCl joint.

are similar to that in the 7 wt% chlorinated rubber before bonding. Thus, a lower contact angle is measured on the failed side 1 sample (60°) due to the increase in polar surface species, which is similar to the contact angle obtained on the failed side 2 sample (62°). The analysis of the surface profile of the side 1 of the debonded 7 wt% TCI treated R joint using SEM (Fig. 9) shows two characteristic different modes of failure: *i*) A mechanically damaged region (Fig. 9a) containing a small concentration of chlorine on the surface, which is consistent with degradation of the rubber with increasing amounts of TCI; *ii*) A region where a clean rupture of the joint is produced (Fig. 9b), which contains higher amounts of chlorine in the outermost layer than in region *i*). The thickness of region *ii*) in the chlorinated layer is about 3 μm, *i.e.* smaller than in the samples treated with smaller amounts of TCI. This result indicates that failure of the joint is produced in the outermost chlorinated layer during the T-peel test. Therefore, the damaged surface of the rubber treated with 7 wt% TCI and the similar chemical composition of the two sides of the debonded joints confirms that the failure in that joint is produced in an external and mechanically weak chlorinated rubber layer which is responsible for the decrease in T-peel strength (Fig. 1). Finally, the ATR-IR spectra of the two sides of the failed joint (Fig. 10) differ slightly. The ATR-IR spectrum of the failed side 1 of 7 wt% TCI treated R shows a higher degree of chlorination (and additional peaks of cyanuric acid) than for 2 wt% TCI treated R. Although there are some bands in the ATR-IR spectrum characteristic of the adhesive in the ATR-IR spectrum of the failed side 2 sample (Fig. 2), chlorinated hydrocarbon, microcrystalline wax and cyanuric acid bands are also shown.

4. CONCLUSIONS

Halogenation of a synthetic vulcanized styrene-butadiene rubber (R) with small amounts of TCI produces improved adhesion (*i.e.* high T-peel strength) of joints produced with a solvent-based polyurethane adhesive. The increase in the amount of chlorination agent up to 7 wt% drastically reduces the T-peel strength. Several factors determine the variation of T-peel strength as a function of the amount of

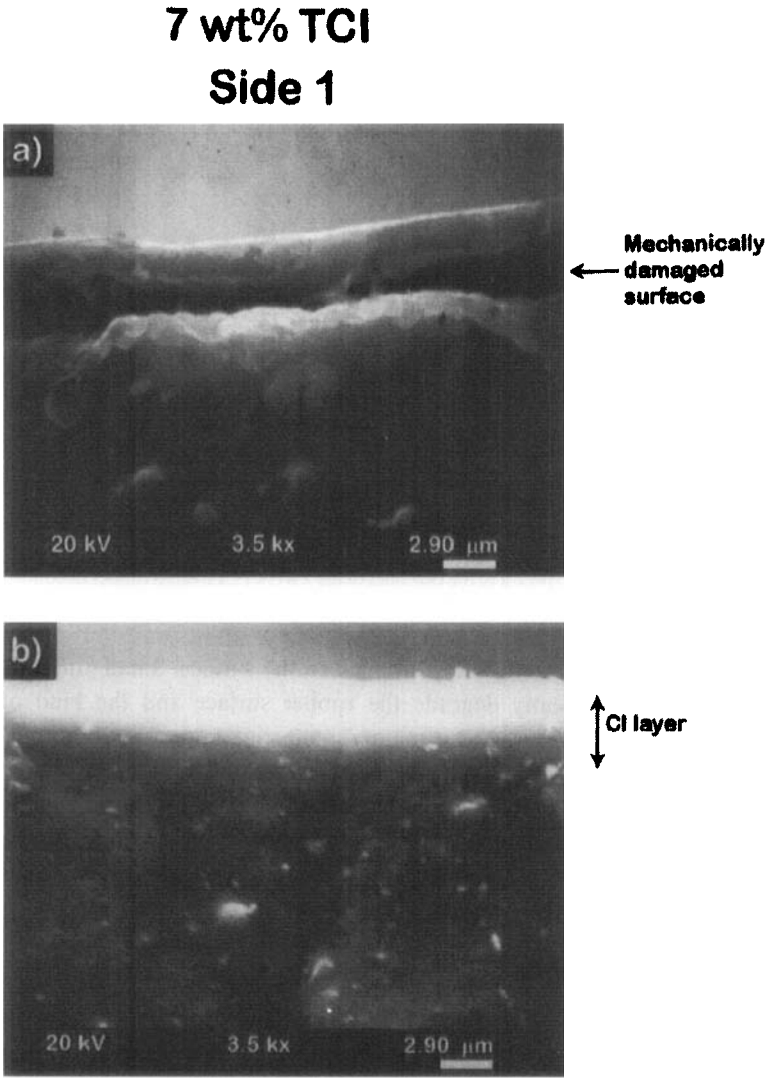

FIGURE 9 SEM micrograph and surface mapping (× 3500) of side 1 of rubber chlorinated with 7 wt% TCI joint.

TCI. Although chlorination with TCI creates a chemistry containing chlorinated hydrocarbon groups and C—O moieties on the rubber surface, a degradation of the rubber surface was also produced and, therefore, the locus of failure of the joints varies in a manner which

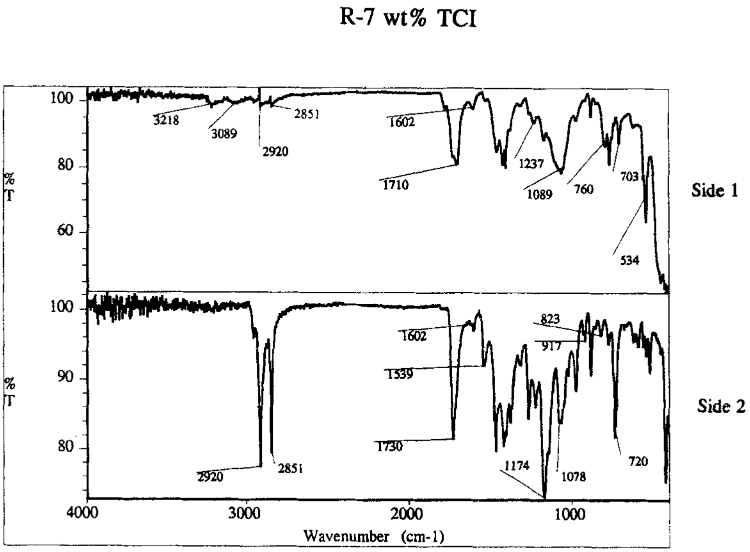

FIGURE 10 ATR-IR spectra of the two sides of the 7 wt% TCI treated rubber debonded joint.

depends on the amount of TCI applied to the surface. Small amounts of TCI do not greatly degrade the rubber surface and the kind of failure of the joint produced is mainly interfacial, until a weak boundary layer which is mechanically weak is created in the outermost chlorinated surface, facilitating the failure in this layer during the T-peel test. The thickness of the chlorinated layer created on the treated R is about 5 µm, and it seems to be independent of the amount of TCI applied to the rubber surface.

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