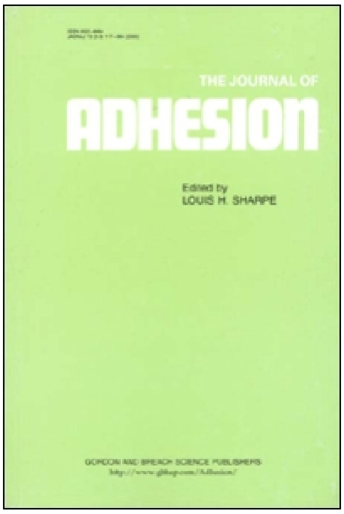

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Surface Characterization of Chlorinated Synthetic Vulcanized Styrene-Butadiene Rubber Using Contact Angle Measurements, Infra-Red Spectroscopy and XPS*

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The surface of a sulfur-vulcanized synthetic styrene-butadiene rubber (SBR) was treated with ethyl acetate solutions containing different amounts of trichloroisocyanuric acid (TCI). The chlorinated SBR surfaces were characterized using contact angle measurements (water, ethane diol, *n*-hexadecane), infra-red (IR) spectroscopy and XPS. Chlorination produced an increase of surface free energy which was mainly due to the enhancement of the acid-base component of the surface free energy, which remained almost unchanged when the amount of TCI was increased. Depending on the amount of chlorination agent, several chemical species were present on the SBR surface: *i*) For low amounts of TCI (up to 2 wt%), mainly chlorinated hydrocarbon and C—O species were present on the surface; *ii*) For medium amounts of TCI (between 2 and 5 wt%), an excess of unreacted TCI remained on the surface and a relatively small amount of isocyanuric acid was deposited; *iii*) For high amounts of TCI (larger than 5 wt%), a weak boundary layer (mainly composed of isocyanuric acid) was formed on the surface and thus the effects due to chlorination were decreased. There was good agreement between the experimental results obtained with contact angle measurements and XPS because both provided information on a surface region close to 100 Å, whereas IR spectroscopy results showed

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deeper penetration of the chlorinating agent into the SBR surface. The estimated thickness of the chlorinated layer was near 5000 Å as estimated from XPS measurements of SBR surfaces modified by argon ion bombardment.

Keywords: Rubber; surface treatment; XPS; chlorination; contact angle, infrared spectroscopy, T-peel strength

INTRODUCTION

Chlorination is a common surface treatment to improve the adhesion of rubber materials to polymers [1–5], metals [6–7] and elastomers [8–12]. Although several chlorination agents have been proposed [1,5,13–19] (sodium hypochlorite, bleach, chlorine), the most common and effective is trichloroisocyanuric acid (TCI) [1,4–7,16,20–24]. Several papers have been published dealing with the nature of the surface modifications on the rubber produced by halogenation with TCI [25–28]. In previous papers [8,13,14,24,29,30], it was established that several factors determine the effectiveness of the chlorination of synthetic vulcanized rubber, such as the nature and compounding of rubber, and the experimental conditions of the chlorination process (time of reaction, solvent and procedure used to apply the halogenation agent on the surface, amount of chlorination agent, kind of postchlorination agent, etc.). On the other hand, the chlorination of SBR with TCI produces an enhanced adhesion due to the improvement of several mechanisms of adhesion [8,13,24,29,31] (mechanical-creation of surface roughness, thermodynamic-increase of surface free energy, chemical-creation of chlorinated hydrocarbon groups and C=O functionality, removal of weak boundary layers), the modification of the physical, mechanical and viscoelastic properties of SBR, and the removal of abhesive moieties. The relative contribution of those modifications is greatly affected by the amount of TCI applied to the rubber surface.

According to previous studies [8,13,24,32], practical adhesion (obtained from a T-peel test) is strongly affected by the amount of TCI applied to the SBR surface. To explain the tendencies in T-peel strength of SBR/polyurethane adhesive joints as a function of the amount of TCI, the creation of a layer of chlorinated SBR surface, which became thicker when the amount of TCI on the SBR surface increased, was proposed. Previous studies [33] showed a disagreement between the experimental results obtained using contact angle measurements and those resulting from ATR-IR spectroscopy. Those differences are probably explained by considering that a different SBR surface thickness is analyzed (the most external surface with contact angle measurements and around 5000 Å with ATR-IR spectroscopy). Therefore, in this study the surface modifications produced by halogenation with TCI of a synthetic vulcanized SBR were studied with three of the most common surface analysis techniques: contact angle measurements, IR spectroscopy and XPS. XPS will provide chemical information within 50–100 Å of the external surface and, thus, the combined use of the information obtained with those techniques will give a better understanding of the variations in surface properties of chlorinated SBR as a function of the amount of TCI.

EXPERIMENTAL

Materials

A sulfur-vulcanized synthetic styrene-butadiene rubber (SBR) was used in this study. The formulation of rubber is given in Table I, and contains carbon black and silica as fillers. Some properties of the rubber were obtained using standardized procedures [34]: °Shore A hardness = 93; Density (20°C) = 1.2 g cm^{-3}; Tensile strength at break = 18.0 MPa; Maximum elongation at break = 397%; Tear resistance = 19.9 kN m^{-1}. The surface treatment applied to the rubber was as follows. The SBR

TABLE I Formulation of vulcanized styrene-butadiene rubber

Compound	*Composition (phr)*
SBR 1502	100
Carbon Black (N330)	23
Silica	25
Sulfur	1.76
Cumarone-indene resin (85°C)	3.52
Zinc oxide	3.81
Stearic acid	0.76
N-cyclohexyl-2-benzothiazole sulphenamide	1.14
Phenolic antioxidant	0.78
Dibenzothiazyl disulphide	0.16
Polyethylene glycol	1.13

was immersed in ethyl acetate for 20 seconds, dried in RT air for 30 min and then was immersed in the chlorination solution (1–7 wt% trichloroisocyanuric acid solution in ethyl acetate). The chlorination process was carried out for one hour. The chlorination deposits solid TCI crystallites and residues of the reaction of TCI with rubber (cyanuric and/or isocyanuric acid); so it has been recommended [29] that a postchlorination treatment also be done. In this study the post-chlorination treatment was carried out by immersing the SBR in an aqueous solution which contains 25 wt% ethanol, removing it and leaving it to evaporate in the open air for one hour.

To determine the T-peel strength, a thermoplastic, one-component polyester-urethane adhesive (*Pearlstick 45-40/15*) manufactured by Merquinsa (Barcelona, Spain) was used. This one-component polyester-urethane has a crystallization time about 20 minutes at room temperature, and a short open time. That polyurethane has a glass transition temperature of −36.8°C and a softening temperature of 50°C (both determined from DSC curves obtained in a *Mettler DSC-30* calorimeter using a heating rate of 10°C/min). The crystallization of the polyurethane adhesive is produced once the solvent is removed, allowing the creation of a polymer network between linear urethane chains [35]. The adhesive was prepared by dissolving 15 wt% PU in 2-butanone in a laboratory mixer (400 rpm, 2 hours), a Brookfield viscosity of 1.3 Pa s (23°C) being obtained.

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 *Instron 1011* test instrument, with a peeling rate of 100 mm/min. Five experimental determinations for each analyzed experimental variable were obtained, the experimental error obtained being less than 5%. The adhesive joints were prepared by applying approximately 150 mg of adhesive to each one of the identically-treated rubber surfaces. After allowing the solvent to evaporate for 30 minutes, the dry adhesive films were melted at 80°C, 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.

Contact Angle Measurements. The surface-treated SBR pieces were introduced into an isothermal 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 advancing contact angles on the surface-treated rubbers were measured on 4 μl drops of bidistilled water, *n*-hexadecane and ethylene glycol; the time required to equilibrate was 15 minutes in every case. The experimental error was ±2 degrees.

The surface energy components for the surface-chlorinated rubbers were calculated from the measured contact angles (Θ) of three suitable liquids (one non polar and two polar) by using the Good equation [36], obtaining separately the dispersive and acid-base components of the surface free energy:

$$Y_L(1+\cos\theta) = 2[(Y_S^{LW}\,Y_L^{LW})^{1/2} + (Y_s^{\oplus}\,Y_L^{\ominus})^{1/2} + (Y_S^{\ominus}\,Y_L^{\oplus})^{1/2}]$$

where the subscripts "L" and "S" refers to the liquid and solid, respectively, and Y_L = surface tension of liquid; $Y^{\oplus}$ = electron acceptor component of surface free energy; $Y^{\ominus}$ = electron donor component of surface free energy; Y^{LW} = dispersive component (Lifshitz-van der Waals) of surface free energy.

Fourier Transformed InfraRed Spectroscopy (FTIR). The IR spectra of rubber treated with different amounts (1–7 wt%) of TCI in ethyl acetate were obtained in a *Nicolet FTIR 205* apparatus, to determine the result of the chemical modifications produced by the surface treatment of the rubbers. The attenuated total multiple reflection method was used (ATR), a germanium crystal being used to reduce the absorption caused by carbon black. More details on this technique were presented earlier [29, 31–33].

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. The treated samples were outgassed for one hour before the analysis to avoid solvent removal during the experiments. In most of the samples this procedure was sufficient to maintain the pressure below 5×10^{-7}

torr during all the experiments. Furthermore, the specimens were cooled down to 0°C to avoid changes in pressure. Rectangular samples (10 mm × 20 mm) were used, although the dimension of the analyzed areas on the samples was 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 emissions (carbon, oxygen, chlorine, zinc, nitrogen, sulfur, silicon) in the survey scan was then carried out. Binding energies of all emissions were referenced to the 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 and carbon-oxygen-containing functional groups [37].

Depth Profile Measurements. The depth profile measurements were conducted using PHI Perkin-Elmer instruments; a *Model 5400 XPS* instrument and a *Model 610 Scanning Auger Electron* spectrometer. In the depth profile experiments using the XPS, the specimen was bombarded with 3.0 kV argon ions at a sputter rate of 5 Å/min. Following the selected bombardment time, XPS spectra were measured. To obtain depth profiles using a faster sputter rate, specimens were argon ion bombarded in the Auger system. In these experiments the specimen was bombarded with 3.0 kV argon ions at a sputter rate of 25 Å/min and then the specimen was removed from the Auger instrument and the sputtered area was analyzed in the XPS system. The surface analysis measurements following ion bombardment were carried out to obtain elemental composition only. Because ion bombardment induces chemical degradation, it was not possible to determine chemical functionality information following ion bombardment.

RESULTS AND DISCUSSION

Chlorination of SBR changes the surface chemistry. IR spectra of chlorinated SBR with different amounts of TCI are given in Figure 1.

In this figure, 0 wt% corresponds to the rubber treated only with solvents under conditions similar to the chlorination (the SBR was immersed in ethyl acetate for 20 seconds, dried in RT air for one hour and then immersed in a 25 wt% ethanol/water solution for 20 seconds, leaving it to evaporate in open air for one hour). The IR spectrum of solvent-treated SBR shows the presence of zinc stearate (1452 and 1539 cm^{-1}, and contribution to CH_2 stretching at 2851–2920 cm^{-1}) and silica (broad band at 1089 cm^{-1}). Halogenation with 2 wt% TCI (Fig. 1) produces a reduction of intensity of C—H (2851, 2920 cm^{-1}) and C=C bands (913, 968 cm^{-1}) due to the formation of chlorinated hydrocarbon (1237, 1387 cm^{-1}) groups in the butadiene units of SBR. Furthermore, C=O functionality (1710 cm^{-1}) and C—O stretching and OH out-of-plane deformation (1420 cm^{-1}) are created on the surface, corresponding to the presence of isocyanuric acid on the rubber and to oxidized C—O species. Increasing levels of TCI (Fig. 1) enhance the chlorination of the SBR surface, and produce a shielding of the SBR, the consequence of which is the decrease in the intensity of zinc stearate bands (1452, 1539, 2851, 2920 cm^{-1}). Furthermore, the intensity of the Si—O band at 1089 cm^{-1} is strongly decreased and N—H bands (1610, 2790, 3089, 3218 cm^{-1}) appear in the IR spectrum as a consequence of the formation of isocyanuric acid (a byproduct of the reaction of TCI and SBR). Therefore, a weak boundary layer is pro-

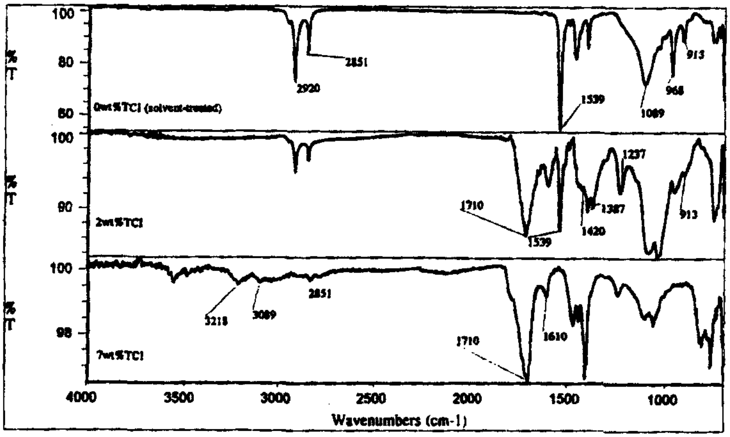

FIGURE 1 ATR-IR spectra of the surface of SBR chlorinated with different amounts of TCI.

duced when high amounts of TCI are applied on the rubber surface, which can be mainly ascribed to noticeable amounts of isocyanuric acid [31, 32].

It was already shown [29–33] that the surface free energy of synthetic vulcanized rubber increases after halogenation. Figure 2 shows the variation of surface free energy of surface-treated SBR as a function of the amount of TCI applied. The halogenation of SBR increases the total surface free energy which mainly corresponds to increases of the acid-base components of surface free energy. The increase in the amount of TCI does not noticeably increase the total surface free energy nor the dispersive or acid-base components of the surface free energy. Thus, the chlorination of SBR creates acid groups (chlorinated hydrocarbon groups, C—O, C=O) on the surface which enhance the surface free energy of rubber. The surface free energies given in Figure 2 cannot be considered as thermodynamic values because some isocyanuric acid exists on the surface of chlorinated SBR (mainly in the sample treated with 7 wt% TCI). Therefore, the data of Figure 2 can be only considered for comparison. On the other hand, although the IR spectra (Fig. 1) show a continuous increase in intensity of chlorinated hydrocarbon groups and C—O functionalities, there is not an effect in the surface free energy of treated SBR. The contact angle measurements provide information on the upper few Angstroms of the treated-SBR surface, whereas ATR-IR spectroscopy gives the chemistry of a thicker surface region (near 5000 Å). Therefore, the information provided by different techniques may differ, and the use of a more surface-sensitive analysis technique may help one to understand the experimental results. Hence, XPS analysis of treated SBR surfaces was carried out.

Although previous studies [24] dealing with XPS analysis of chlorinated rubbers with TCI have been published, no correlations with contact angle measurements and IR spectroscopy were presented. The XPS spectra for the C 1s, Cl 2p and N 1s regions are given in Figures 3 to 5, respectively. According to these figures, the solvent-treated SBR contains carbon as hydrocarbon and approximately 10 atomic % oxygen, as the principal chemical species (Tab. II); the oxygen concentration includes contributions from precipitated silica ($\sim$4 at.%), zinc stearate ($\sim$3.5 at.%) and other oxygenated functionalities (stearic acid, antioxidant, etc). Furthermore, small amounts of zinc (binding energy, BE = 1023.1 eV), and sulfur (BE = 163.2 eV) and sulphate or other

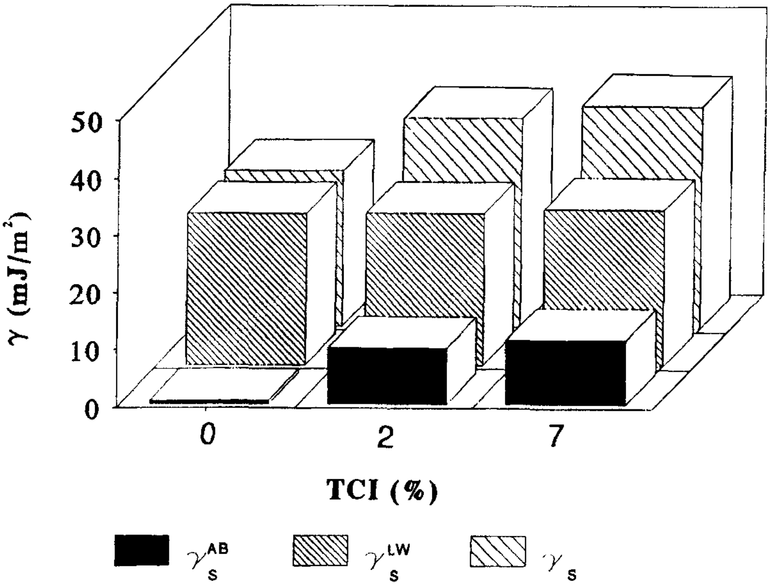

FIGURE 2 Surface free energy (γ) of the surface of SBR chlorinated with different amounts of TCI. Good method [35]. γ_s = total surface free energy; γ_s^{LW} = dispersive component (Lifshitz-van der Waals) of surface free energy; γ_s^{AB} acid-base component of surface free energy.

oxidized sulfur species (BE = 169.2 eV) are present on the solvent-treated SBR surface (Tab. II). Carbon 1s photopeak curve fitted results (Tab. III) show C—O and COO^- (from zinc stearate) groups on the solvent treated SBR surface. Chlorination of SBR with 2 wt% TCI produces several modifications of the surface chemistry:

1. After chlorination, the atomic concentration of carbon is reduced, whereas an increase of oxygen moieties is produced. No noticeable changes of chemical moieties and atomic concentrations of silicon, sulfur and zinc are produced.
2. Halogenation introduces chlorine (Cl 2p, BE = 199.9 eV) and nitrogen (N 1s, BE = 400.4 eV) functionalities on the SBR surface (Figs. 4 and 5, Tab. II). The binding energy of chlorinated SBR corresponds to organic chlorine from unreacted TCI and/or C—Cl moieties on the surface. On the other hand, nitrogen arises from unreacted TCI and from isocyanuric acid. According to Table II, the atomic per-

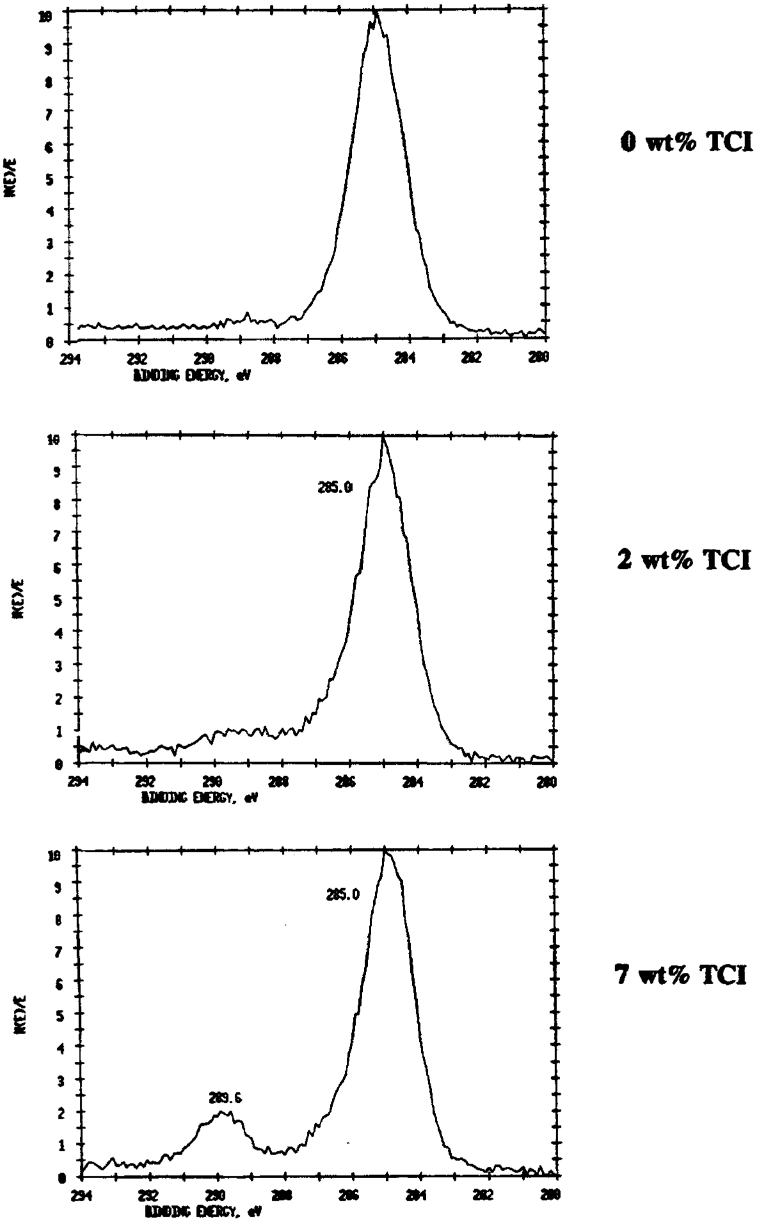

FIGURE 3 XPS spectra of the surface of SBR chlorinated with different amounts of TCI. C 1s photopeaks.

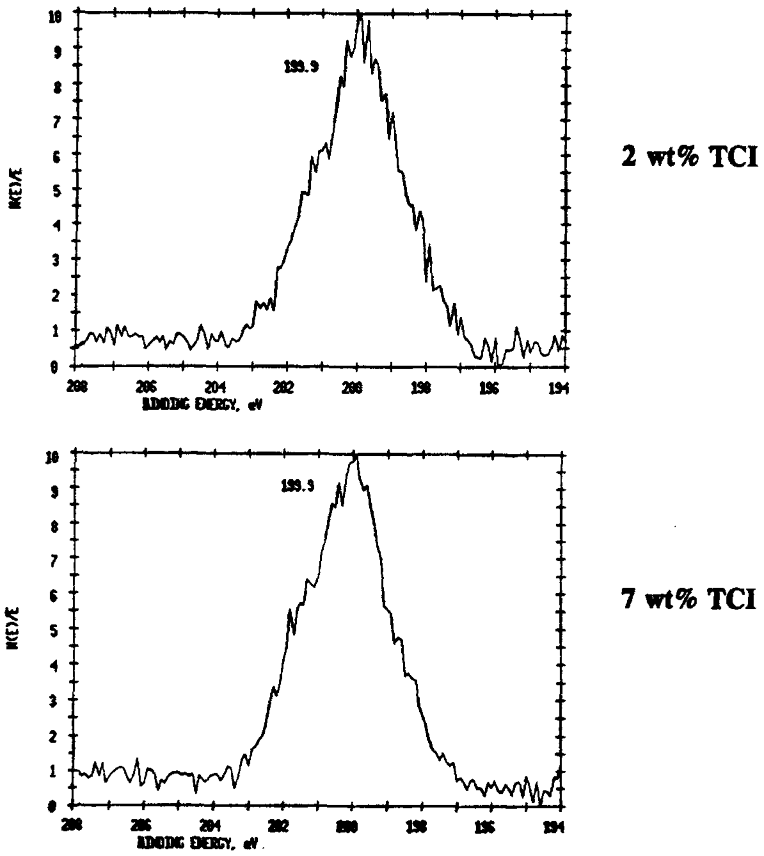

FIGURE 4 XPS spectra of the surface of SBR chlorinated with different amounts of TCI. Cl 2p photopeaks.

centage of Cl is about 1 at.% higher than for N, suggesting that around 1 at.% Cl may correspond to C—Cl species.

3. C 1s photopeak curve fitting of SBR treated with 2 wt% TCI (Fig. 6) shows the existence of C—O (BE = 286.7 eV), N—C=O (BE = 288.7 eV), and COO^- (BE = 290.1 eV) functionalities. The C 1s photopeak of solid TCI shows the intense band due to N—C=O groups, indicating the existence of unreacted solid TCI on the SBR surface treated with 2 wt% TCI.

The XPS analysis of SBR treated with 7 wt% TCI produces a modification of surface chemistry quite similar to that for 2 wt% TCI

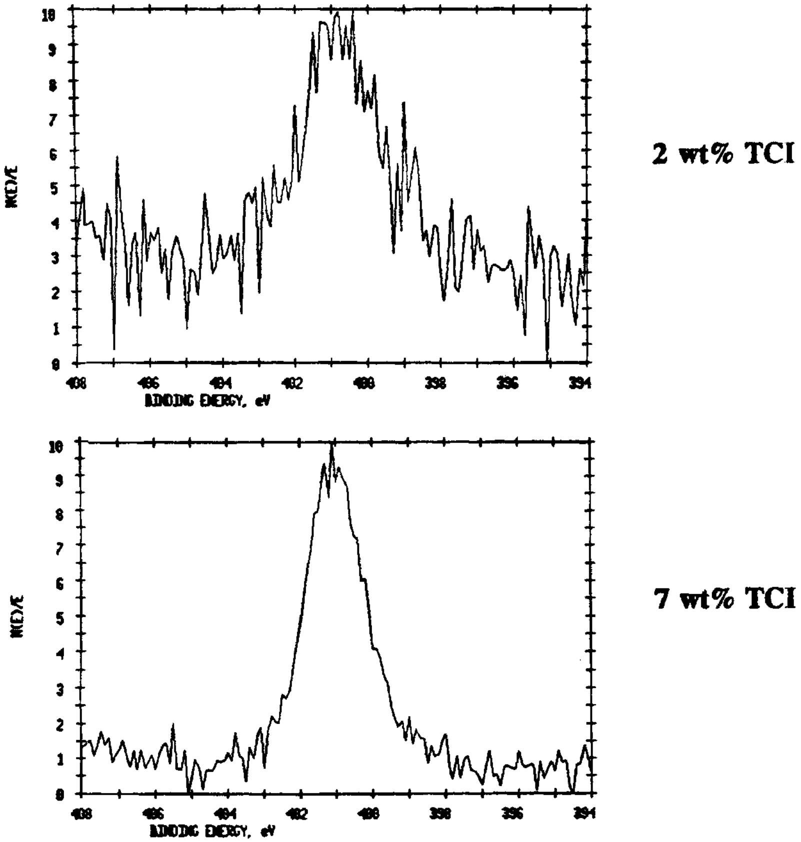

FIGURE 5 XPS spectra of the surface of SBR chlorinated with different amounts of TCI. N 1s photopeaks.

TABLE II Atomic concentration (%) of elements on chlorinated SBR obtained with XPS

Element	*0 wt % TCI*	*2 wt% TCI*	*7 wt% TCI*
C	86.9	76.7	71.3
O	9.4	13.5	14.0
Si	2.0	2.5	1.0
N	–	2.7	8.6
Cl	–	3.7	4.2
S	0.6	0.3	0.4
Zn	1.1	0.6	0.5

TABLE III Carbon species (atomic %) on chlorinated SBR obtained with XPS. C 1s photopeak curve fitting

Species	*0 wt% TCI*	*2 wt% TCI*	*7 wt% TCI*
C—C, C—H	92.8	81.5	73.3
C—OH, C—OR, C—Cl	4.6	9.8	11.1
—N—C=O	-	5.3	3.1
$—COO^-$	2.6	3.4	12.5

treated rubber. According to Table II, the chlorination with 7 wt% TCI produces a reduction of carbon concentration and a significant increase in the atomic concentration of nitrogen. The atomic percentages of oxygen, chlorine, sulfur and zinc are quite similar to 2 wt% TCI treated SBR, but there is a reduced amount of silicon. Furthermore, the C 1s photopeak curve fitting shows a noticeable increase of COO^- groups on the surface (Fig. 6); there is no increase in the atomic concentrations of chlorine and oxygen, and there is an important increase of nitrogen on the surface, indicating the existence of noticeable amounts of isocyanuric acid and a carboxylated species on the surface. These compounds may constitute a weak boundary layer on the surface of chlorinated SBR.

Figure 7 presents the T-peel strength of chlorinated SBR/polyurethane adhesive joints. Chlorination of SBR with small amounts of TCI produces a noticeable increase in practical adhesion, giving cohesive failure of the rubber. The increase in the amount of chlorinating agent produces a sudden decrease of T-peel strength and the failure mode changes to adhesive. The treatment of SBR with 7 wt% TCI does not give any adhesion to the polyurethane adhesive, due probably to the formation of a weak boundary layer. The variations in T-peel strength in Figure 7 are in good agreement with the experimental results provided by contact angle measurements and XPS. Thus, the chlorination of SBR with small amounts of TCI (lower than 2 wt%) produces an enhancement of surface free energy and the formation of C—Cl and C—O groups on the rubber which may be associated with the important increase in T-peel strength. The increase of the amount of chlorinating agent does not modify the surface free energy (Fig. 2); there is an increase of COO^- groups on the surface of treated SBR, and poor adhesion to polyurethane adhesive is obtained due to the existence of a weak boundary layer.

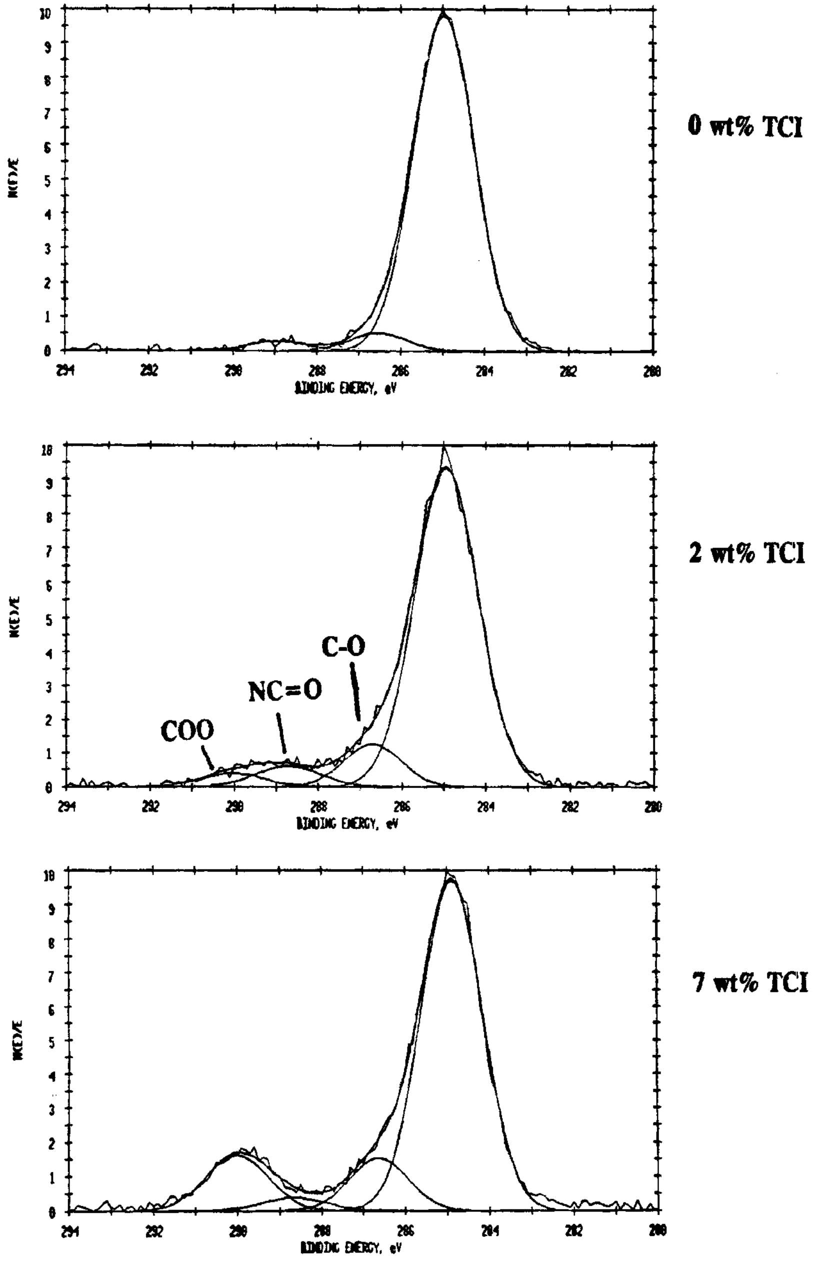

FIGURE 6 C 1s photopeak curve fitting for the surface of SBR chlorinated with different amounts of TCI.

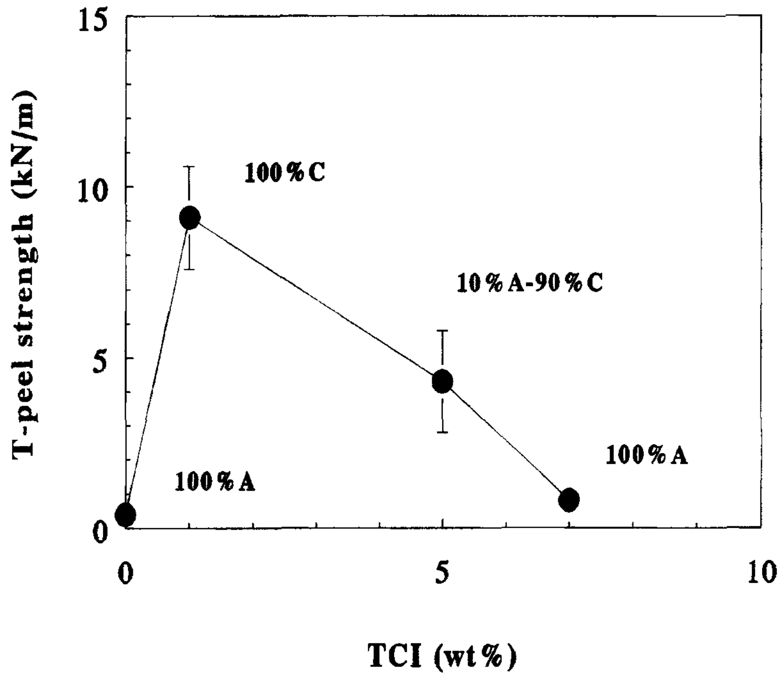

FIGURE 7 T-peel strength of chlorinated SBR/polyurethane joints as a function of TCI percentage. Locus of failure: A = adhesive failure; C = cohesive failure of rubber.

The features of the IR spectra of chlorinated SBR (Fig. 1) do not correlate well with the variation in T-peel strength as a function of the amount of TCI. This finding is probably because the information provided by IR spectroscopy corresponds to a relatively thick layer of rubber surface. Therefore, the chlorinating agent may react with the SBR surface and penetrate into the bulk rubber. In this study, removal of layers of chlorinated SBR was carried out by bombarding the sample surfaces inside the XPS with argon ions (around 5 Å of rubber was eliminated per minute). Using this procedure it was possible to carry out an *in situ* chemical analysis of the SBR after each bombardment cycle. Chemical analyses of the resulting rubber surfaces after ion bombardment are given in Figures 8a and 8b for chlorinated SBR with 2 and 7 wt% TCI, respectively. There is a decrease in the atomic concentration of nitrogen and oxygen in the most external 25 Å of chlorinated surface, the changes being less noticeable until a depth of 100 Å. However, in the most external 25 Å of SBR surface, the atomic concentration of nitrogen is reduced to 3 at.% in the SBR treated with 2 wt% TCI, but it was still around 6.5 at.% nitrogen on the 7 wt% TCI treated SBR, confirming the existence of a weak boundary layer of isocyanuric acid on the SBR treated with high amounts of chlorinating agent (further, the atomic percentage of chlorine is not greatly modified by removing rubber layers).

Table IV shows the XPS analysis of SBR surfaces bombarded with argon ions at a sputter rate of 5 Å/min for 20 min (surface depth 100 Å) together with the XPS analysis of the SBR surfaces bombarded in the Auger spectrometer with argon ions at a sputter rate of 25 Å/min (the surface depth obtained were 2625 Å and 5250 Å). Independently of the TCI percentage, there is a noticeable decrease of chlorine (to ~2 at.%) and nitrogen (to ~ 1.3 at.%) when 5000 Å of SBR surface is removed. Furthermore, the atomic concentration of silicon increases, as a

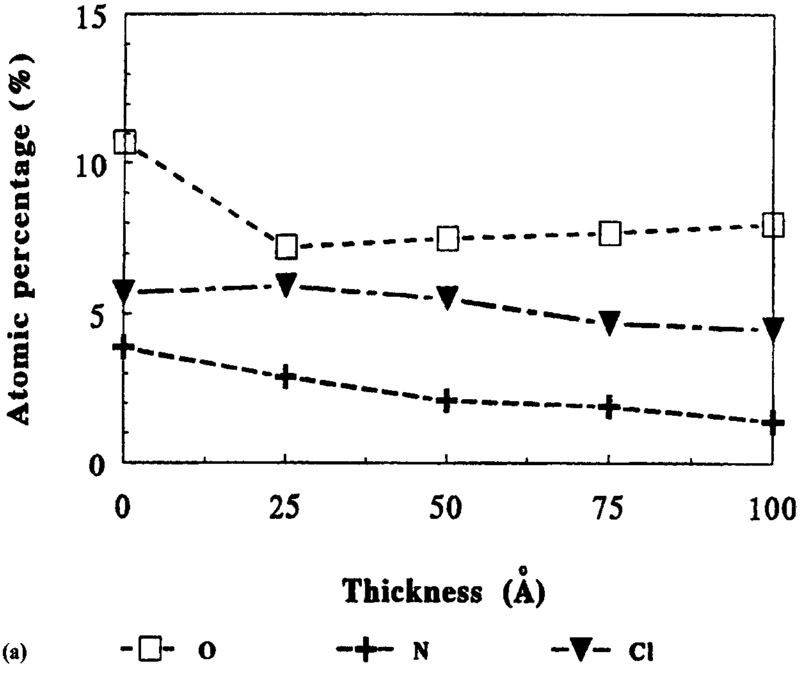

FIGURE 8 Evolution of atomic concentrations of oxygen, nitrogen and chlorine in SBR chlorinated with TCI as a function of the depth of surface layer removed.

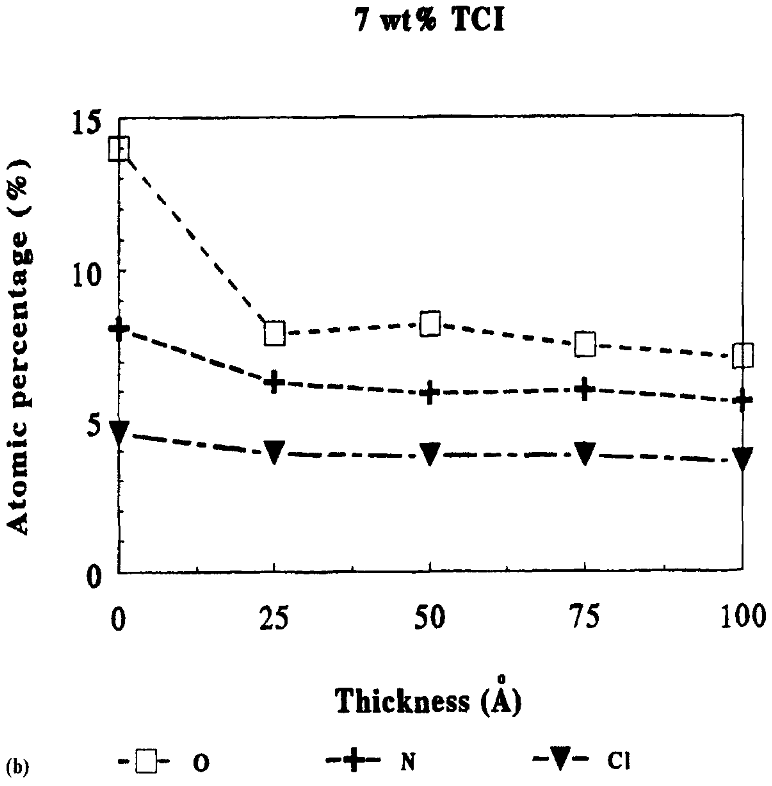

FIGURE 8 (Continued).

TABLE IV Atomic concentration (%) of elements on 2 wt% TCl chlorinated SBR obtained with XPS after argon ion bombardment in an XPS (up to 100 Å) and in an Auger (2625 and 5250 Å) spectrometers

Element	*Surface depth*			
	0 Å	*100 Å*	*2625 Å*	*5250Å*
C	76.0	81.7	82.6	80.0
O	10.7	8.0	9.7	12.8
Si	1.6	2.8	2.7	3.4
N	3.9	1.4	0.6	1.3
Cl	5.7	4.5	3.5	2.0
S	0.2	0.2	0.4	0.2
Zn	1.9	1.3	0.5	0.3

consequence of the removal of non-rubber layer on the SBR surface. In other words, the depth of the chlorinated layer is at least 5000 Å, and thus an explanation of the results obtained using IR spectroscopy can be provided.

CONCLUSIONS

1. The variation of T-peel strength of chlorinated SBR/polyurethane adhesive joints as a function of the TCI percentage can be related to the change in contact angle measurements and to the surface chemistry obtained with XPS. IR spectroscopy does not provide a similar trend because a thicker SBR surface layer is analyzed.
2. For low amounts of TCI applied to the SBR surface, there is an increase of the acid-base contribution to the surface free energy which can be related to the formation of chlorinated hydrocarbon chains and C—O functionalities. The increase in the amount of TCI gradually produces a detrimental effect in adhesion due to the creation of a weak boundary layer consisting of isocyanuric acid.
3. The thickness of the chlorinated layer in surface treated SBR is at least 5000 Å.

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