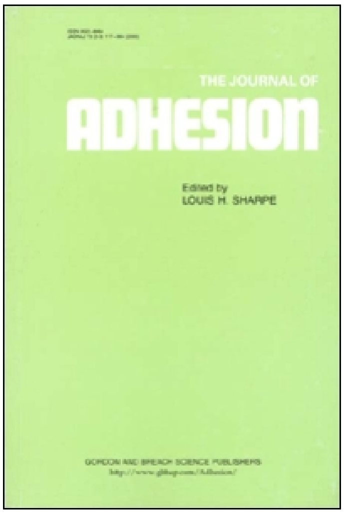

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Influence of Chlorinating Solution Concentration on the Interactions Produced Between Chlorinated Thermoplastic Rubber and Polyurethane Adhesive at the Interface

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INFLUENCE OF CHLORINATING SOLUTION CONCENTRATION ON THE INTERACTIONS PRODUCED BETWEEN CHLORINATED THERMOPLASTIC RUBBER AND POLYURETHANE ADHESIVE AT THE INTERFACE

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Chlorination of a thermoplastic styrene-butadiene-styrene rubber (S0) with different amounts of trichloroisocyanuric acid (TCI) solutions in ethyl acetate improved its adhesion to polyurethane adhesives. A strong interaction of the PU (polyurethane) adhesive and the chlorinated S0 rubber chains is produced at the interface. The increase in the concentration of TCI from 0.5 wt% up to 2–7 wt% resulted in the deposition of crystallites of unreacted TCI on the rubber surface. The remaining TCI on the rubber surface migrates through the PU adhesive producing some chlorination of the PU chains. The failure of the joint is located in this interface composed of both chlorinated S0 rubber and partially-chlorinated PU adhesive.

Keywords: Chlorination; Trichloroisocyanuric acid; SBS rubber; Interface; Polyurethane adhesive

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INTRODUCTION

Given the incompatibility between a non-polar rubber surface and the polar polyurethane (PU) adhesive, synthetic rubbers require a surface treatment prior to bonding [1]. Footwear and automotive industries widely use synthetic thermoplastic rubber, which needs to be bonded to different substrates using polyurethane (PU) adhesives. To improve the adhesion between the rubber and the PU adhesive, chlorination with trichloroisocyanuric acid (TCI) [2, 3] is commonly performed. Chlorination is the most widely used chemical treatment for synthetic rubber. Its success is due to the increase in polarity of the rubber surface with a consequent increase in surface energy, the removal of antiadherent compounds from the rubber surface and the increase of the mechanical interlocking between the rubber and the adhesive due to rubber surface roughness [4]. Recent studies [5] have shown that chlorination with TCI produces a crosslinking of the rubber surface as well as improved interactions between the uppermost-chlorinated layer and the PU adhesive. As a consequence, diffusion of the PU chains at the chlorinated rubber/adhesive interface may contribute to enhanced adhesion of chlorinated rubbers.

On the other hand, an excess of TCI usually produces a degradation of the rubber surface [6–9] and a modification of the PU adhesive in contact with the rubber. The aim of this study is to investigate the influence of the chlorinating solution concentration on the interactions produced between the chlorinated rubber and the polyurethane adhesive at the interface. Furthermore, the differences produced by the remaining unreacted TCI on the treated rubber surface will be assessed.

EXPERIMENTAL

Materials

The synthetic unvulcanized styrene-butadiene rubber (S0) used in this study—provided by REPSOL QUíMICA (Santander, Spain)- does not contain oils, plasticizers or fillers. The styrene block content of S0 rubber is 30%, its tensile strength is 17 MPa, and the Shore A hardness is 72°. Samples (30 mm width and 150 mm length) were prepared by injection molding the polymer in a heated mold (150°C).

To determine the T-peel strength, one-component thermoplastic polyester-urethane pellets (*Pearlstick 45–40/15*) manufactured by MERQUINSA S.A. (Barcelona, Spain) were used. This one-component polyester-urethane has a relatively high crystallization rate (near 20 min at room temperature) and short open time. The adhesive was prepared by dissolving 18 wt% polyurethane pellets in methyl ethyl ketone in a laboratory mixer (500 rpm for 2.5 hours). The adhesive solution obtained had a Brookfield viscosity of 4.9 Pa.s (23°C).

Experimental Techniques

Chlorination Procedure

The chlorination procedure of S0 rubber was as follows. The rubber was immersed for 20 seconds in the chlorination solution (0.5–7 wt% TCI in ethyl acetate). A postchlorination treatment, which consists of immersion of the chlorinated rubber in an aqueous solution of ethanol (25 wt%) for 20 seconds followed by drying at room temperature in the open air for 1 h, was carried out.

T-peel Strength Measurements

Adhesive joints were made using two rubber strip test pieces (150 mm × 30 mm) that had been similarly treated. The PU adhesive was applied with a brush (150 mg of dried adhesive was placed on each adherend). After allowing the solvent to evaporate for 1 h, the dry adhesive was melted at 80°C under IR radiation (reactivation process). The coated rubber samples were placed into contact immediately for 10 seconds under a pressure of 0.8 MPa at room temperature. The adhesive joints were kept at 23°C and 50% relative humidity for 72 hours before undergoing the T-peel test. The strength of the adhesive joints was determined using a T-peel test (European Standard: PREN 1391) [10] in an Instron 1123 test instrument, with a peeling rate of 100 mm/min. Five replicates for each analyzed experimental variable were obtained. The standard deviation was less than 0.7 kN/m.

Fourier Transform Infrared Spectroscopy (FTIR)

A *Nicolet Magna IR 760* spectrophotometer was used to obtain the infrared spectra of the chlorinated rubbers and solid residues. The IR spectra of chlorinated rubber were obtained using a *Nic-Plan*^{TM} IR microscope accessory and a *IR-Plan*^{TM} *Spectra Tech.* objective. To avoid deep penetration of the IR radiation into the sample, the attenuated total multiple reflection (ATR-IR) method was employed. A zinc selenide crystal located at the microscope objective was used. The incident angle was 45°. A total of 512 scans were obtained and averaged to generate a IR spectrum with a resolution of 4 cm^{-1}.

To obtain the transmission-IR spectra of the solid TCI and the solid residues, KBr pellets containing the sample were prepared using a *Spectra Tech. Qwik Handi-Press*. A KBr background was collected prior to obtaining the IR spectrum of the samples. Thirty-two scans were obtained and averaged with a resolution of $4\,\mathrm{cm}^{-1}$.

X-ray Photoelectron Spectroscopy (XPS)

XPS was used to determine the modifications produced on the outermost (50–100 Å) rubber surface. The surface-treated rubber materials were analyzed using a *Perkin Elmer PHI 5400* spectrometer with a Mg Kα achromatic X-ray source (1253.6 eV) operating at 14 keV and 300 watts with an emission current of 30 mA. Pressure inside the analysis chamber was held below 5×10^{-7} torr (6.6×10^{-5} Pa) during the course of the analysis. Samples were mounted onto the spectrometer probe with double-stick tape. Rectangular sample pieces (10 mm × 20 mm) were used, although the dimension of the analyzed areas on the samples was 1 mm × 3 mm. The measurements were done using a take-off angle of 45°. The spectrometer was calibrated to the $4f_{7/2}$ photopeak of gold at 83.8 eV and the $2p_{3/2}$ photopeak of copper at 932.4 eV. Survey scans up to 1100 eV and high-resolution scans were obtained on all significant peaks in the survey spectra. Binding energies of all photopeaks were referenced to the C 1s photopeak position for C-C and C-H species at 285.0 eV. Atomic concentration calculations and curve fitting were carried out on an Apollo 3500 work station. 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 carbon 1s fit was adjusted to the high binding energy side of the photoelectron peak [11]. At least 3 analyses and curve fits were independently performed for each treated sample to assure reproducibility.

Scanning Electron Microscopy (SEM)

The external modifications of the surface chlorinated S0 samples were analyzed in an ISI SX 400 SEM instrument at an acceleration voltage of 20 kV. The rubber samples were gold-coated. The failed chlorinated S0 rubber samples were cut perpendicularly to the surface to determine the depth of penetration of the chlorinating agent into the rubber. The cross-section surfaces were then analyzed in the same instrument, which is coupled with an energy dispersive X-ray (EDX) system (Noran 5402), having a micro Z series detector able to detect elements with an atomic number higher than 5 (boron). Chemical composition was assessed by mapping the cross-section of each specimen, analyzing simultaneously the relative concentration of chlorine, carbon, silicon and nitrogen.

Contact Angle Measurements

The surface-treated rubber pieces were placed in a 25°C thermostated chamber of a Ramé Hart 100–00 115 NRL goniometer. The chamber was previously saturated with the vapor of the test liquid for at least 10 min before placing a liquid drop on the surface of the rubber. Advancing contact angles on the chlorinated rubber were measured after placing 4 µl drops of twice-distilled water, *n*-hexadecane and ethylene glycol.

The surface energy components for the surface-chlorinated rubbers were calculated from the contact angles values using the Good equation [12], obtaining separately the dispersive and acid-base components of the surface energy:

$$\gamma_L(1+\cos\theta) = 2[(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + (\gamma_S{}^{\oplus}\gamma_L{}^{\ominus})^{1/2} + (\gamma_S{}^{\ominus}\gamma_L{}^{\oplus})^{1/2}]$$

where the subscripts "*L*" and "*S*" refer to the liquid and solid, respectively, and γ_L = surface tension of liquid; $\gamma^{\oplus}$ = electron acceptor component of surface energy; $\gamma_S{}^{\ominus}$ = electron donor component of surface energy; γ^{LW} = dispersive component (Lifshitz-van der Waals) of surface energy.

Ellipsometry

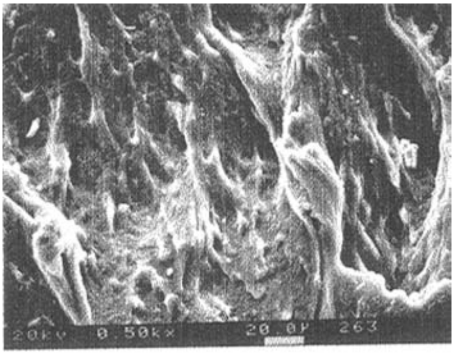
Thicknesses of films of PU-adhesive spin coated on ferroplate substrates from solutions of PU in MEK were approximated using a *J. A. Woollam Variable Angle Spectroscopic Ellipsometer VASE* and *WVASE 32* software. The instrument was calibrated before each set of experiments using a silicon wafer. Data were collected at 60, 65, 70 and 75° angles of incidence and at wavelengths of 300 to 1000 nm by increments of 10 nm. A Cauchy model [13] was used to fit the data of polyurethane films and the optical constants for chromium [13] were used to fit the data of a flamed cleaned ferroplate substrate.

RESULTS AND DISCUSSION

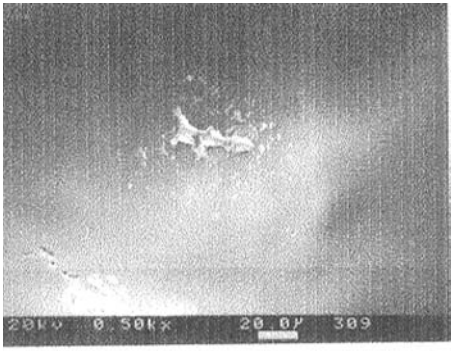
In order to investigate the interactions between the chlorinated S0 rubber and the polyurethane adhesive at the interface, the surface modifications produced on the non-bonded S0 rubber by the chlorinating treatment were studied. The locus of failure was also assessed from the analysis of the failed surfaces obtained after T-peel tests of chlorinated-S0 rubber/PU adhesive joints.

Surface Modifications on S0 Rubber Surface Produced by Halogenation with TCI

Figure 1 shows the relatively rough surface of the as-received S0 rubber. A solvent wipe with MEK dissolves the external rubber surface producing a smoother topography. The effects produced on the S0 rubber surface by chlorination depend on the percentage of TCI in the chlorinating solution. Chlorination with 0.5 wt% TCI creates holes on the surface (about 20–50 μm diameter) produced by a selective reaction of the TCI with the rubber. The addition of more concentrated TCI solutions produces a more pronounced degree of roughness and a higher degree of heterogeneities. Furthermore, some cracks appear in

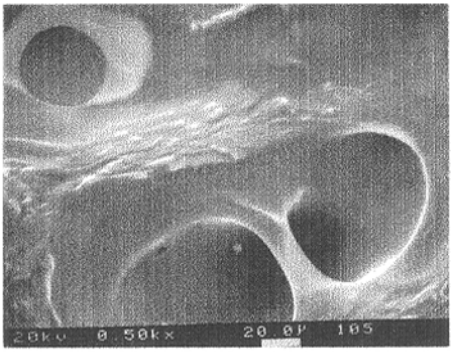


(a) As received

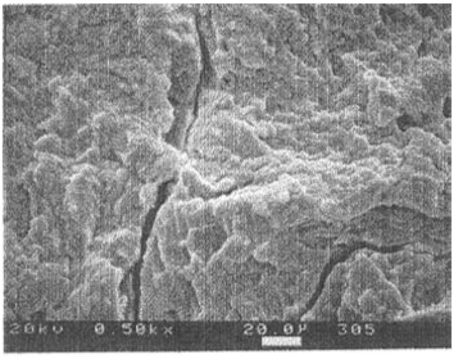


(b) Solvent wiped

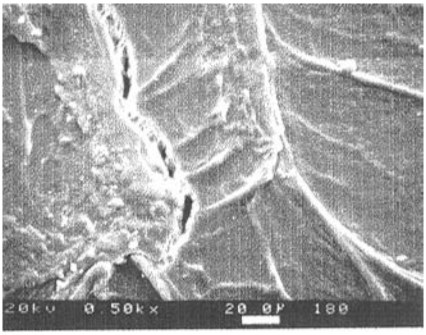
FIGURE 1 SEM micrographs (×500) of as-received, solvent-wiped and chlorinated S0 rubber (0.5–7 wt% TCI).



(c) 0.5 wt% TCI



(d) 2 wt% TCI



(e) 7 wt% TCI

FIGURE 1 (*continued*).

the S0 rubber surface treated with TCI percentages equal to or higher than 2 wt%.

As-received S0 rubber is a block copolymer of butadiene and styrene. The ATR-IR spectrum (Figure 2) shows the typical absorption bands for both polymers. Thus, butadiene absorption occurs at $\sim 3000\,cm^{-1}$ (=CH stretching), 2915 and $2848\,cm^{-1}$ (C-H stretching), $1448\,cm^{-1}$ (-CH_2 scissoring), $1380\,cm^{-1}$ (-CH_2 twisting) and $968\,cm^{-1}$ (*trans*-1,4-C=C). Styrene bands appear at 713, 760 and $913\,cm^{-1}$ (C-H out of plane of vinyl group), aromatic C-C stretching at $1601\,cm^{-1}$, and aromatic C-H stretching at $3034\,cm^{-1}$. Halogenation with 0.5 wt% TCI produces a change in the chemistry of the S0 rubber surface: there is a reduction of C=C bands ($968\,cm^{-1}$) and C-H stretching bands (2915, $2848\,cm^{-1}$) compared with the styrene absorption band at $713\,cm^{-1}$ (this band is not affected by chlorination). This decrease is due to the creation of chlorinated hydrocarbon moieties in the butadiene units (764, 818, 1235, $1400\,cm^{-1}$). Furthermore, C=O ($1740\,cm^{-1}$) groups are created as a consequence of the oxidation of the rubber and/or the deposition of TCI. Upon treating the rubber with 2 and 7 wt% TCI, the effect of chlorination is enhanced, *i.e.*, the deposition of TCI on the rubber surface occurs.

Figure 3 shows the transmission-IR spectrum of solid TCI. Typical bands of both TCI and isocyanuric acid (a by-product of TCI reaction with rubber) are present: N-H stretching (3529, $3463\,cm^{-1}$), N-H in plane deformation ($1155\,cm^{-1}$) and N-H out of plane deformation (698, $804\,cm^{-1}$) of isocyanuric acid and N=C=O asymmetric ($2265\,cm^{-1}$), C=O stretching ($1740\,cm^{-1}$), N-C=O stretching ($1600\,cm^{-1}$), C-N stretching ($1361\,cm^{-1}$) of both isocyanuric acid and TCI. By comparing with Figure 2, it is clear that unreacted TCI is present on the 2 and 7 wt% TCI-chlorinated S0 rubber (the higher the TCI amount, the higher the TCI deposition).

In order to analyze the rubber surface to a depth of only a few nanometers, XPS was used. Table 1a shows the chemical composition of S0 before and after chlorination. As-received S0 rubber is mainly composed of carbon as hydrocarbon (Figure 4), and also contains significant amounts of oxygen and silicon (probably due to a mold-release agent, *i.e.*, silicone on the surface, as well as some degree of surface oxidation). There is a decrease in the carbon percentage on S0 rubber surface after chlorination. This treatment introduces chlorine and nitrogen functionalities on the S0 surface. The binding energy of chlorine (Cl 2p, BE = 199.9 eV) on chlorinated S0 corresponds to organic chlorine from unreacted TCI and/or C-Cl moieties on the surface. On the other hand, nitrogen (N 1s, BE = 400.4 eV) comes from

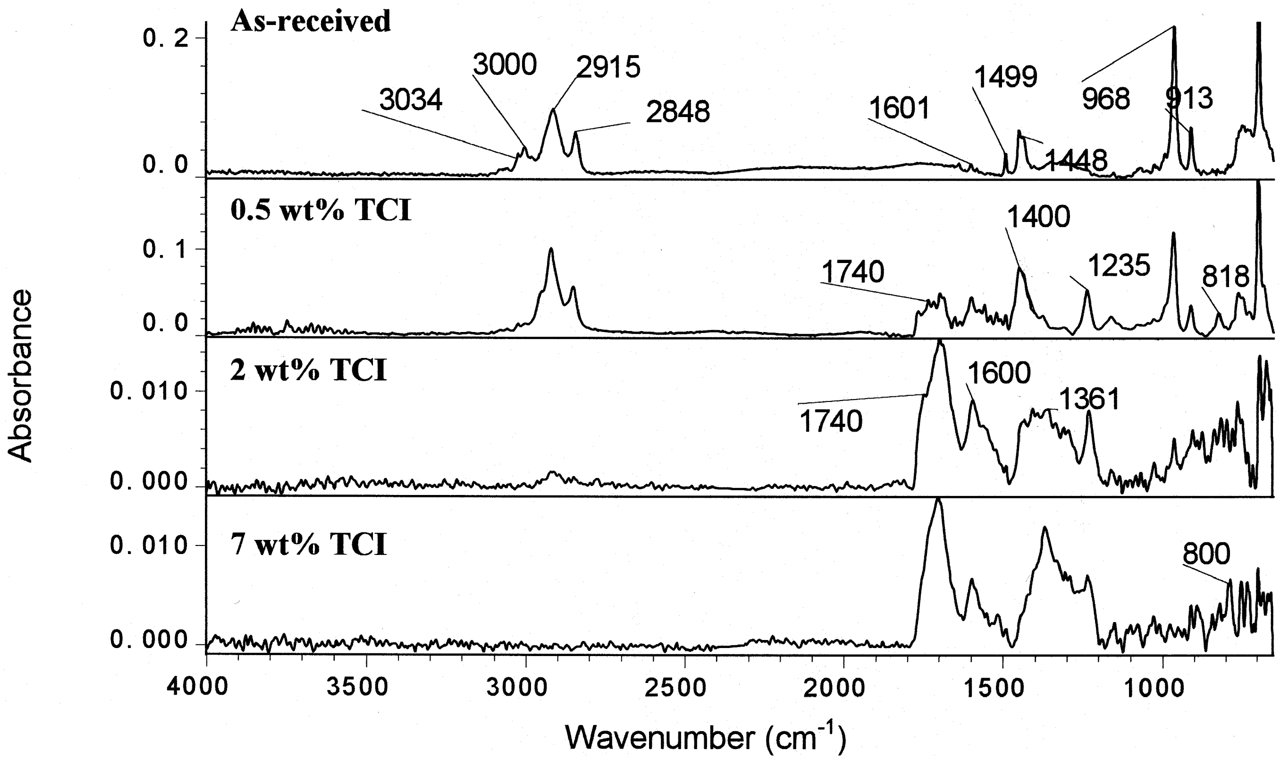


FIGURE 2 ATR-IR spectra of the as-received and chlorinated S0 rubber.

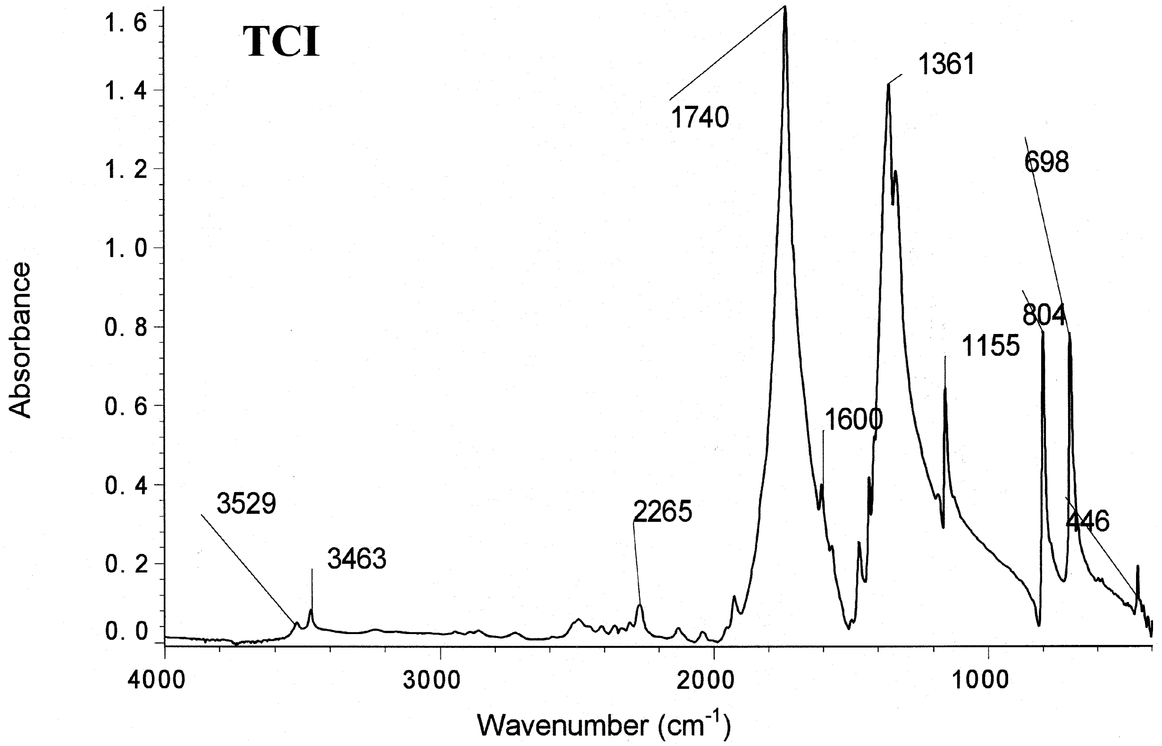


FIGURE 3 Transmission-IR spectrum of solid TCI.

TABLE 1a Surface Chemical Composition (at %) of Chlorinated-S0 Rubber Analyzed by XPS

Element	As-received	0.5 wt% TCI	2 wt% TCI	7 wt% TCI
C	95.6	82.3	72.9	73.8
O	3.2	11.0	14.3	9.2
Si	1.2	0.9	1.3	0.3
N	—	2.2	3.5	6.1
Cl	—	3.6	8.0	10.6

TABLE 1b Carbon Species (Curve Fitting of C 1s Photopeak) of Chlorinated S0 Rubber Analyzed by XPS

Species	As-received	0.5 wt% TCI	2 wt% TCI	7 wt% TCI
C-C, C-H	91.3	77.8	65.0	61.8
C-O, C-Cl	5.3	13.9	24.7	24.8
>C=O, N-C=O	—	4.4	4.3	4.9
-COOR	—	2.9	5.1	6.5
π-π^*	3.4	1.0	0.9	2.0

unreacted TCI and from isocyanuric acid. Both chlorine and nitrogen contents on the rubber surface increase with increasing TCI percentage. Furthermore, the carbon, chlorine and nitrogen concentrations in S0 treated with 7 wt% TCI are higher than for samples treated with 2 wt% TCI, indicating the existence of a non-rubbery layer on the 7 wt % TCI-treated S0 rubber. This non-rubbery layer is rich in carbon, chlorine and nitrogen, and it is suggested that this is likely composed of unreacted TCI on the surface.

Halogenation also produces some oxidation of the rubber surface. C 1s photopeak curve fitting (Figure 4, Table 1b) of chlorinated S0 shows the existence of C-C, C-H (BE = 285.0 eV), C-O (BE = 286.7 eV), N-C=O (BE = 288.7 eV) and COOR (BE = 290.1 eV) functionalities. The C 1s photopeak of solid TCI shows the intense band due to N-C=O groups, and this indicates the existence of unreacted solid TCI on the S0 rubber treated with 2 and 7 wt% TCI. Furthermore, the C 1s photopeak fitting shows a noticeable increase in carboxylated species on the rubber surface, which are not due to TCI or by-products of the reaction of TCI with the rubber surface.

Figure 5 shows the variation of the surface energy of chlorinated S0 as a function of the amount of TCI applied to the surface. Halogenation

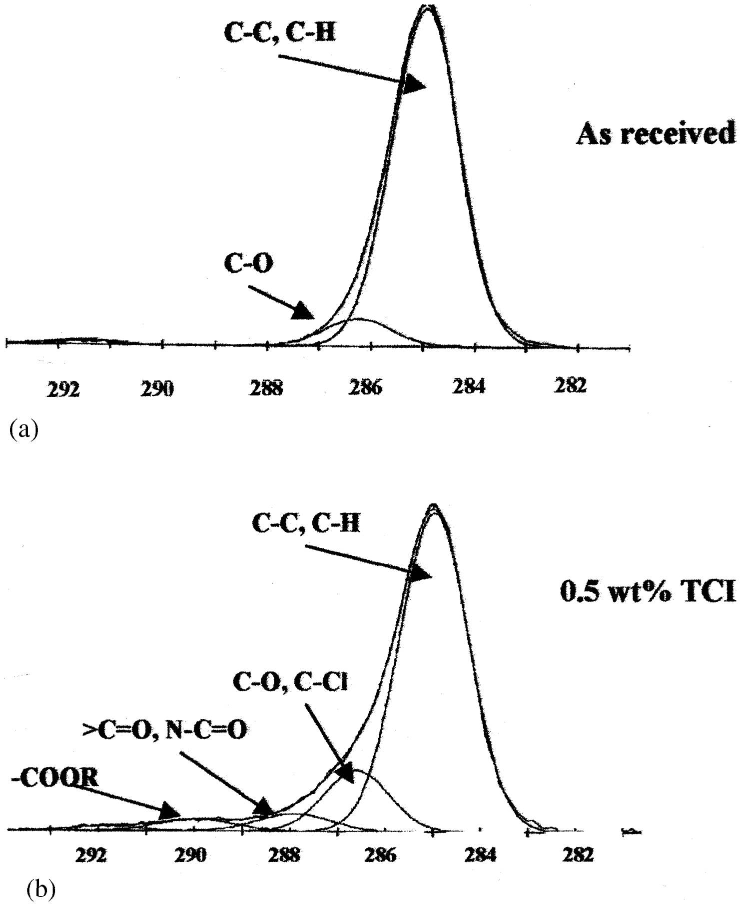


FIGURE 4 C 1 s photopeak curve fit (XPS) of the as-received and chlorinated S0 rubber.

with TCI increases the total surface energy, which mainly corresponds to an increase in the acid-base components of the surface energy. However, the increase in adhesion is achieved only when a relatively high percentage of TCI (2 wt%) is used (Figure 6). EDX mapping of the cross-section of the chlorinated rubber (Figure 7) shows that the increase in the TCI percentage in the chlorinating solution produces a thicker chlorinated layer on the rubber surface.

Consequently, improvement in the adhesion of chlorinated rubbers can be ascribed to a contribution of the mechanical (heterogeneities,

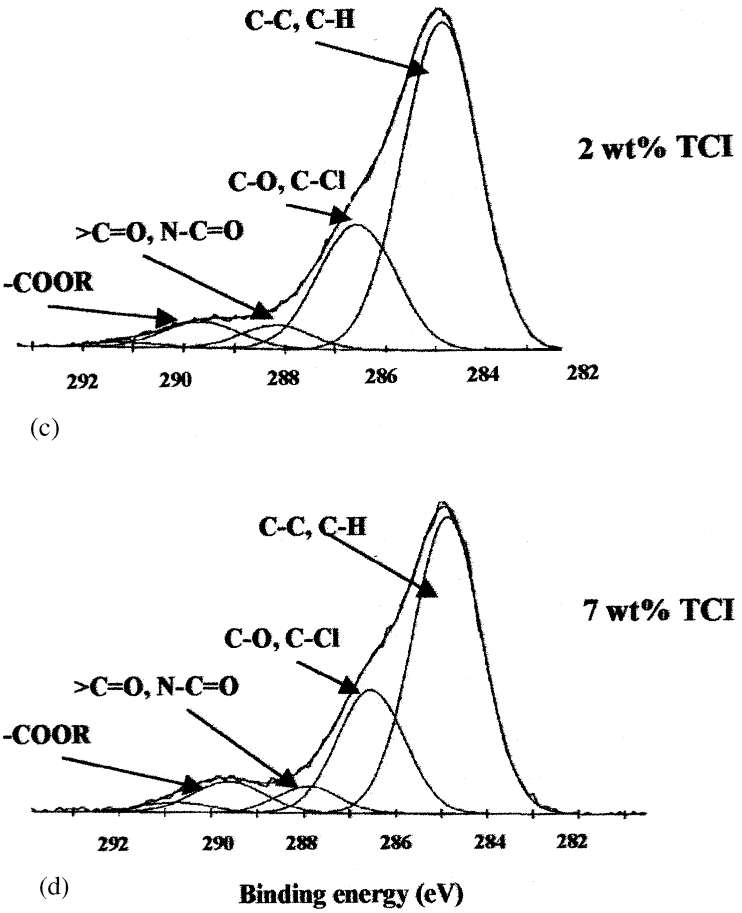
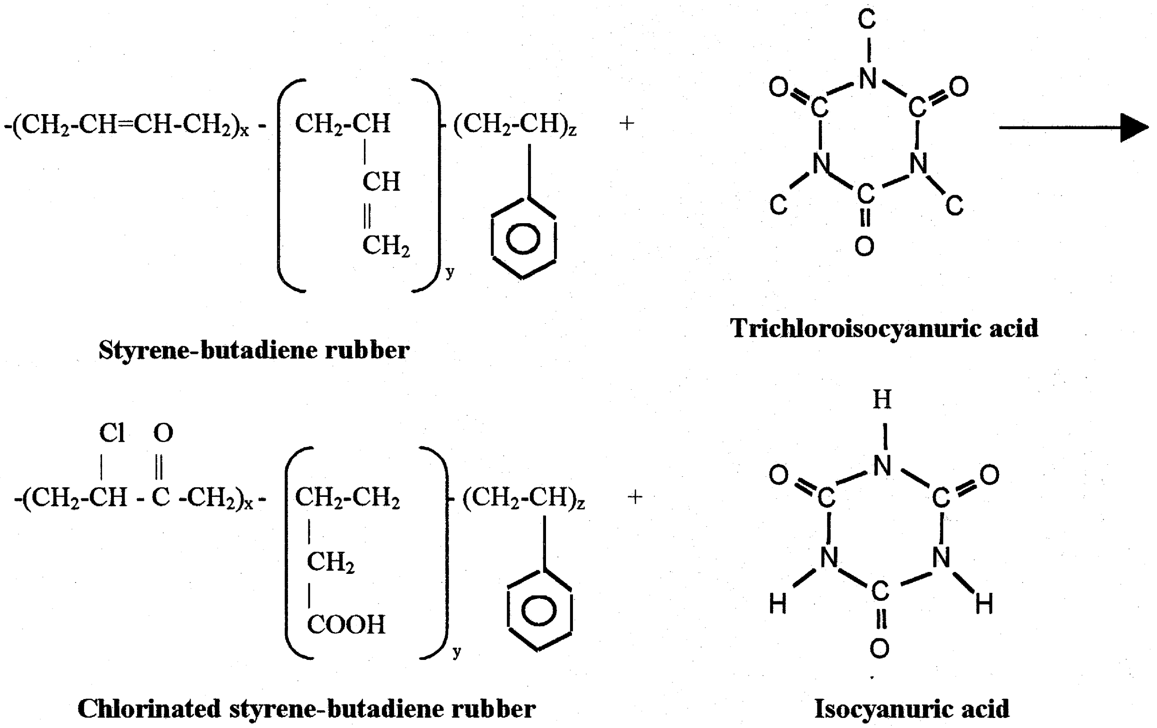


FIGURE 4 (*continued*).

cracks), thermodynamic (increase of the acid-base contribution to the surface energy) and chemical (chlorination) rubber surface modifications. The strong adhesion between the chlorinated S0 rubber and the PU adhesive is also likely ascribed to the presence of oxidized species (C-O, >C=O and -COOR) on the rubber surface, as shown in Scheme 1.

However, the lack of adhesion of the 0.5 wt% TCI-treated rubber cannot be understood and thus, the analysis of the failed surfaces obtained after T-peel testing was carried out to obtain more precise information about the effects produced by chlorination with TCI.



SCHEME 1 Reaction between Styrene-Butadiene Rubber and Trichloroisocyanuric Acid.

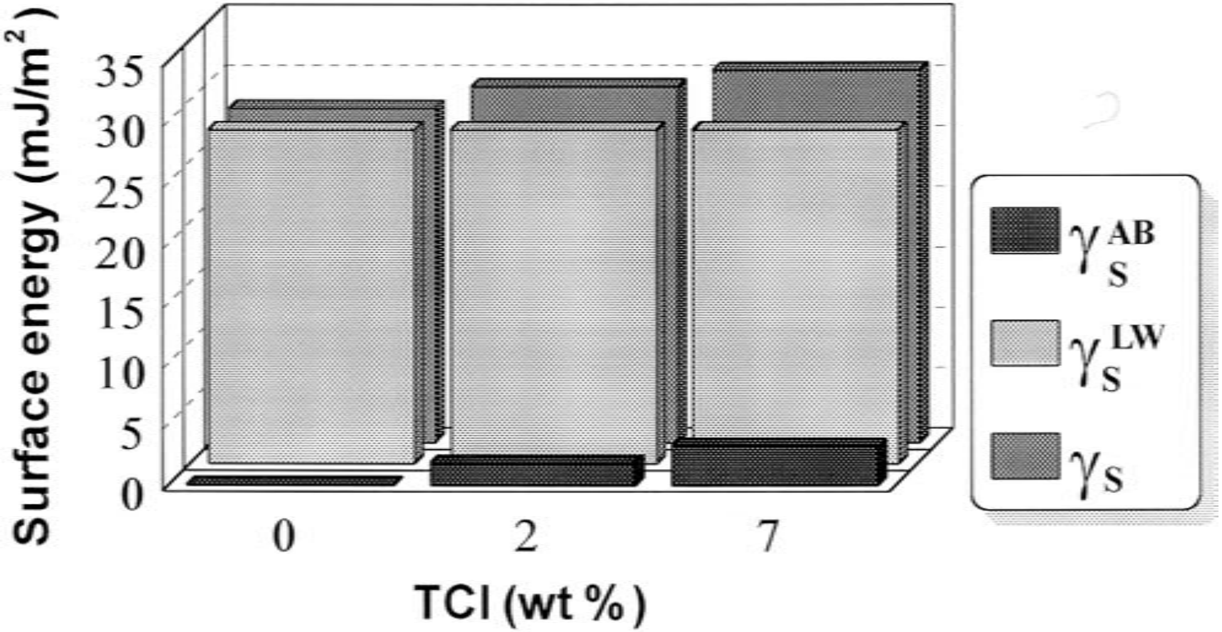


FIGURE 5 Surface energy (mJ/m^2) of chlorinated-S0 rubber.

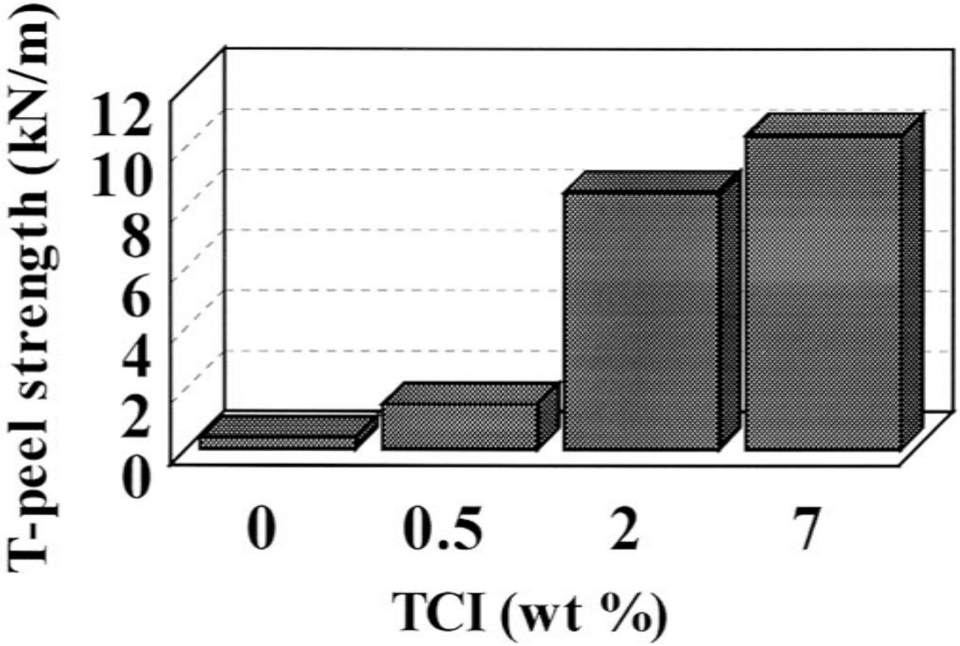
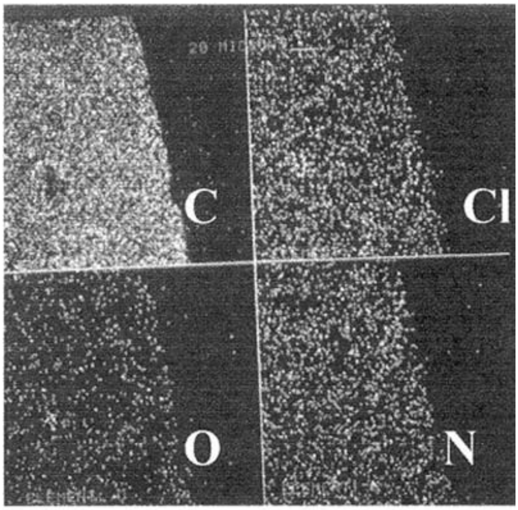
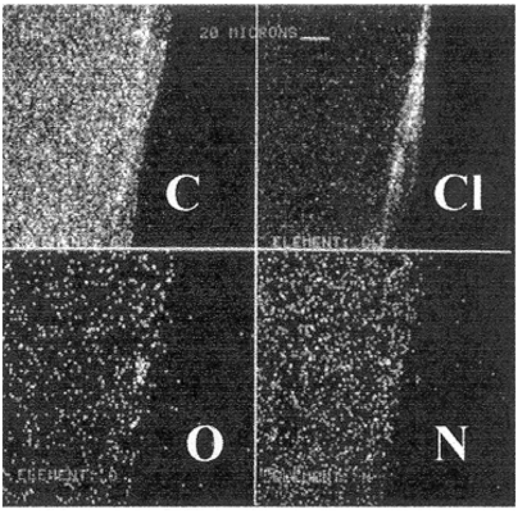


FIGURE 6 T-peel strength (kN/m) of chlorinated-S0 rubber/PU adhesive joints.

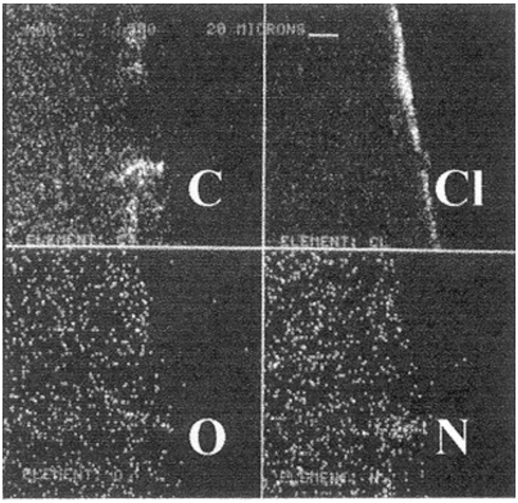


(a) 0 wt% TCI

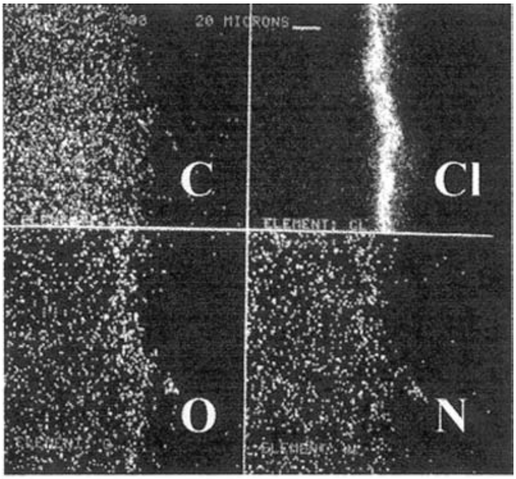


(b) 0.5 wt% TCI

FIGURE 7 EDX mapping of the solvent wiped and chlorinated S0 rubber.



(c) 2 wt% TCI



(d) 7 wt% TCI

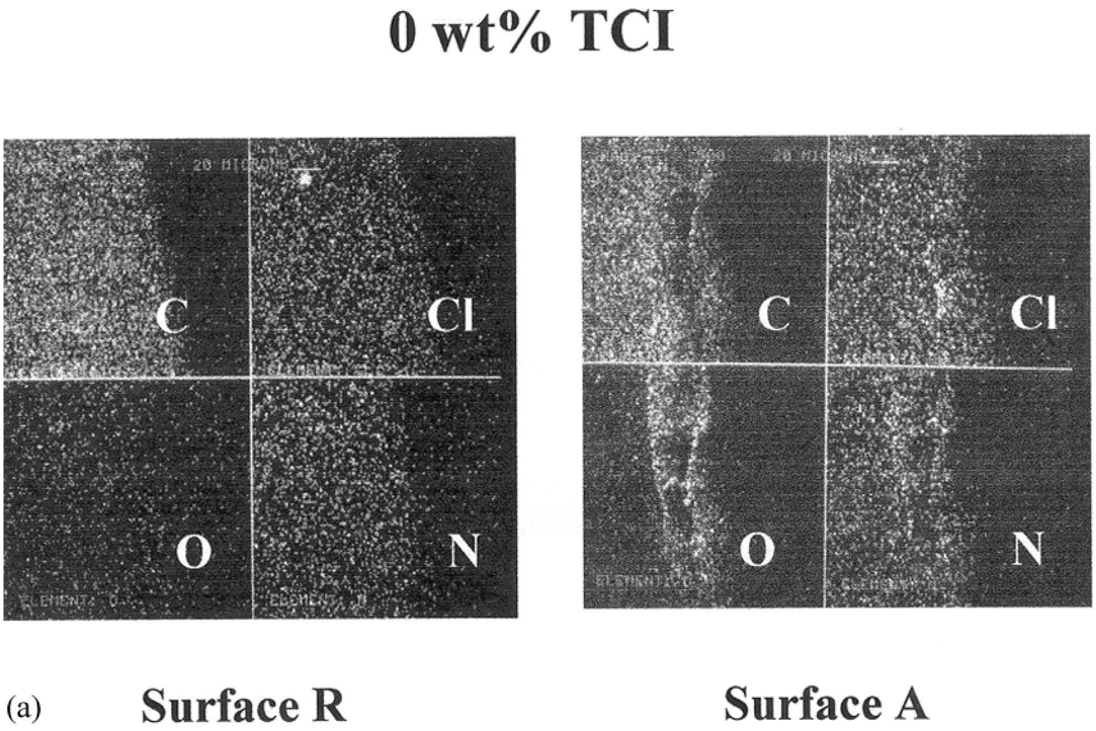
FIGURE 7 (*continued*).

Analysis of the Failed Surfaces Obtained after T-peel Testing of Chlorinated-S0 Rubber/PU Adhesive Joints

The locus of failure of the joints (visually assessed) was always adhesional, *i.e.*, one of the failed specimens exclusively corresponds to the rubber (R-surface) and the other one corresponds to the adhesive (A-surface). The following nomenclature was used: S0(0) for the non-chlorinated rubber; and S0(0.5), S0(2) and S0(7) for the chlorinated S0 rubber with 0.5, 2 and 7 wt% TCI treatments, respectively. The surface profile (EDX) of the cross-section of the failed surfaces corresponding to S0(0)/PU joint (Figure 8a), shows oxygen only on the A-surface, which suggest that the locus of failure is adhesional. The mapping of the S0(0.5)/PU failed joint does not show any chlorine in the R-surface nor the A-surface (Figure 8b). On the other hand, the cross-section of the joints produced with S0 chlorinated with 2 and 7 wt% TCI shows chlorine, oxygen and nitrogen on both failed surfaces, indicating that the failure is located in the chlorinated layer.

The ATR-IR spectrum for the PU adhesive film (Figure 9) shows typical C-H stretching bands (2939, 2860 cm^{-1}), N-H bending and N-C=O symmetric stretching peaks (1533 cm^{-1}), C=O stretching (1717 cm^{-1}), C-O stretching (bands at 1100–1240 cm^{-1}), C-N stretching (1250 cm^{-1}) and N-H out of plane deformation ($\sim$700 cm^{-1}). The ATR-IR spectra of R and A failed surfaces of the S0(0)/PU adhesive joint (Figure 10a) are quite similar to the corresponding ATR-IR spectra of the as-received S0 rubber and the PU adhesive film, respectively (Figure 9). The IR spectra are consistent with an adhesional failure of the joint. There is no further modification of the ATR-IR spectra (relative to S0 and pure PU) obtained for the failed R and A surfaces of the S0(0.5)/PU adhesive joint (Figure 10b). The ATR-IR spectra for the failed surfaces correspond to as-received rubber and pure polyurethane, respectively. No chlorine or oxidation absorption is found, which is consistent with the absence of chlorine and oxygen in the mapping of the failed surfaces (Figure 8a). Therefore, the failure appears to be produced near the interface but slightly below the chlorinated layer.

Chlorination with 2 wt% TCI produces a different locus of failure. The ATR-IR spectrum of the failed R-surface (Figure 10c) partially corresponds to the non-bonded S0(2) chlorinated rubber (Figure 2), except that TCI bands are not present. The ATR-IR spectrum of the A-surface corresponds to the PU and some styrene absorption (700 cm^{-1}) from the rubber is also present. These findings suggest that a mixed failure mode between adhesional and cohesive in the rubber is produced, a result that is consistent with the EDX mapping (Figure 8).


0 wt% TCI

(a) Surface R

Surface A

FIGURE 8 EDX mapping of failed surfaces obtained after T-peel testing.

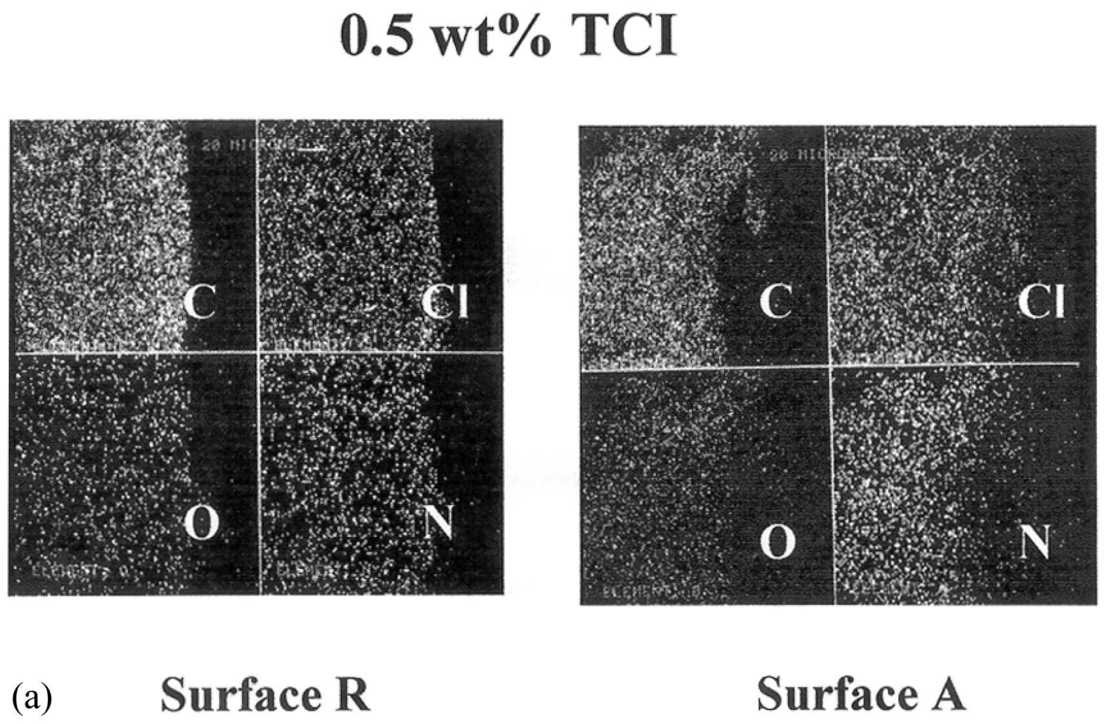
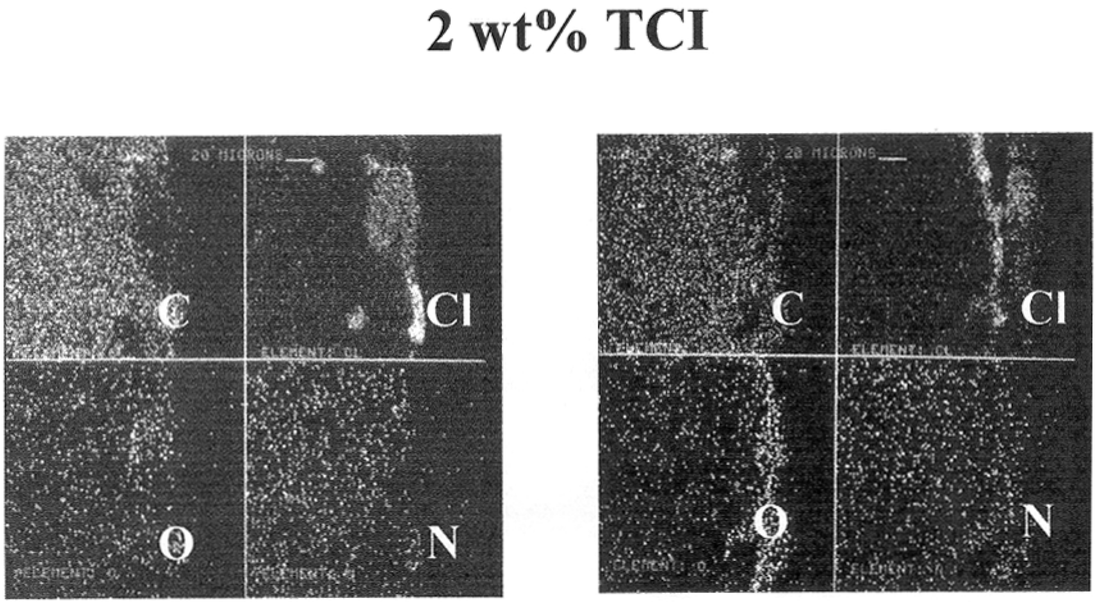


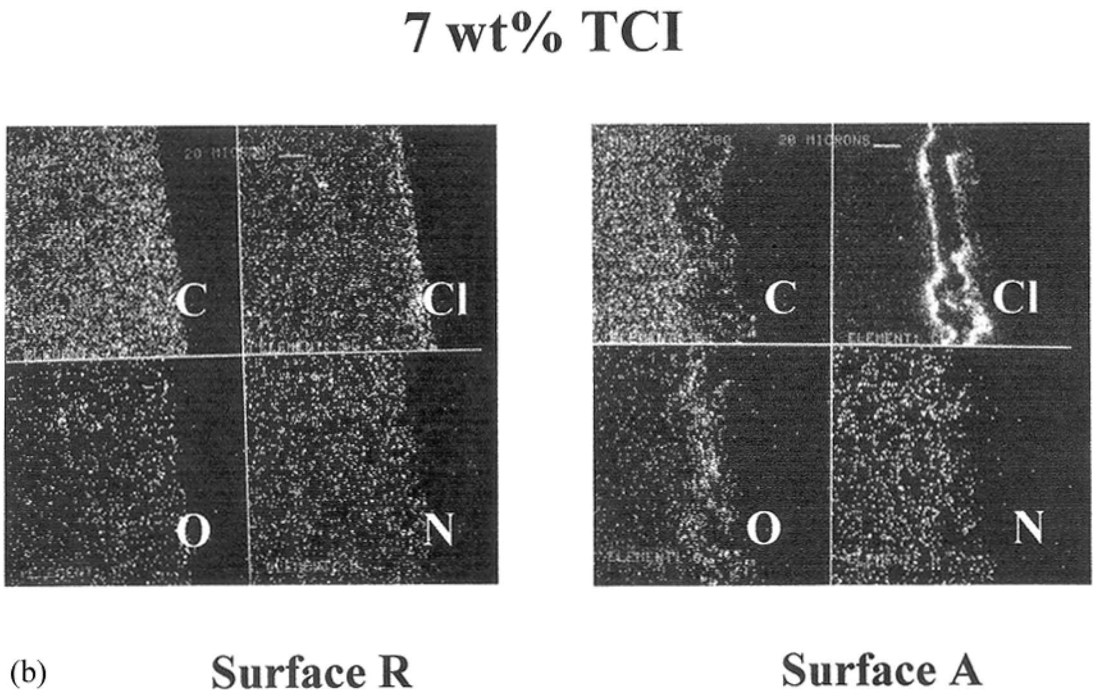
FIGURE 8 *(continued)*.



(b) Surface R

Surface A

FIGURE 8 (*continued*).



7 wt% TCI

(b) Surface R

Surface A

FIGURE 8 (*continued*).

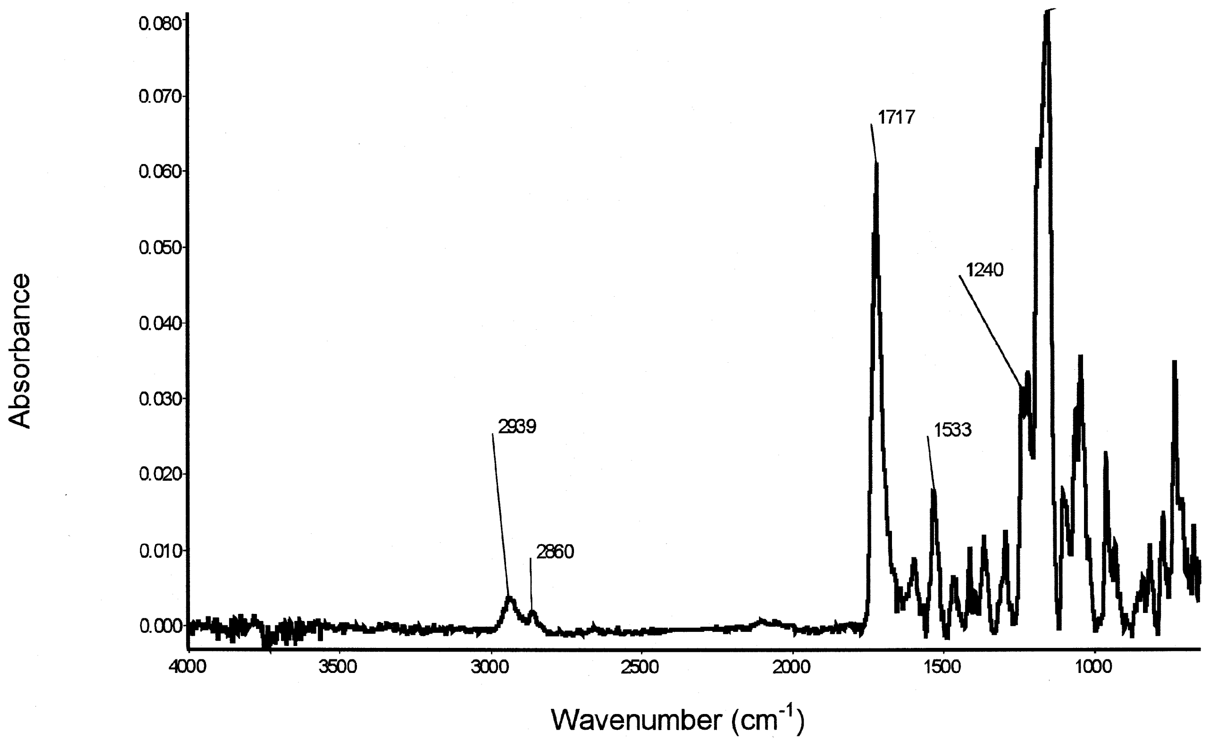


FIGURE 9 ATR-IR spectrum of the PU adhesive film.

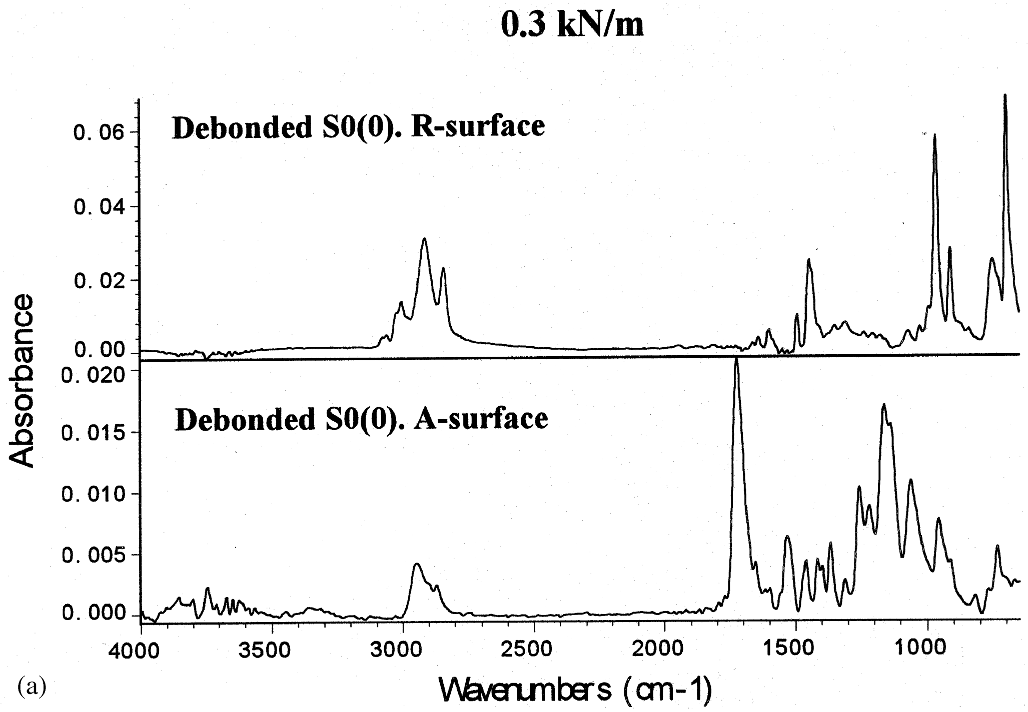
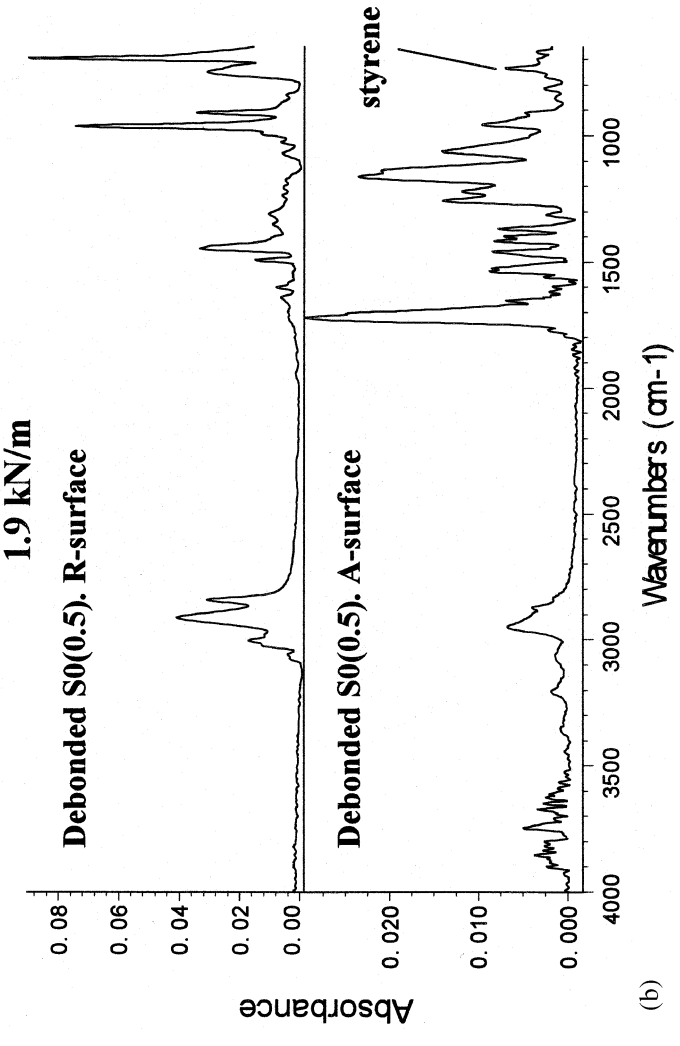


FIGURE 10 ATR-IR spectra of failed surfaces of the joint (a) S0(0)/PU adhesive; (b) S0(0.5)/PU adhesive; (c) S0(2)/PUadhesive and (d) S0(7)/PU adhesive.



(b)

FIGURE 10 *(continued)*.

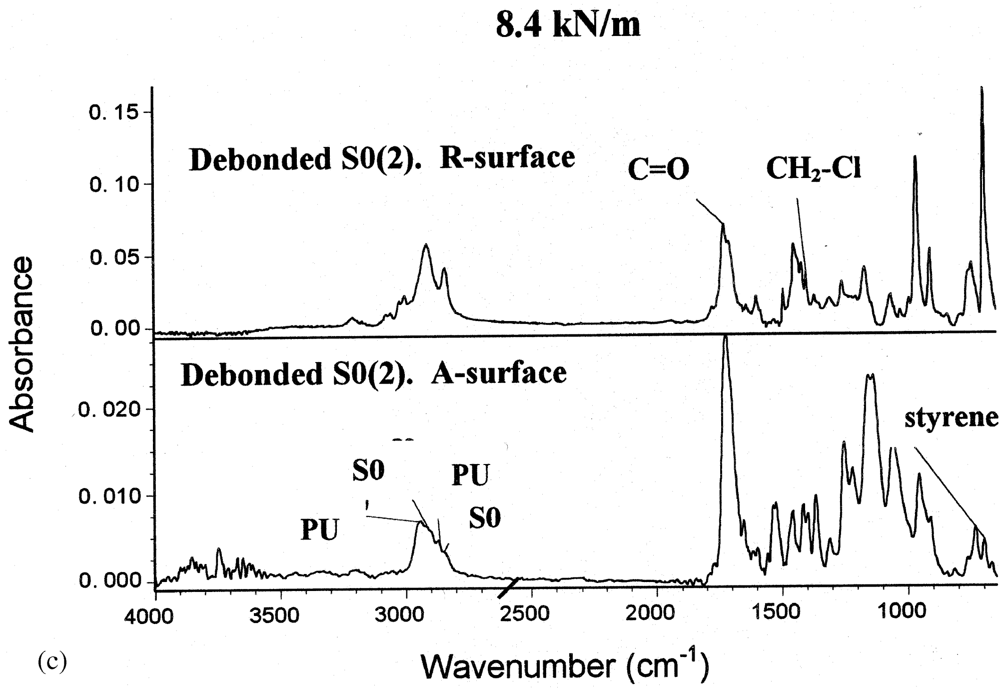


FIGURE 10 (*continued*).

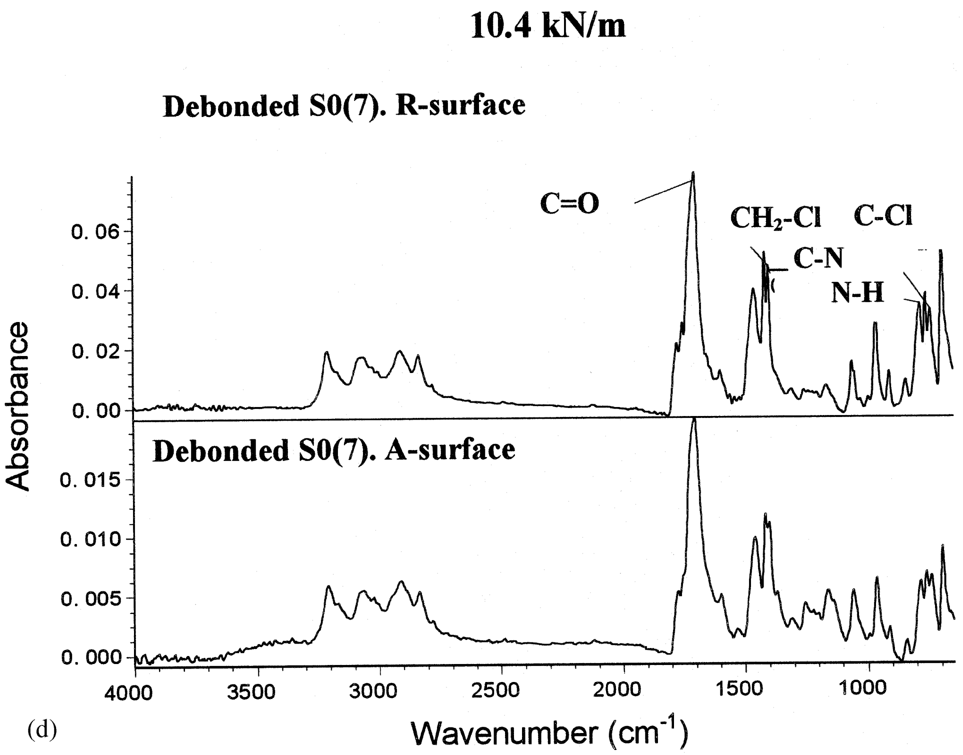


FIGURE 10 (*continued*).

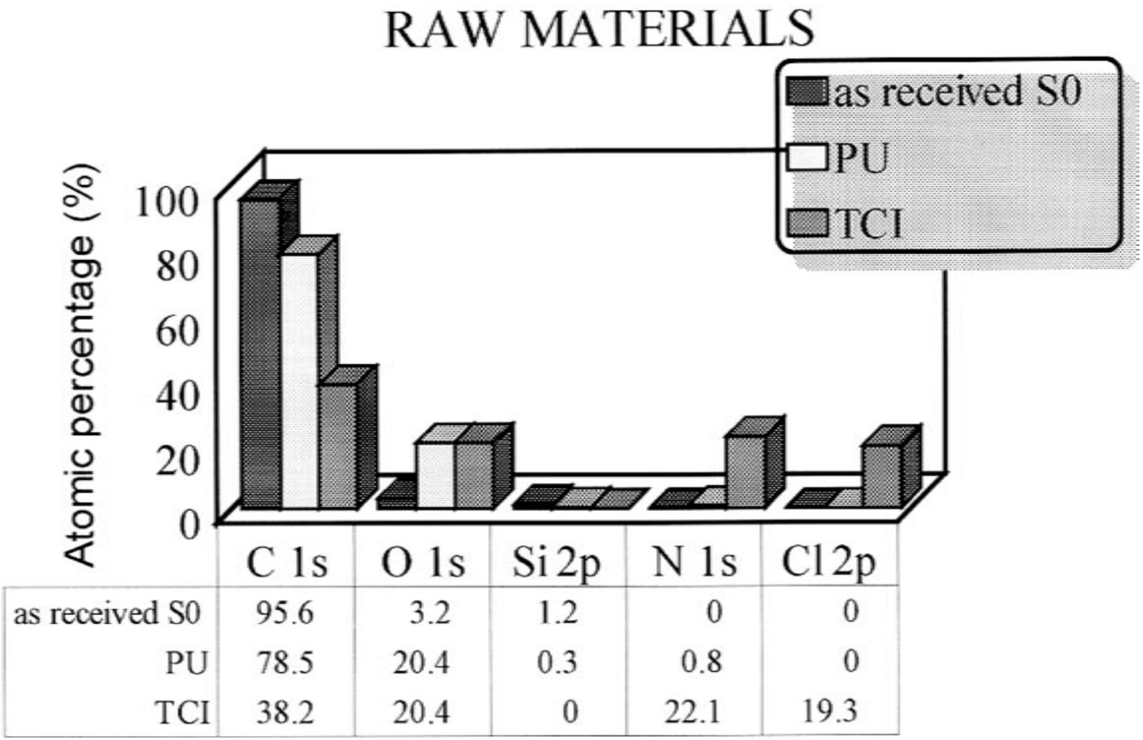
The ATR-IR spectra of the failed surfaces corresponding to the S0(7)/PU adhesive joint (Figure 10d) are identical and show bands of chlorinated hydrocarbon groups (760, 818, 1235, 1400, 1448 cm^{-1}). Furthermore, C=O functionalities (1710–1740 cm^{-1}), C-N stretching (1361 cm^{-1}) and N-H out of plane deformation (~800 cm^{-1}) are present, which correspond to TCI and isocyanuric acid (a by-product of the reaction of TCI with the rubber). Therefore, the failure mode is cohesive in the chlorinated rubber layer, in agreement with EDX analysis (Figure 8).

Figure 11 shows the XPS surface analysis data for the raw materials. The PU adhesive contains 0.3 at% silicon, 0.8 at% nitrogen and a large noticeable amount of oxygen (20.4 at%) and carbon (78.5 at%). The C:O:N:Cl ratio in TCI does not correspond exactly with the percentages expected from the TCI formula ($C_3N_3O_3Cl_3$). An unexpectedly high carbon percentage (38.2 at%), compared with the oxygen and nitrogen contents, is probably due to the presence of some impurities in the TCI.

Atomic percentages on the A-surface of the S0(0)/PU adhesive joint (Figure 12a) correspond to polyurethane (Figure 11). The R-surface data show approximately the same composition as that for the as-received S0 rubber, although a smaller oxygen percentage is found. No nitrogen from the PU was found on the R-surface. This suggests that the failure mode is adhesional, which is consistent with ATR-IR spectroscopy and EDX analysis, as well as with the lack of compatibility between the S0 rubber and the PU adhesive (peel strength = 0.4 kN/m).

Chlorination with 0.5 wt% TCI produces a change in the locus of failure of the joint. Chlorine, silicon and oxygen percentages on the R-surface are much smaller than those on the non-bonded 0.5 wt% TCI-chlorinated rubber (Table 1a), and the carbon percentage is higher (Figure 12b). On the other hand, the A-surface shows a slight amount of chlorine, similar to that on the R-surface and a higher amount of nitrogen than on the PU adhesive. Therefore, the failure is produced close to the interface but a thin layer of rubber is transferred to the A-surface as a result of the T-peel test.

Chlorination with 2 and 7 wt% TCI (Figures 12c and d, respectively) produces an increase in the oxygen, chlorine and nitrogen contents on the failed R-surface, but these percentages are always lower than those corresponding to the chlorinated but non-bonded S0 rubber surfaces. The failed A-surface shows smaller oxygen content than in the PU adhesive and a similar chlorine percentage to that in the corresponding R-surface. These results suggest that the failure of the joint takes place in a chlorinated layer with characteristics somewhat different from those for the chlorinated rubber itself (Figure 13). Therefore, the chlorinated rubber/PU adhesive interface was



	C 1s	O 1s	Si 2p	N 1s	Cl 2p
as received S0	95.6	3.2	1.2	0	0
PU	78.5	20.4	0.3	0.8	0
TCI	38.2	20.4	0	22.1	19.3

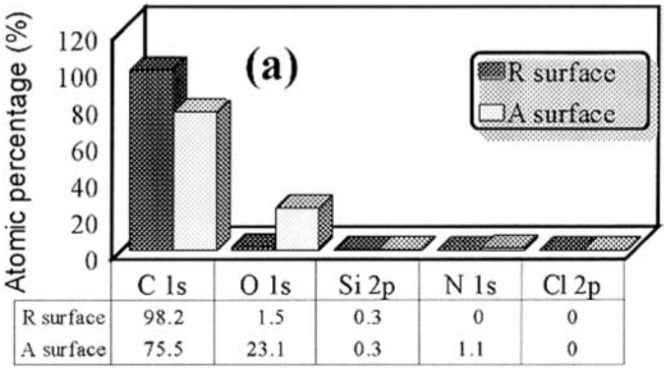
FIGURE 11 Surface atomic percentages (XPS) of raw materials.

analyzed in more detail to investigate the nature of the interactions produced between the S0 rubber and the PU adhesive.

Study of the Chlorinated S0-rubber/Polyurethane Adhesive Interface

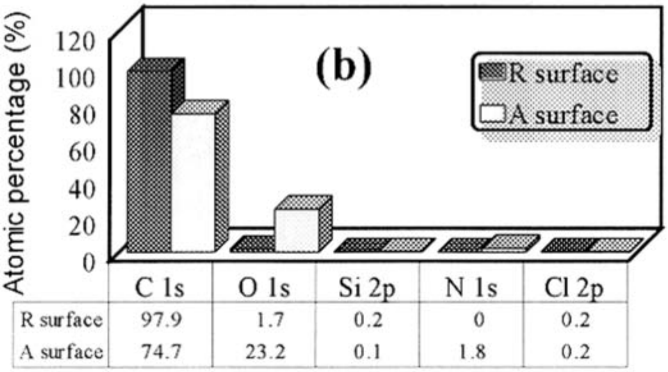
Solutions of different concentrations of PU adhesive in MEK (0.36, 1.0, 1.8 and 3.6 wt%) were spin coated on the as-received and on the chlorinated S0 rubber, and the corresponding ATR-IR spectra were

S0-0 wt % TCI



	C 1s	O 1s	Si 2p	N 1s	Cl 2p
R surface	98.2	1.5	0.3	0	0
A surface	75.5	23.1	0.3	1.1	0

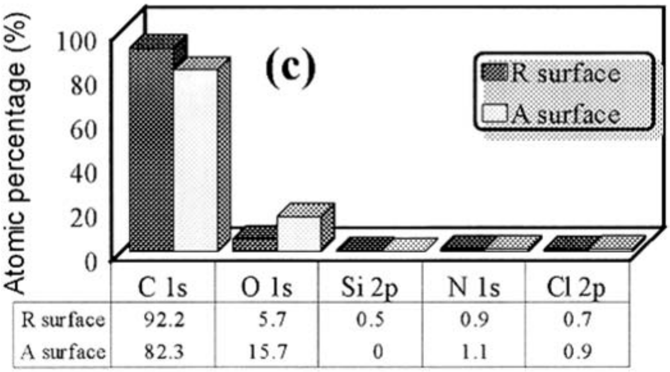
S0-0.5 wt % TCI



	C 1s	O 1s	Si 2p	N 1s	Cl 2p
R surface	97.9	1.7	0.2	0	0.2
A surface	74.7	23.2	0.1	1.8	0.2

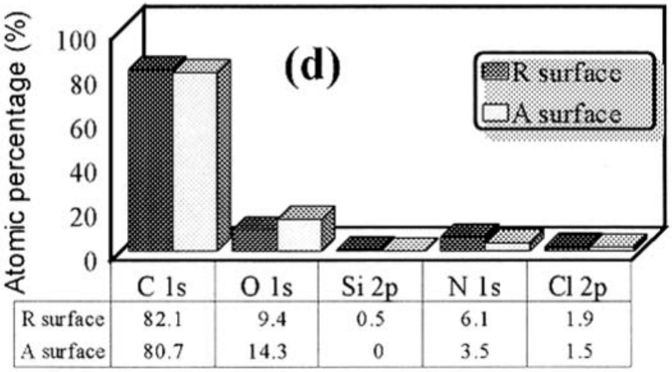
FIGURE 12 Surface atomic percentages (XPS) of failed specimens.

S0-2 wt% TCI



	C 1s	O 1s	Si 2p	N 1s	Cl 2p
R surface	92.2	5.7	0.5	0.9	0.7
A surface	82.3	15.7	0	1.1	0.9

S0-7 wt% TCI



	C 1s	O 1s	Si 2p	N 1s	Cl 2p
R surface	82.1	9.4	0.5	6.1	1.9
A surface	80.7	14.3	0	3.5	1.5

FIGURE 12 (*continued*).

obtained. The nomenclature used was as follows: PU(0.36)/S0(0) corresponds to the as-received S0 rubber which was spin-coated with a solution of 0.36 wt% PU in MEK; PU(0.36)/S0(0.5) corresponds to the S0 rubber chlorinated with a solution of 0.5 wt% TCI and coated with a solution of 0.36 wt% PU in MEK. The thickness of the PU layers was obtained from ellipsometry measurements of PU films spin coated onto a ferroplate. A Cauchy model was used to fit the data [10] (Table 2).

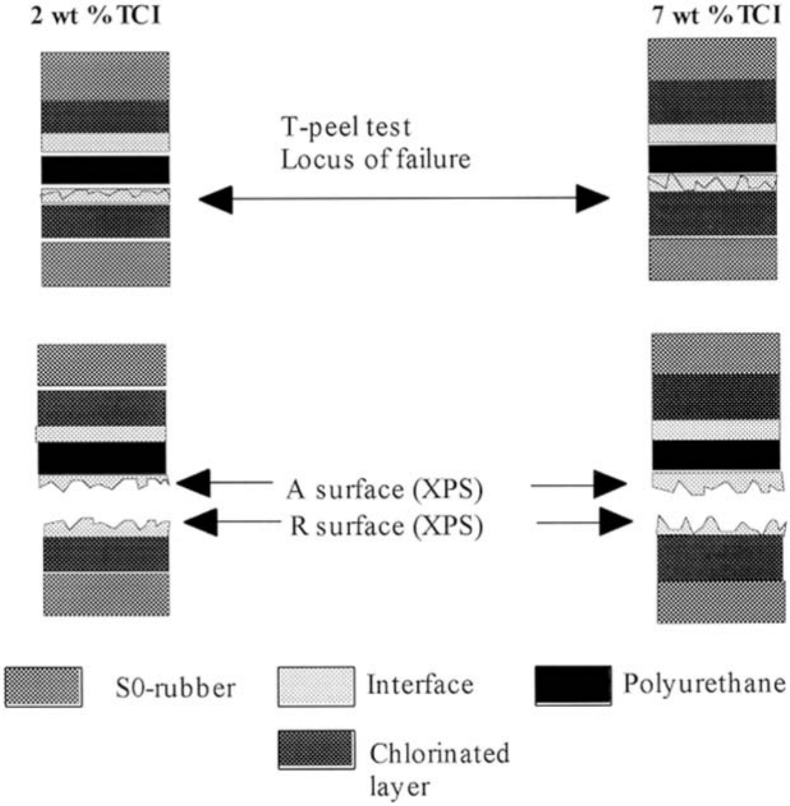


FIGURE 13 Locus of failure in chlorinated-S0 rubber/PU adhesive joints.

Figure 14 shows the ATR-IR spectra of the spin-coated rubber chlorinated with 0.5 wt% TCI. The PU(0.36)/S0(0.5) spectrum is similar to the S0(0.5) (Figure 2), except that the increase of the PU concentration enhances the bands due to PU (Figure 9).

TABLE 2 Thickness of PU Films Obtained by Spin Coating PU/MEK Solutions on Ferroplate

PU/MEK (wt%)	Thickness (Å)
0.36	230.45 ± 1.56
1.0	636.21 ± 6.11
1.8	1223.1 ± 10.5
3.6	3363 ± 101

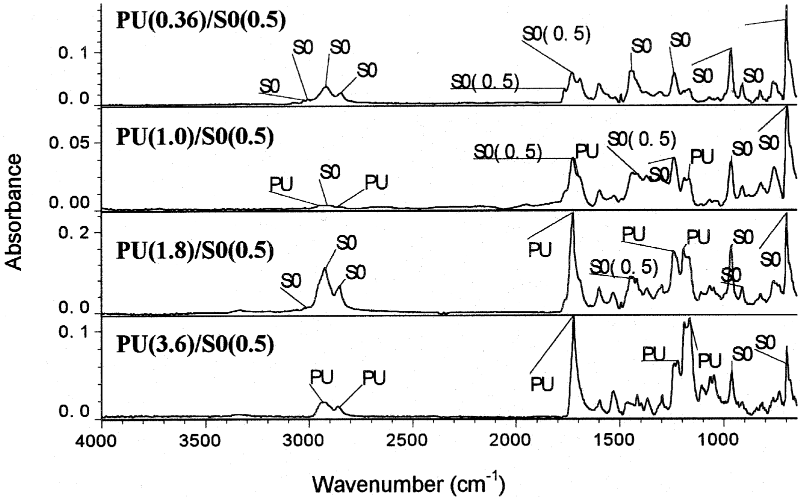


FIGURE 14 ATR-IR spectra of PU spin-coated S0 rubber chlorinated with 0.5 wt% TCI.

The ATR-IR spectra of PU(0.36)/S0(2) (Figure 15) and PU(0.36)/S0(7) (Figure 16) differ from those of the PU/S0(0.5). The spectra of PU(0.36)/S0(2) and PU(0.36)/S0(7) are similar to the chlorinated rubbers S0(2) and S0(7), respectively (Figure 2). Even when the concentration of the PU solution deposited on the rubber surface increases (*i.e.*, thicker PU film on the S0 rubber), the corresponding ATR-IR spectra show only bands of TCI, which are actually hiding those of the PU. This suggests a migration of the unreacted TCI from the rubber surface through the PU adhesive.

In order to determine if a reaction between the PU and the TCI is produced, a PU film was prepared by placing a PU solution (18 wt%) on *Pyrex*-glass and allowing the solvent (MEK) to evaporate. The dry PU films were chlorinated with 0.5, 2 and 7 wt% TCI/EA solutions using the same chlorination procedure. Figure 17 shows that in PU + 7% TCI, C=O stretching bands of both PU (1717 cm^{-1}) and TCI (1740 cm^{-1}) are present, and new bands from isocyanuric acid (by-product of the reaction of TCI) (N-H stretching at 3208, 3079 cm^{-1}) and chlorinated hydrocarbons (C-Cl bending at 1464, 1400 cm^{-1}) are present. Thus, a chlorination of the PU hydrocarbon chains is probably produced.

In order to investigate the interaction between the chlorinated rubber and the PU, pieces of as-received and chlorinated S0 rubber previously spin coated with PU from a 1 wt% PU/MEK solution

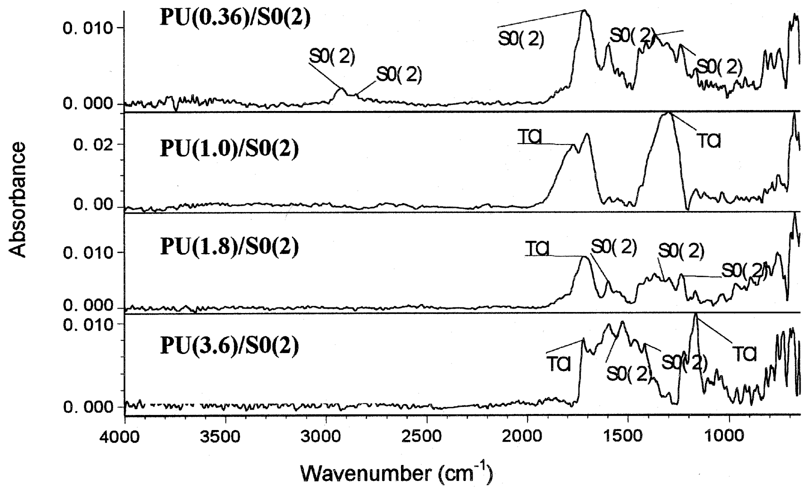


FIGURE 15 ATR-IR spectra of PU spin-coated S0 rubber chlorinated with 2 wt% TCI.

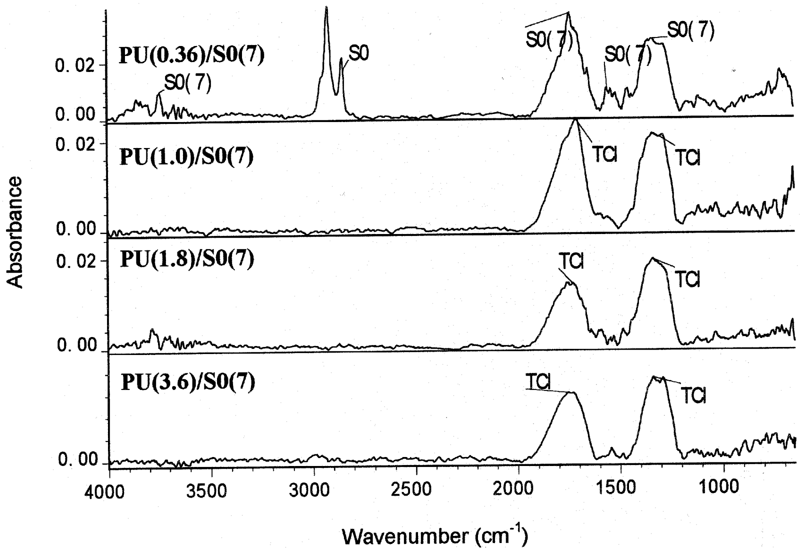


FIGURE 16 ATR-IR spectra of PU spin-coated S0 rubber chlorinated with 7 wt% TCI.

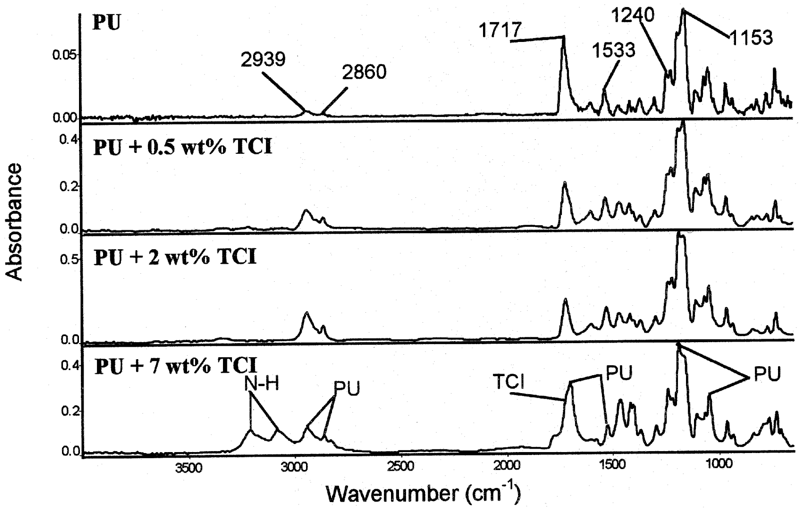


FIGURE 17 ATR-IR spectra of PU film chlorinated with solutions of TCI/EA.

(resulting PU film was 636 Å thick) were immersed in toluene and mechanically shaken for one hour. In this experiment, the PU adhesive, which is insoluble in toluene, remained as a film in the solution (ATR-IR spectra of both sides were obtained), and the chlorinated rubber became partially insoluble (transmission-IR spectra of the precipitate and of the remaining solution were also obtained). Both sides of the PU film that were in contact with the as-received rubber showed ATR-IR spectra similar to those of the raw PU. However, the ATR-IR spectra of the PU in contact with the chlorinated S0 rubber (Figure 18) show bands of PU and some of rubber S0 on side #1 and only bands of chlorinated S0 appeared on the other side, which indicates that there is a strong adhesion between the outermost chlorinated rubber surface and the PU adhesive.

The outermost rubber surface, which does not interact with the PU but is crosslinked by the chlorination treatment, remained insoluble as a precipitate in the toluene. The solution was filtered-off and both the precipitate and the solution were analyzed by transmission-IR (Figure 19). The IR spectrum of the precipitate shows bands of chlorinated rubber (Figure 19a), and the remaining solution (Figure 19b) corresponds to the non-chlorinated rubber. Thus, crosslinking of the S0 rubber surface is produced by chlorination. The remaining TCI on the rubber surface migrates through the PU adhesive producing some chlorination of the PU chains. Furthermore, a strong adhesion

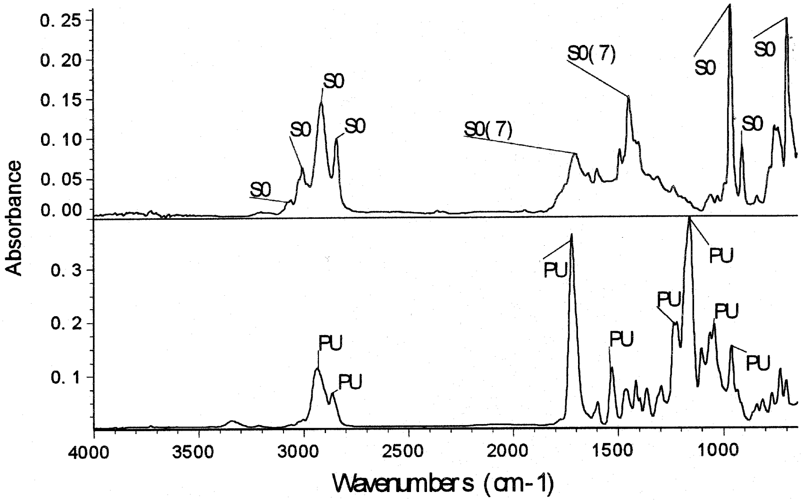


FIGURE 18 ATR-IR spectra of both sides of PU film in contact with S0 rubber chlorinated with 7 wt% TCI.

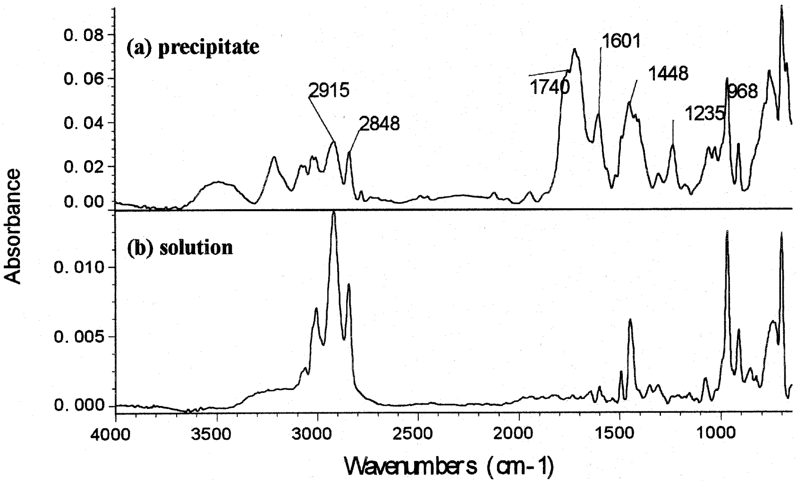


FIGURE 19 Transmission-IR of (a) precipitate and (b) solution of S0 rubber chlorinated with 7 wt% TCI spin coated with PU and dissolved in toluene.

between the chlorinated rubber and PU adhesive chains is produced. The failure of the joint is located in this interface composed of both chlorinated S0 rubber and partially-chlorinated PU adhesive.

CONCLUSIONS

1. Halogenation of S0 rubber with trichloroisocyanuric acid increased adhesion to PU adhesives due to the improved mechanical (heterogeneities, microcracks), thermodynamic (increase of acid-base contribution to the surface energy), chemical (creation of C-Cl groups) surface modifications and also strong interactions between the PU adhesive and chlorinated S0 rubber chains at the interface.
2. Chlorination produces a crosslinking of the outermost rubber surface, which becomes insoluble in toluene. A deposition of TCI on the rubber surface is produced when a highly concentrated chlorinating solution is used (2–7 wt%). Unreacted TCI is able to migrate from the rubber surface through the PU adhesive, and chlorination of the PU is produced.
3. There is a strong interaction between the PU adhesive and chlorinated S0 rubber at the interface, which increased the strength of the adhesive joint. Nevertheless TCI percentages of 2–7 wt% TCI/EA are necessary to obtain good adhesion levels. The concentration of the chlorinating solution affects not only the adhesion strength but also the locus of failure during a peel test. Thus, the failure of the non-chlorinated S0 rubber/PU adhesive joint is adhesional. Chlorination of S0 rubber with 0.5 wt% TCI produces a failure in the outermost rubber surface. Chlorination with 2 wt% TCI produces a mixed failure mode (adhesional and cohesive in the interface). The failure mode progressed to cohesive in the interface when 7 wt% TCI was used.

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