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IMPROVED PEEL STRENGTH IN VULCANIZED SBR RUBBER ROUGHENED BEFORE CHLORINATION WITH TRICHLOROISOCYANURIC ACID

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The effectiveness of chlorination as surface treatment to improve the adhesion of synthetic vulcanized styrene-butadiene rubber (SBR) depends on several experimental variables. Solutions of trichloroisocyanuric acid (TCI) in methyl ethyl ketone (MEK) have been used as effective chlorination agents for several rubbers. In this study, the influence of roughening prior to chlorination treatment of a SBR rubber (R2) and the durability of the modifications produced as the time after chlorination increased have been considered. Two concentrations of the chlorination agent (0.5 and 2 wt% TCI/MEK) have been used and the chlorination treatment was applied on the R2 rubber surface using a brush. Characterization of the treated surfaces was carried out using contact angle measurements, ATR-IR spectroscopy and Scanning Electron Microscopy (SEM). T-peel tests of treated R2 rubber/polyurethane adhesive joints have been carried out to determine the adhesion properties. Roughening was an effective treatment to remove paraffin waxes (antiadherent moieties) from the R2 rubber surface. When the chlorination is produced on the roughened R2 rubber, more noticeable chemical and morphological modifications were produced, and higher adhesion was obtained. On the other hand, TCI particles appeared on the roughened and unroughened chlorinated R2 rubber surface, and the size of these TCI particles were decreased by increasing the time after treatment. Furthermore, similar peel strength values were obtained for time after halogenation higher than 2 hours; for shorter time, a decrease in peel strength was found by increasing the time, due to the migration of paraffin wax to the rubber surface.

Keywords: SBR rubber; Surface treatment by halogenation; Roughening; Contact angle measurements; Infrared spectra; SEM; T-peel strength

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INTRODUCTION

Chlorination with trichloroisocyanuric acid (TCI) is the most common surface treatment applied to increase the wettability and the adhesion properties of styrene-butadiene rubbers used in the footwear and automotive industry [1–9]. TCI is a strong oxidizing and chlorinating agent for rubbers [10]. It is a white organic powder, soluble in ketones and esters. It reacts with the solvent and gradually releases chlorinating species from the solution [1].

The nature of the modifications produced by halogenation with TCI on the rubber surface depends on different experimental parameters [1, 11, 12]. In general, halogenation is a treatment able to produce chemical (creation of polar groups), thermodynamical (improved wettability), and morphological (roughness, heterogeneities) modifications on the rubber surface, which lead to better adhesion [13, 14]. Experimental variables such as the concentration of the chlorinating agent, type of solvent, time of chlorination, formulation and components of the rubber [15–22], among others, influence the extent of the modifications produced on the rubber surface.

Although chlorination generally produces some roughness on the rubber surface, in this study a roughening treatment has been carried out prior to chlorination of a vulcanized styrene-butadiene rubber (R2). It is expected that deeper penetration of the adhesive (improved mechanical interlocking) into the roughened rubber surface occurs during the formation of the joint, because the mechanical adhesion must be increased. Also, roughening removes contaminants or oils from the rubber surface [23] and, therefore, adhesion is enhanced. In this study the effects produced by chlorination of roughened and unroughened R2 rubber using two different concentrations of TCI are compared.

In a previous paper [16] the time between the chlorination of the rubber and the adhesive application has been shown to be a key factor in the effectiveness of the treatment. Thus, the influence of roughening prior to chlorination on the durability of the chlorination treatment has also been investigated.

EXPERIMENTAL

Materials

A sulfur-vulcanized styrene-butadiene rubber (R2) has been used in this study. It was prepared using a moulding process (150°C for 50 min) after open-mill mixing. R2 rubber contains precipitated silica as filler, and also paraffin wax and zinc stearate as

antioxidants/antiozonants were added. Furthermore, zinc oxide and stearic acid react during vulcanization to produce more zinc stearate. Both zinc stearate and paraffin wax have been described [24] as moieties responsible for the poor adhesion of R2 rubber. The formulation of R2 rubber is given in Table 1.

To determine the adhesion properties of surface treated R2 rubber, roughened or unroughened + chlorinated R2 rubber/polyurethane adhesive joints were prepared. The polyurethane adhesive solution was prepared by dissolving 18 wt% Desmocoll 530[®] pellets (provided by Bayer, Leverkusen, Germany) in methyl ethyl ketone (MEK) in a laboratory mixer (2000 rpm for 2 h). The Brookfield viscosity of the polyurethane solution was 2700 mPa.s (23°C). Desmocoll 530 is a thermoplastic polyester urethane (*i.e.*, low hard segment content and without free isocyanate groups) having a high crystallization rate and low thermoplasticity [25].

Chlorination Procedure

The influence of roughening of R2 rubber prior to chlorination has been considered in this study. The roughening of R2 rubber surface was produced in a *Superlema S.A.* (Zaragoza, Spain) instrument operating at 2800 rpm. A P100 aluminium oxide abrasive cloth was used to produce roughening, and about 0.5 mm thickness of rubber was removed.

The effects of the chlorination produced on the R2 rubber surface were compared with those produced by chlorination of freshly-

TABLE 1 Formulation of Vulcanized Synthetic Styrene-butadiene Rubber R2. Composition in Parts per Hundred Parts of Rubber (phr)

| Ingredient | Percentage (phr) |
|--|------------------|
| SBR 1502 | 100 |
| Precipitated silica | 42 |
| 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 disulfide | 2.5 |
| Microcrystalline paraffin wax | 0.8 |
| Hexamethylene tetramine | 1.0 |
| Zinc stearate | 5.4 |

roughened R2 rubber surface. Two concentrations of chlorinating agent were used (0.5 and 2 wt% TCI/MEK). The chlorination solutions were applied using a brush and, in general, the polyurethane adhesive was applied on the treated R2 rubber 15 h after the chlorination treatment was performed.

The durability of the chlorination treatment of both the roughened and unroughened R2 rubber surface was studied between 30 min and 1 week after chlorination. The polyurethane adhesive solution was always applied 30 min before joints were produced.

Experimental Techniques

Contact Angle Measurements

The roughened or unroughened + chlorinated R2 rubber were placed into a hermetic, isothermal (25°C) and saturated chamber of a *Ramé-Hart 100* goniometer. The chamber of the goniometer was previously saturated with water vapour for at least 10 min before placing the drop. Drops (4 μl) of twice-distilled and deionized water were placed on the treated R2 rubber surface. For the unroughened + chlorinated R2 rubber, equilibrium contact angle values (on both sides of the drops) were measured 15 min after the water drop was placed on the surface as this is the time necessary to obtain a constant contact angle. For the roughened + chlorinated R2 rubber the advancing and receding contact angles using the tilting plate method were measured [26]; those contact angle values were obtained 15 minutes after the water drop was placed on the R2 rubber surface. At least three drops on two identically treated samples were measured and averaged. The experimental error was ± 2 degrees.

Fourier Transform Infrared Spectroscopy (FTIR)

A *Nicolet FTIR 205* spectrometer was used to obtain the IR-spectra of the treated R2 rubber surfaces. The attenuated total multiple reflection technique (ATR) was used to analyze the chemical modifications produced on the most external (about 5 μm) R2 rubber surface. A KRS-5 (thallium bromiodide) crystal was used. Two hundred scans were obtained and averaged with a resolution of 4 cm^{-1} . The incident angle of the IR radiation was 45°.

The failed surfaces obtained after T-peel testing of joints were also characterized using ATR-IR spectroscopy. Although this technique is not especially surface sensitive, it is useful in the analysis of chlorinated rubber because the chlorination agent penetrates into the rubber about 2 μm [1], and the modifications produced in that region can be assessed. On the other hand, ATR-IR spectroscopy could fail to

detect a thin film of polyurethane adhesive on the rubber substrate and to mistake a cohesive failure in the adhesive for an adhesive failure at the interface.

Scanning Electron Microscopy (SEM)

The morphological modifications produced on the roughened or unroughened + chlorinated surfaces were analyzed using a *JEOL JSM-840 SEM* system, provided with a Mamiya 6×7 camera. The R2 rubber samples were gold-coated before analysis and the energy of the electron beam in the microscope was 20 kV.

T-peel Strength Test

Treated R2 rubber/PU adhesive/treated R2 rubber joints were prepared by applying the PU adhesive solution (about 0.8 ml was applied on each rubber piece) on each unroughened and roughened + chlorinated R2 substrate (dimensions = $150 \times 30 \times 6$ mm). The solvent of the adhesive was allowed to evaporate for 45 min. Then, the dried adhesive films were melted (reactivation process) at 100°C under IR irradiation and immediately placed into contact under a pressure of 0.8 MPa for 10 seconds. T-peel test (72 h after joint formation) was carried out using an Instron 4411 instrument (European Standard: PREN 1391), a peeling rate of 0.1 m/min was used. Five replicates for each experimental variable were tested and the peel strength values were averaged. The error was lower than 0.7 kN/m.

RESULTS AND DISCUSSION

Three aspects are considered in this section: (i) Surface modifications produced by roughening of R2 rubber; (ii) Effects of the roughening of R2 rubber before chlorination; (iii) Durability of the effects produced by chlorination of unroughened and roughened R2 rubber.

Surface Modifications Produced by Roughening of R2 Rubber Surface

The equilibrium contact angle of unroughened R2 rubber (Table 2) is high (106 degrees) probably due to the presence of a low surface energy hydrocarbon layer. This non-rubber layer is mainly composed of paraffin wax. A paraffin wax film was obtained and the water contact angle was measured. A value of 102 degrees was obtained. Because the contact angle of water on styrene-butadiene rubbers (without additives) is about 90 degrees [17, 18], the presence of a layer of paraffin wax is confirmed. Paraffin waxes are included as antiozonants in

TABLE 2 Contact Angle Values (Water, 25 °C) of As-received and Roughened R2 Rubber Chlorinated with 0.5 and 2 wt% TCI/MEK

| TCI (wt%) | Contact Angle (degrees) | | | |
|-----------|-------------------------|-------------|-----------|----------|
| | Unroughened | Roughened | | |
| | Equilibrium | Equilibrium | Advancing | Receding |
| 0 | 106 | 119 | 120 | 108 |
| 0.5 | 69 | 63 | 67 | 59 |
| 2 | 73 | 66 | 67 | 62 |

rubber formulation. These waxes are soluble in the rubber and they diffuse to the surface by supersaturation in the rubber to form a thin layer on the surface [27]. Furthermore, the ATR-IR spectrum of unroughened R2 rubber shows typical bands due to paraffin wax at 2919 and 2851 cm^{-1} (C-H stretching), and intense bands at 720 and 730 cm^{-1} (CH_2 rocking). Other bands of the unroughened R2 rubber are CH_2 in-plane deformation (1456 cm^{-1}), $-\text{CH}_2$ wagging motion (1380 cm^{-1}), and *trans*-1,4-C=C stretching (968 cm^{-1}) from butadiene. Styrene absorption occurs at 705 cm^{-1} and 912 cm^{-1} (C-H out-of-plane deformation) and 1602 cm^{-1} (aromatic C-C). The band at 1080 cm^{-1} due to silica filler (Si-O stretching) is also present, although its intensity is relatively low. The band at 1537 cm^{-1} ascribed to C=O from the stearic acid is not observed and, thus, migration of this compound to the unroughened R2 rubber surface is not produced. Moreover, bands due to S-containing compounds from the vulcanizing agent or N-compounds are not observed on the R2 rubber surface, which can also confirm the existence of a wax layer on the unroughened R2 rubber surface.

Because the unroughened R2 rubber contains a non-rubber layer on the surface, the roughening should remove this layer, as is shown in the ATR-IR spectrum of Figure 1 where a noticeable reduction in the intensity of the bands at 720, 730, 2919 and 2851 cm^{-1} (removal of CH_2 groups), and the increase in the relative intensity of the Si-O band at 1080 cm^{-1} are produced, indicating a decrease in $\text{CH}_2\text{-CH}_3$ containing species. The presence of a more intense band due to the silica filler is also a consequence of the removal of the thin layer of hydrocarbon moieties. On the other hand, due to the creation of roughness on the R2 rubber, the equilibrium contact angle of the roughened R2 rubber is slightly higher than that of the unroughened R2 rubber. For the roughened R2 rubber, advancing and receding contact angles have been measured because of the roughness of the surface; values of 120

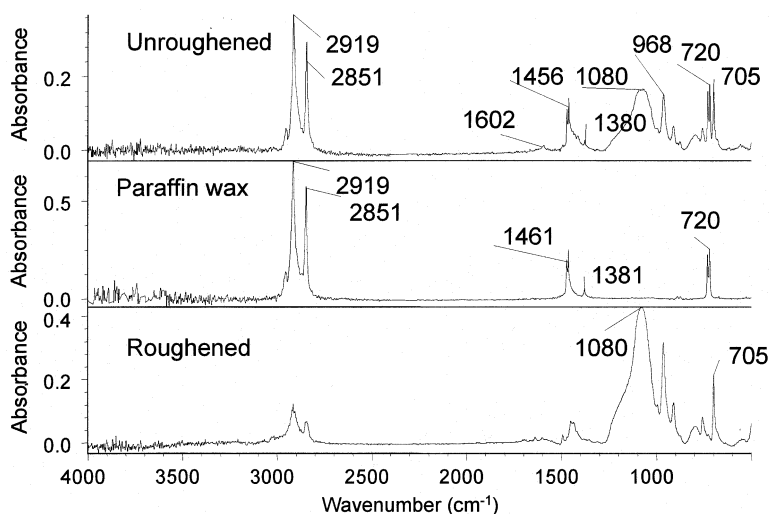


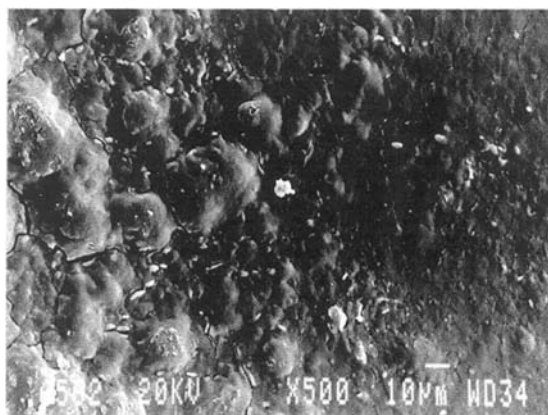
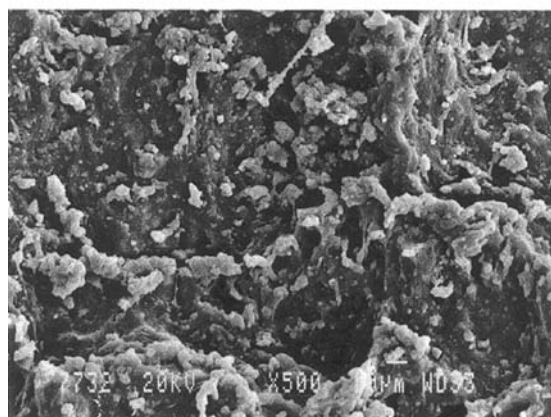
FIGURE 1 ATR-IR spectra of unroughened and roughened R2 rubber.

degrees and 108 degrees for the advancing and receding contact angles, respectively (Table 2), were obtained.

As expected, the morphology of the R2 rubber was affected by roughening. SEM micrographs (Figure 2) show the removal of external layers (which contain contaminants) from the R2 rubber surface and the creation of a non-flat surface containing asperities and rubber particles.

When the peel tests of R2 rubber/PU adhesive joints were carried out (72 h after joints were produced), a higher peel strength was obtained in the joint produced with roughened R2 rubber (0.2 kN/m for the joint made with the unroughened R2 rubber compared with 3.1 kN/m for that of the roughened R2 rubber). This increase can be mainly ascribed to the removal of the non-rubber layer and to the creation of roughness which favours the mechanical interlocking of the adhesive and the rubber surface, in agreement with previous results [28]. It was established [29], that the pitting of the surface is generally a positive factor for adhesion as it offers mechanical anchoring sites. Nevertheless, pitting alone is not enough to increase adhesion since cracks of a low surface energy substrate may not be available to the adhesive.

There is not only an increase in the T-peel strength value in the joint produced with the roughened R2 rubber but differences in the locus of failure are obtained. In order to assess more precisely the locus

**Unroughened****Roughened****FIGURE 2** SEM micrographs of unroughened and roughened R2 rubber.

of failure in the joints, the ATR-IR spectra of the failed surfaces obtained after peel strength were measured. In this study, the A-surface corresponds to the failed surface which visually corresponds to the adhesive surface, and the R-surface to that corresponding to the R2 rubber surface.

Figure 3 shows the ATR-IR spectrum of the PU adhesive film before joint formation. The main bands are due to the NH_2 stretching absorption at 3350 cm^{-1} , typical C-H stretching bands of polyurethane ($2939, 2860\text{ cm}^{-1}$), C=O stretching (1730 cm^{-1}), N-C=O symmetric stretching absorption (1531 cm^{-1}), C-O stretching (bands at $1177\text{--}1240\text{ cm}^{-1}$), and N-H out-of plane deformation at 731 cm^{-1} . Figure 4a shows the ATR-IR spectra of the failed surfaces obtained

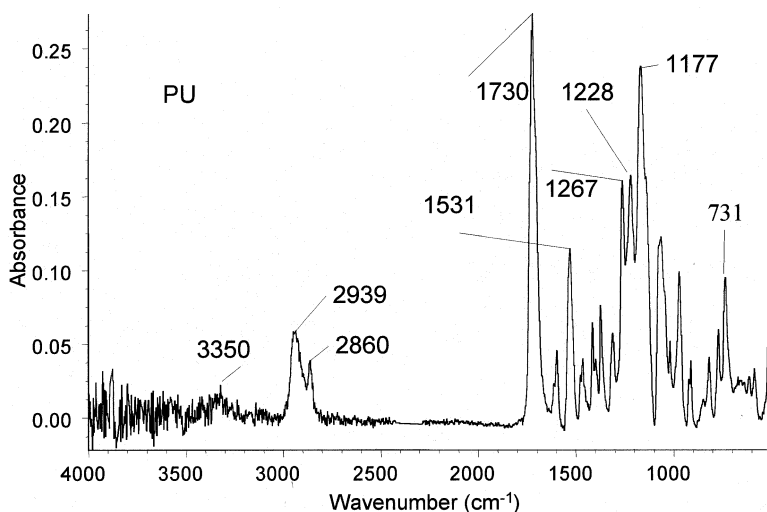


FIGURE 3 ATR-IR spectrum of the PU adhesive film.

after peel testing of the unroughened R2 rubber/PU adhesive joint. Both ATR-IR spectra show intense bands at 2851 and 2919 cm^{-1} due to paraffin wax, indicating that the failure of the joint is produced in a weak non-rubber layer. Furthermore, as a consequence of the wax transfer from the R2 rubber to the PU surface, the intensity of the band due to Si-O (1080 cm^{-1}) on the R surface increases (Figure 4a) with respect to that in the unroughened rubber before joint formation (Figure 1). On the other hand, the roughened R2/PU joints show apparently an adhesion failure as the ATR-IR spectrum of the A-surface (Figure 4b) is similar to that of the PU before joint formation (Figure 3). The ATR-IR spectrum of the R surface shows a band at 1537 cm^{-1} due to zinc stearate, which cannot be seen in the ATR-IR spectrum of the roughened rubber before joint formation. The bands at 2919, 2851 and 1456 cm^{-1} can also be ascribed to zinc stearate [30]. Therefore, once the adhesive joint in the roughened R2 rubber is produced, zinc stearate seems to migrate from the bulk roughened R2 rubber to the interface, and is partially transferred to the PU adhesive surface during peel testing. Therefore, the failure is mainly produced in a weak layer of zinc stearate. There is no evidence of migration of paraffin wax to the interface in the joint produced with roughened R2 rubber. Thus, the improved peel strength in roughened R2 rubber/PU adhesive joints is mainly due to creation of roughness and removal of paraffin wax.

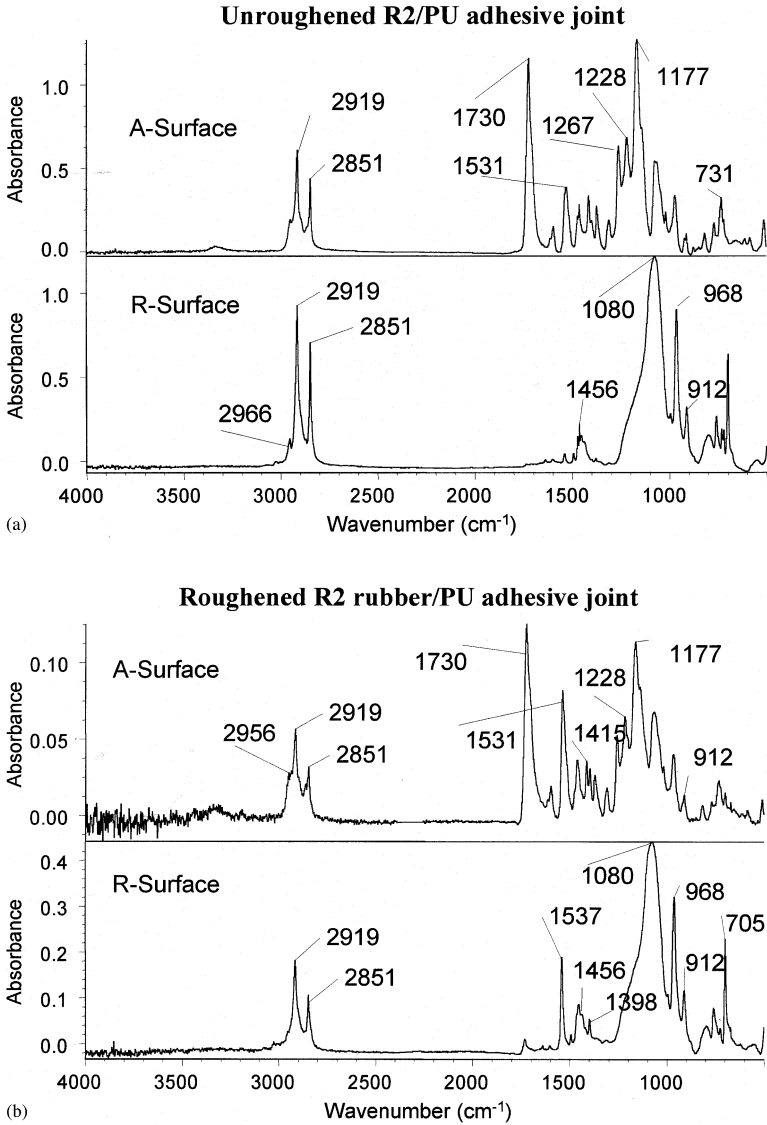


FIGURE 4 ATR-IR spectra of failed surfaces after peel test is carried out. **a)** Unroughened R2 rubber/PU adhesive joint; **b)** Roughened R2 rubber/PU adhesive joint.

Roughening vs Unroughening Prior to Chlorination of R2 Rubber

The chlorination treatment of roughened or unroughened R2 rubber was carried out by using two concentrations of TCI (0.5 and 2 wt% TCI/MEK). The chlorination solutions were applied using a brush and the analysis of the surface modifications were carried out 15 hours after chlorination of R2 rubber was done.

Chlorination of the roughened R2 rubber (R2R) with 0.5 wt% TCI/MEK produced a noticeable decrease in contact angle value which is similar to that for the unroughened + chlorinated R2 rubber (Table 2). By increasing the concentration to 2 wt% TCI/MEK the contact angle slightly decreases (Table 2) and, therefore, a small amount of TCI is sufficient to produce the modifications on the R2 rubber surface. The increase in TCI concentration probably produces a thicker chlorinated rubber layer, *i.e.*, deeper penetration of the chlorination agent into the R2 rubber occurs.

Chlorination of unroughened R2 rubber with 2 wt% TCI/MEK solution removes paraffin wax, and typical bands due to chlorination (1420, 539 cm^{-1}) and by-products of the reaction (1710, 1780 cm^{-1}) appear (Figure 5). Similar, although less marked, effects are obtained by chlorination with 0.5 wt% TCI/MEK. On the other hand, the

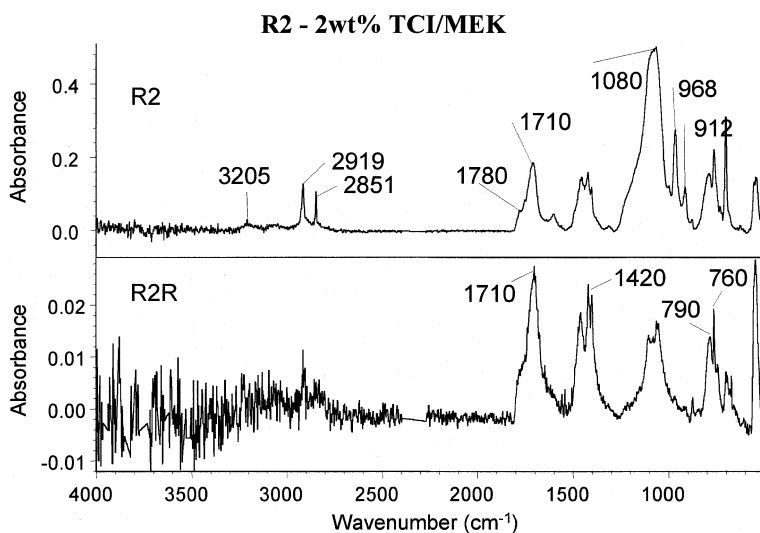


FIGURE 5 ATR-IR spectra of unroughened and roughened R2 rubber chlorinated with 2 wt% TCI/MEK solution.

relative intensity of the IR bands due to C=C is decreased (968 cm^{-1}). The effects due to chlorination are much more marked in the roughened + chlorinated R2 rubber, showing intense bands at 539, 760, 790, 1710 and 1420 cm^{-1} and the bands due to hydrocarbon chains of the rubber (2851 , 2919 and 705 cm^{-1}) can hardly be seen (Figure 5). In fact, the ATR-IR spectrum of the roughened + 2 wt% TCI/MEK treated surface corresponds to a layer of chlorinated moieties which could be as thick as $5\text{ }\mu\text{m}$ (depth provided by the ATR-IR spectroscopy method used in this study). However, a similar degree of chlorination is obtained by treating the unroughened R2 rubber with 0.5 and 2 wt% TCI/MEK, indicating that the roughening prior to chlorination favours the reaction of TCI with the roughened R2 rubber.

After chlorination with TCI/MEK solutions, some deposition of solid TCI particles was observed on the unroughened + chlorinated and roughened + chlorinated R2 rubber surfaces. On the roughened + chlorinated R2 rubber surface, the TCI particles are mainly deposited into the heterogeneities created by roughening. The increase in the TCI concentration favours the deposition of solid TCI particles on the R2 rubber surface (Figure 6). On the other hand, the TCI particles are homogeneous in size (about $2\text{ }\mu\text{m}$ in length) and shape (prismatic). Those particles are homogeneously distributed on the rubber surface, and similarly on the surfaces of unroughened and roughened R2 rubber.

The peel strength of joints produced with surface chlorinated R2 rubber is higher than for the unchlorinated rubber due to improved wettability and creation of polar moieties (Figure 7). The chlorination with 0.5 wt% TCI/MEK is sufficient to produce a higher adhesion, and the increase in the amount of TCI only produced a slight (joints produced with the roughened R2 rubber) or pronounced (joints produced with the unroughened R2 rubber) increase in peel strength. Always, the joints produced with roughened + chlorinated R2 rubber provide higher peel strength values than those for unroughened + chlorinated R2 rubber. This improvement is due to the higher roughness and degree of chlorination of the roughened R2 rubber. Those differences in peel strength are also associated with a different locus of failure in the joints. The ATR-IR spectra of the failed surfaces obtained after peel testing were used in this study to assess precisely the failure mode in the joints.

The failure mode in the chlorinated R2 rubber/PU joints varies depending on whether the roughening of the rubber is produced prior to chlorination and on the concentration of the chlorinating solution. The ATR-IR spectra of the failed surfaces corresponding to the joint produced with the roughened + 0.5 wt% TCI/MEK R2 rubber surface

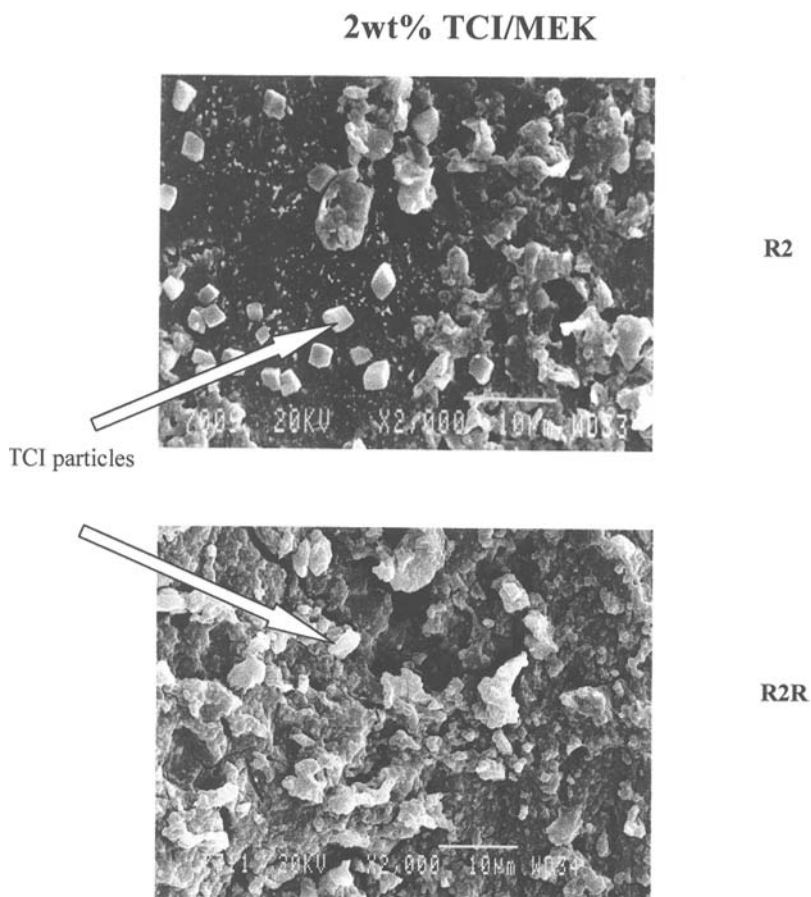


FIGURE 6 SEM micrographs of unroughened and roughened R2 rubber chlorinated with 2 wt% TCI/MEK.

shows bands due to rubber and chlorinated moieties of the rubber ($1420, 1730 \text{ cm}^{-1}$) on both surfaces (Figure 8), indicating that the failure occurs in the chlorinated rubber layer. This layer is thicker than for the similarly treated unroughened R2 rubber surface, because deeper chlorination is favoured by the non-rubber layer removal from the R2 rubber by roughening. Therefore, higher peel strength can be expected when R2 rubber is roughened before chlorination.

When the concentration is increased to 2 wt% TCI/MEK the failure in the joints was different. For the joint produced with roughened + 2 wt% TCI/MEK chlorinated R2 rubber, the ATR-IR spectra of

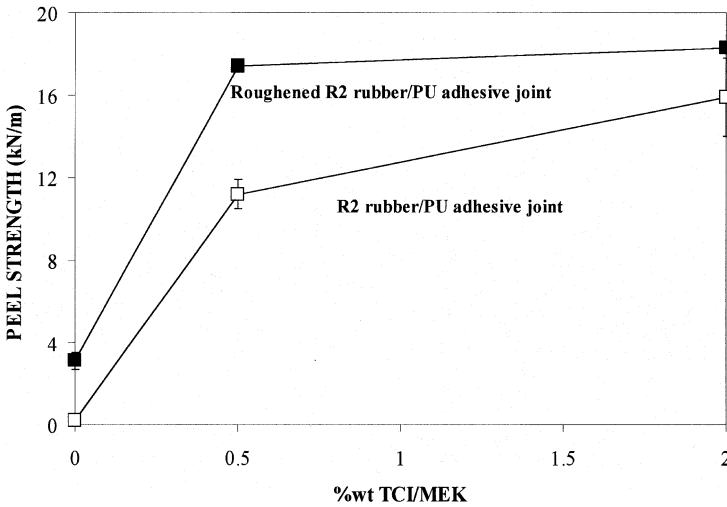


FIGURE 7 T-peel strength values (kN/m) of unroughened and roughened R2 rubber chlorinated with 0.5 and 2 wt% TCI/PU adhesive joints. Values obtained 72 h after joint formation.

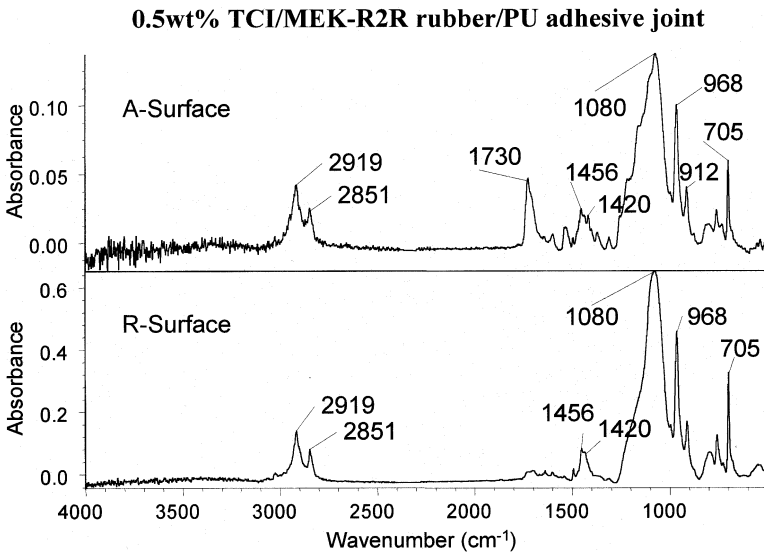


FIGURE 8 ATR-IR spectra of the failed surfaces of roughened R2 rubber chlorinated with 0.5 wt% TCI/MEK/PU adhesive joint.

the A and R surfaces are similar (Figure 9) and correspond to the rubber. There is no evidence of chlorination bands, and the ATR-IR spectrum of the A surface does not show bands due to the polyurethane. Therefore, a cohesive failure in the rubber is produced.

Figure 10 shows a schematic summary of the different loci of failure in the joints.

Time between the Chlorination of R2 Rubber and the Application of the Polyurethane Adhesive

The time between the chlorination treatment and the adhesive application is a key economical aspect in the footwear industry. Due to the presence of paraffin wax in the formulation of R2 rubber which tends to migrate to the surface as the time increases, it was considered of interest to determine the durability of the modifications produced by chlorination on the R2 rubber surface and its effect on adhesion. To carry out the study, a concentration of 2 wt% TCI/MEK was chosen, and was applied on the R2 rubber surface using a brush. Furthermore, the chlorination was also applied to unroughened and roughened R2 rubber, to monitor the evolution of the paraffin wax migration once it was removed from the surface by roughening. The treated R2 rubber

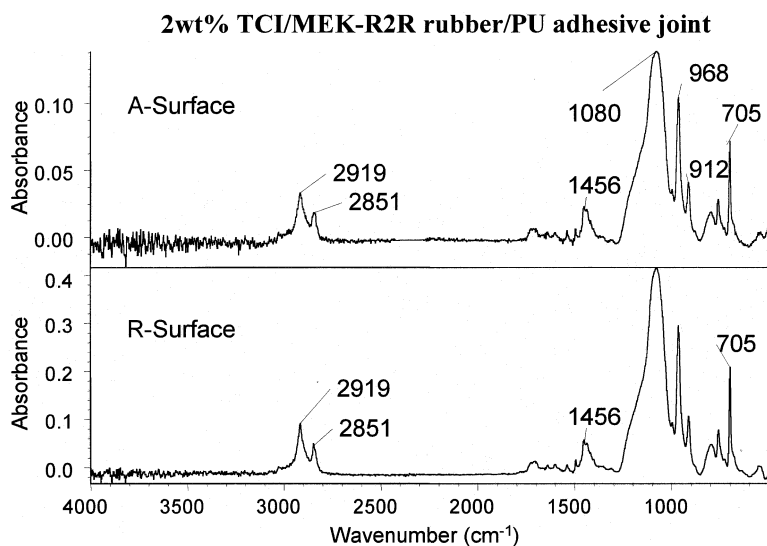


FIGURE 9 ATR-IR spectra of the failed surfaces of roughened R2 rubber chlorinated with 2 wt% TCI/MEK/PU adhesive joint.

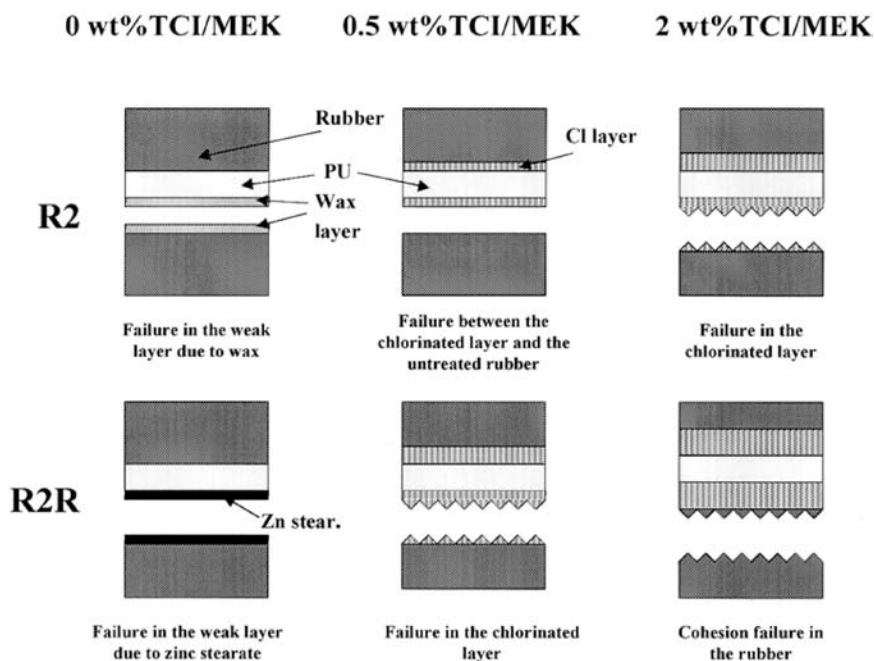


FIGURE 10 Scheme of the different loci of failure in unroughened + chlorinated or roughened + chlorinated R2 rubber/PU adhesive joints.

surfaces were characterized 30 min, 2 h, 15 h, 48 h and 168 h (1 week) after chlorination was carried out.

The chlorination of unroughened R2 rubber produces a decrease in the water contact angle to 78 degrees measured 30 min after chlorination was carried out (Figure 11). This value of contact angle does not change by increasing the time after chlorination up to 1 week. However, the contact angle on the roughened + chlorinated R2 rubber (30 min after treatment) is lower (62 degrees) and increases by increasing the time after chlorination up to 2 hours, reaching a value of 72 degrees. A further increase in the time of chlorination does not vary the contact angle values. The ATR-IR spectra of roughened + chlorinated R2 rubber are quite similar for different times after chlorination, and absorptions typical of chlorination (539 , 1420 , 1710 cm^{-1}) are obtained (Figure 12). The chlorination of the unroughened R2 rubber produced similar effects but a lower degree of surface modification and less intense bands due to chlorination. Those

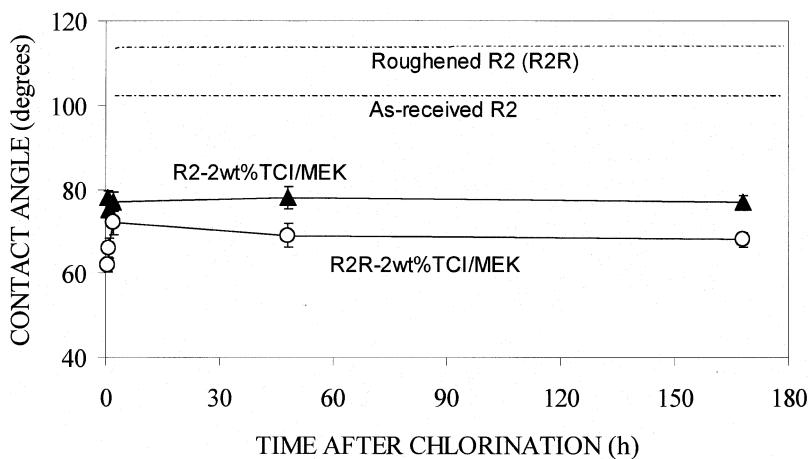


FIGURE 11 Contact angle values (water, 25°C) of unroughened + 2 wt% TCI/MEK and roughened rubber + 2 wt% TCI/MEK as a function of the time after chlorination.

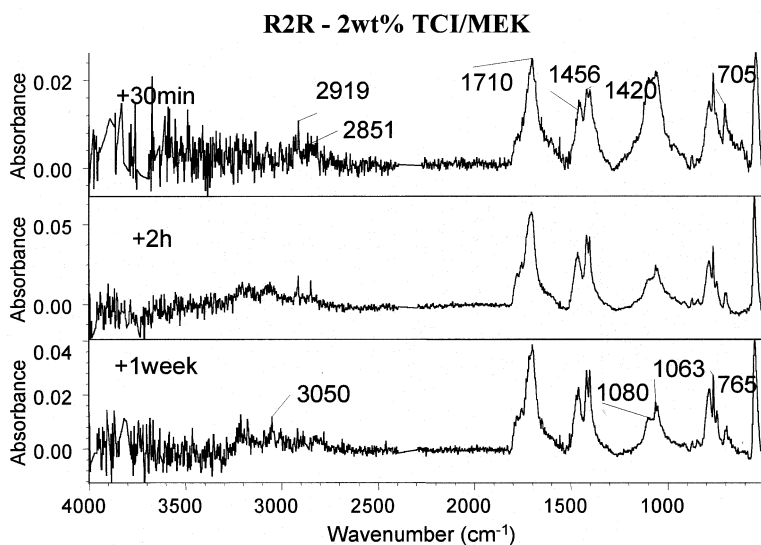


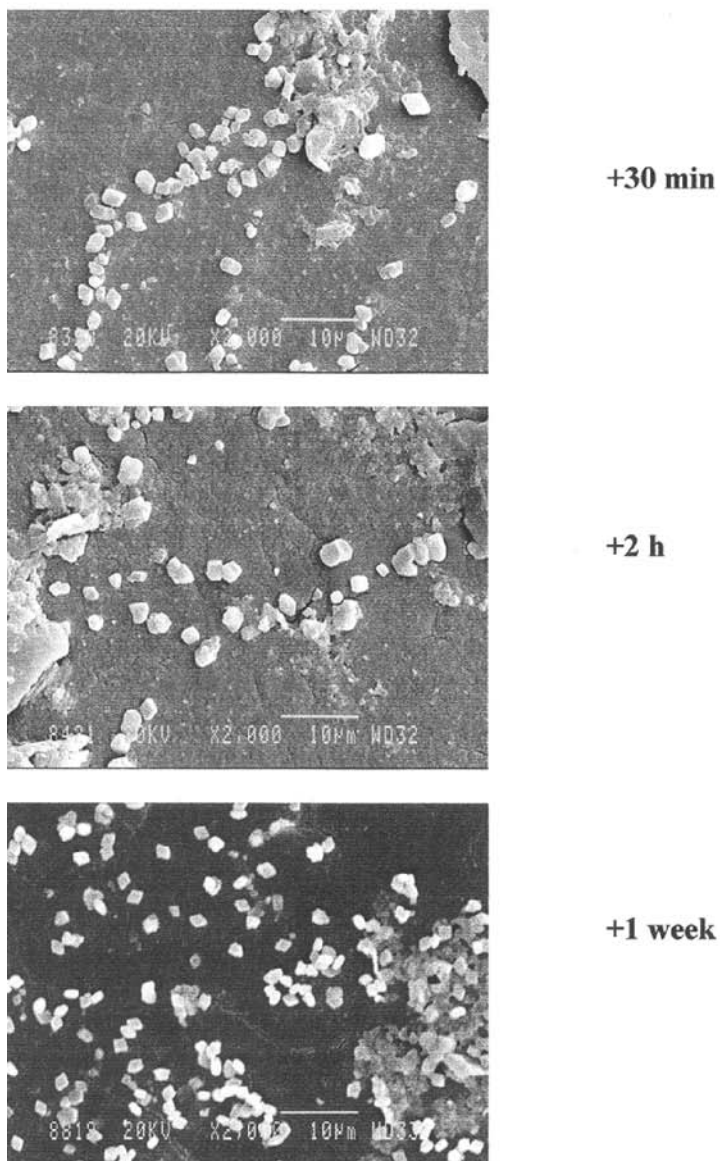
FIGURE 12 ATR-IR spectra of roughened R2 rubber chlorinated with 2 wt% TCI/MEK as a function of the time after chlorination.

modifications are similar for times of chlorination higher than 2 h. For lower time of chlorination, less intense bands due to chlorination are obtained (Figure 12), indicating that a higher degree of chlorination was obtained by increasing the time up to 2 hours. There are no important differences in the relative intensity of these bands by increasing the chlorination time.

The SEM micrographs of unroughened + chlorinated R2 rubber show deposition of TCI particles on the surface, the size of which is decreased by increasing the chlorination time (Figure 13a). TCI particles on the roughened + chlorinated R2 rubber surface are bigger for a short chlorination time, but the reduction in TCI particle size is more important as the time after chlorination increases (Figure 13b). One week after chlorination, TCI particles have about the same size on unroughened + chlorinated and roughened + chlorinated R2 rubber surfaces.

The joints produced with the unroughened + chlorinated R2 rubber show a slight increase in T-peel strength (Figure 14) upon increasing the chlorination time. For the roughened + chlorinated R2 rubber/PU adhesive joints, a decrease in the T-peel strength for short chlorination time (up to 2 hours) is obtained, which is in agreement with the increase produced in the contact angle values (Figure 11).

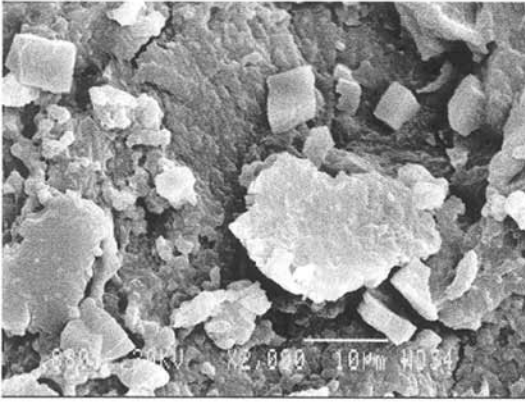
The ATR-IR spectra of the failed surfaces after peel testing have been obtained in order to assess the loci of failure more precisely in the different joints. Whereas the unroughened + chlorinated R2 rubber/PU adhesive joints show similar ATR-IR spectra whatever the chlorination time is, there are some differences in the roughened + chlorinated R2 rubber/PU adhesive joints. For short chlorination times (30 min after treatment), the roughened + chlorinated R2 rubber/PU adhesive joints show similar ATR-IR spectra for the A and R failed surfaces (Figure 15a). The relatively low intensity of the bands at 2919 and 2851 cm^{-1} due to C-H bonds compared with those of the unroughened + chlorinated R2 rubber (+30 min) failed surfaces confirm the greater degree of chlorination in roughened R2 rubber. The locus of failure is also somewhat different being deeper into the rubber bulk. By increasing the chlorination time up to 2 h a decrease in T-peel strength is obtained (Figure 14) which is in agreement with the change in the locus of failure in the joint. The ATR-IR spectra of the A and R failed surfaces show chlorination and isocyanuric acid bands (1780 and 3208 cm^{-1}). Thus, the failure in the joint produced with roughened + 2 wt% TCI treated R2 rubber (2 hours) is produced in the chlorinated layer (Figure 15b). When the adhesive is applied 1 week after chlorination of roughened R2 rubber, a cohesive failure in the chlorinated layer is also obtained (Figure 15c).

R2-2wt% TCI/MEK

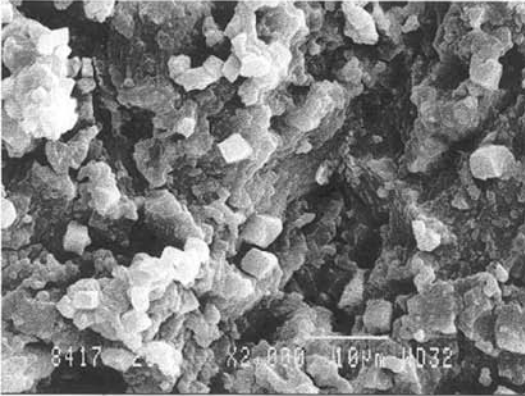
(a)

FIGURE 13 SEM micrographs of 2 wt% TCI/MEK chlorinated R2 rubber as a function of the time after chlorination. **a)** Unroughened R2 rubber; **b)** Roughened R2 rubber.

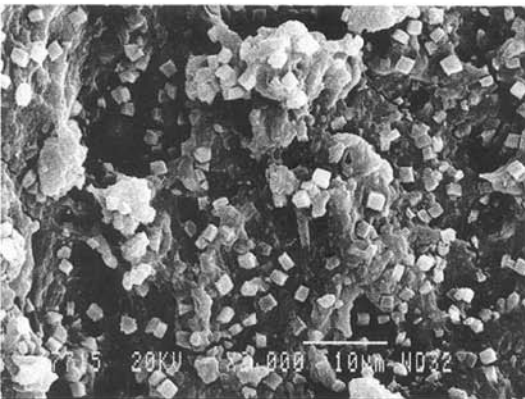
R2R-2wt% TCI/MEK



+30 min



+2 h



+1 week

(b)

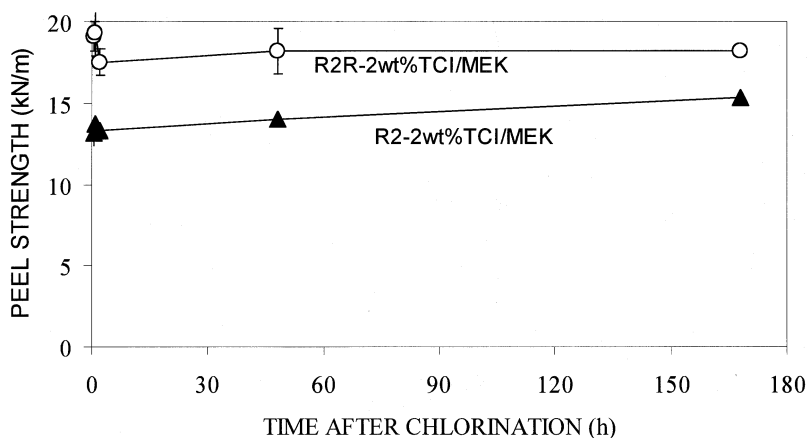


FIGURE 14 T-peel strength values of unroughened and roughened + 2 wt% TCI/MEK chlorinated R2 rubber/PU adhesive joints as a function of the time after chlorination. Values obtained 72 h after joint formation.

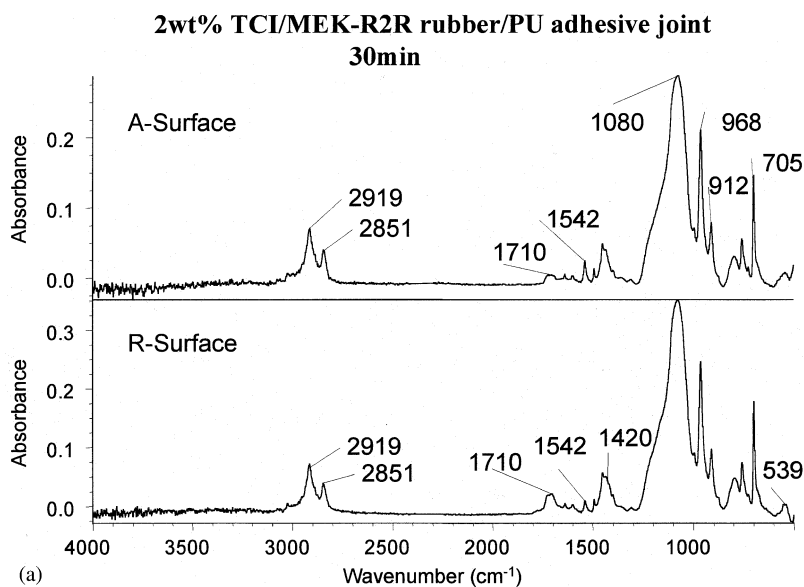


FIGURE 15 ATR-IR spectra of failed surfaces of roughened + 2 wt% TCI/MEK chlorinated R2 rubber/PU adhesive joints as a function of the time after chlorination. **a)** 30 min; **b)** 2 hours; **c)** 1 week after chlorination.

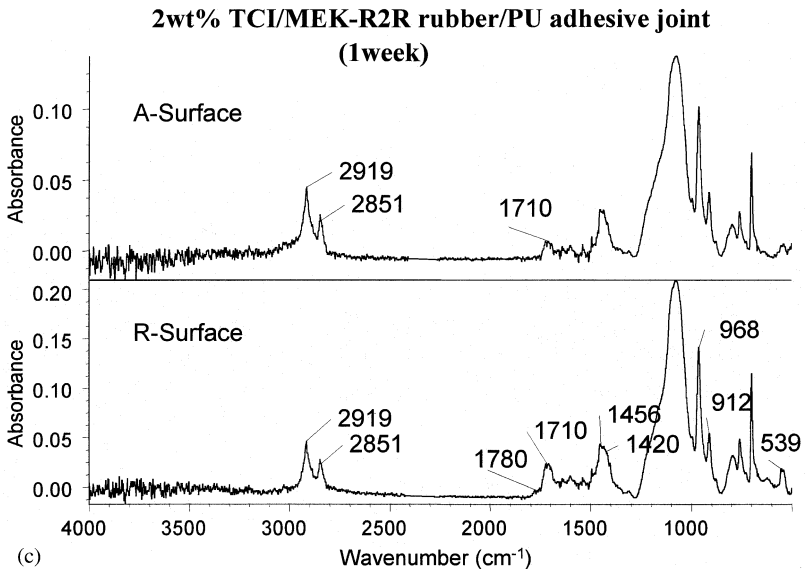
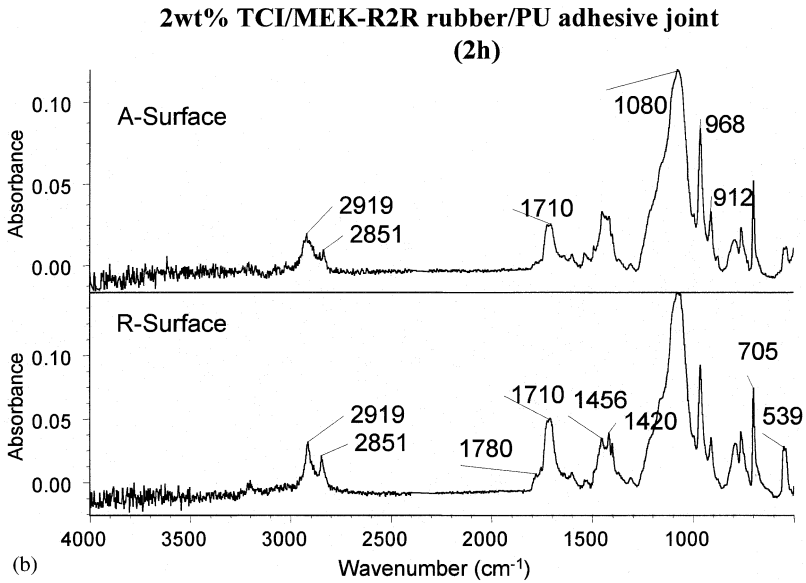


FIGURE 15 (continued).

CONCLUSIONS

1. Roughening removes the non-rubber paraffin wax layer from the R2 rubber surface. When chlorination is produced on roughened R2 rubber, a higher degree of chlorination is produced and more important surface modifications and deposition of TCI particles into the cracks and holes are produced, facilitating the reaction of TCI with the R2 rubber. An increase in T-peel strength values is obtained, mainly when 2 wt% TCI/MEK solution is used.
2. Reaction of TCI with R2 rubber continues with time, and a decrease in the size of TCI particles on the rubber surface is produced. Increasing the time after chlorination in the roughened + chlorinated R2 rubber joints leads to a decrease in T-peel strength which can be ascribed to a different locus of failure, deeper in the rubber bulk as the time increases.

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