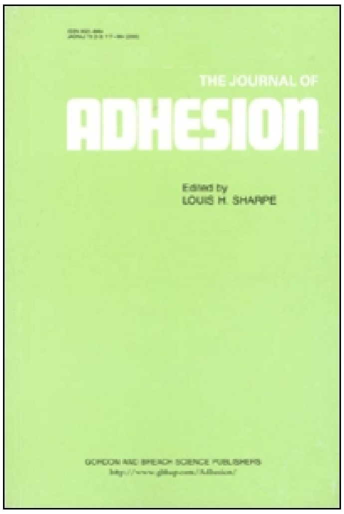

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Surface Characterization of Vulcanized Rubber Treated with Sulfuric Acid and its Adhesion to Polyurethane Adhesive*

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Modifications produced on a vulcanized styrene–butadiene rubber surface by treatment with sulfuric acid were studied and several experimental variables were considered.

The treatment of R1 rubber with sulfuric acid produced a noticeable decrease in contact angle which was mainly ascribed to an increase in surface energy due to the formation of sulfonic acid moieties and C=O bonds, and the removal of zinc stearate. The rubber surface swelled and became brittle as a result of the treatment, and when flexed microcracks were created. A rubber surface layer modification was produced with a consequent decrease in tensile strength and elongation-at-break values. The treatment enhanced the *T*-peel strength of R1 rubber/polyurethane adhesive joints and the locus of failure was cohesive in the rubber.

The optimum immersion time in H_2SO_4 solution was less than 1 min., and the reaction time in air was not found to be critical; the neutralization with ammonium hydroxide and the high concentration of the sulfuric acid (95 wt%) were essential to produce adequate effectiveness of the treatment.

Keywords: SBR rubber; Surface treatment; Sulfuric acid; Contact angle; ATR-IR spectroscopy; SEM; *T*-peel strength

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INTRODUCTION

Rubbers are widely used in applications which require a bond of the rubber to dissimilar substrates by means of an adhesive. Due to the non-polar nature and the relatively low surface energy of the rubber, incompatibility with most adhesives (mainly with polar nature) and lack of adhesion is produced. Furthermore, some additives in the formulation of synthetic rubber may produce poor adhesion (antioxidants, mould-release agents); these additives can migrate from the bulk to the surface once the adhesive joint is formed and contribute to facilitate a lack of adhesion. In consequence, a rubber surface treatment must be carried out prior to the application of the adhesive.

The most common surface treatments for rubber materials are mechanical, physical and chemical. Solvent wiping produces a swelling of the rubber surface, giving rise to improved adhesion in some rubber formulations [1]. Roughening has been proposed as an effective mechanical surface treatment to remove zinc stearate and waxes from the rubber surface, but a progressive migration of these compounds from the bulk to the surface with time may occur [2, 3]. On the other hand, some residual particles produced during the treatment can be trapped in the roughened rubber surface, constituting an undesirable source of contamination. On the other hand, chemical surface treatments (organic peroxides [4], reactive polyisocyanates [5], halogenation [6–8]), although effective, pose potential environmental threats. Finally, physical surface treatments (plasma and corona discharge) [9] have also been proposed but they are relatively expensive techniques.

In this study, the treatment of R1 rubber with sulfuric acid (cyclization) has been proposed and the surface modifications responsible for the increased adhesion towards polyurethane adhesives have been studied.

Although a number of studies in the literature discuss the treatment of polymers with sulfuric acid [10–12], surface modification by sulfuric acid of vulcanized styrene–butadiene rubbers (SBR) has not been well described. The term "cyclization" refers to the fact that during the reaction of natural rubber (polyisoprene) with sulfuric acid cyclic hydrocarbon structures are produced. Cyclization has often been used for bonding rubber to metal with epoxy or phenol formaldehyde adhesives [12] and appears to be most successful when applied to unsaturated diene rubbers. The surface of vulcanized diene rubbers such as natural rubber (NR), nitrile-butyl rubber (NBR) and styrene – butadiene rubber (SBR) can be treated with concentrated sulfuric acid to yield a cyclized layer of rubber on the surface. This layer is quite brittle and, when flexed, develops microcracks, which are believed to help in subsequent bonding by acting as centers for the mechanical interlocking of the adhesive to the rubber. However, the residual acid left in the cyclized layer may accelerate aging or assist moisture attack at the bond line [11, 12]. The thickness of this layer depends on the length of the treatment with sulfuric acid and the cohesive strength of the surface layer has been shown to be a limiting factor in the adhesion properties.

The proposed mechanism for cyclization is sulfonation, *i.e.*, the hydrogen of the C—H bond is removed and replaced by a SO_3 molecule, which is then hydrogenated to form a sulfonic acid at the site of attachment. The sulfonic acid created during sulfonation can be neutralized to create more stable species. Neutralization with ammonium hydroxide extracts the hydrogen from the sulfonic acid and leave a stabilized ion pair ($SO_3^+NH_4^-$). Neutralization can also be performed using various amines (methyl amine, isobutylamine, tetramethylene pentamine). Practically all engineering plastics which contain tertiary C—H bonds are suitable for sulfonation. This includes most of the engineering resins, with the exception of fluorocarbons and some silicones [11].

In this study, surface modifications produced by treatment of a synthetic vulcanized rubber with sulfuric acid have been carried out. On the other hand, considering that cyclization effectiveness is influenced by different experimental variables, in this study the concentration of H_2SO_4 (50 – 95 wt%), the influence of the immersion time in H_2SO_4 solution (0.5 – 15 min.), the reaction time in air (0.5 – 5 min.), and the neutralization with or without NH_4OH were considered.

EXPERIMENTAL

Materials

A sulfur-vulcanized synthetic styrene – butadiene rubber (R1), manufactured by Caster S.A. (Elche, Spain), was used in this study. The formulation of the rubber is given in Table I. This rubber contains silica and carbon black as fillers, as well as zinc oxide and stearic acid. During vulcanization, zinc oxide and stearic acid react to produce zinc stearate, which seems to be one of the components which is responsible for the poor adhesion of this rubber [2].

Some properties of the rubber were obtained using standardized procedures: Hardness = 93°Shore A; Density (20°C) = $1.2\,\mathrm{g \cdot cm^{-3}}$; Tensile strength = 18.0 MPa; Maximum elongation-at-break = 397%; Tear resistance = $19.9\,\mathrm{kN \cdot m^{-1}}$.

The treatment of R1 with sulfuric acid was carried out following different consecutive steps: (i) The rubber was immersed in concentrated sulfuric acid for a given time (immersion time); (ii) It was then removed from the acid and allowed to continue to react in air for a given time (reaction time in air); (iii) The acid was neutralized using hot distilled water + ammonium hydroxide (15 wt% ammonia) + exhaustive washing under distilled water, the neutralization being carried out until a pH = 7 was obtained in the wash water; (iv) The treated rubber (a continuous film of liquid remained on the rubber surface) was dried off under infrared radiation at moderate temperature (lower than 60°C) for 30 minutes.

To determine the adhesion strength of surface-treated R1 rubber, two identically-treated specimens (150 mm × 30 mm) were joined using an adhesive in solution, based on one-component thermoplastic polyester urethane (*Desmocoll 510*) provided by Bayer AG (Leverkusen,

TABLE I Formulation of R1 synthetic styrene-butadiene rubber

Component	*Percentage (phr)*[a]
SBR 1502	65
SBR 1904	35
Precipitated silica	25
Carbon black	23
Sulphur	1.8
Cumarone-indene resin (85°C)	3
Zinc oxide	3.8
Stearic acid	0.8
N-Cyclohexiyl-2-benzothiazole sulphenamide	1.1
Phenolic antioxidant	0.8
Polyethylene glycol (*MW* = 4000)	1.1
Tetramethylthiuram-disulphide	0.2

[a] Data are expressed in parts per hundred of rubber (phr).

Germany). The adhesive solution was prepared by mixing 18 wt% polyurethane in 2-butanone. A solution with a Brookfield viscosity of 1.7 ± 0.1 Pa · s (20°C) was obtained. The dried adhesive film on the R1 surface was 0.4 mm thick, which corresponds to about 100 mg polyurethane adhesive spread on an area approximately 140 mm × 30 mm. The strength of the joints was evaluated using *T*-peel tests.

EXPERIMENTAL TECHNIQUES

Contact Angle Measurements

The surface-treated rubber pieces were introduced into the thermostated chamber of a *Ramé Hart 100* goniometer. The chamber was previously saturated with the vapor of the test liquid at 25°C for at least 10 minutes before placing a drop of liquid on the surface of the rubber. At least three droplets were placed and their contact angles measured on each treated rubber surface. At least three replicates of similarly-treated rubber were analyzed. The contact angles on the surface-treated rubbers were measured 15 minutes after placing 4 μL drops of doubly-distilled deionized water or ethanediol on the sample. The experimental error was ± 2 degrees. The components of the total surface energy (γ_S) were obtained by applying the Owens and Wendt equation:

$$\gamma_L(1+\cos\theta) = 2\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{1/2} + 2\left(\gamma_S^P\gamma_L^P\right)^{1/2}$$

where the subscripts "*L*" and "*S*" refer to the test liquid and rubber, respectively, γ_L = surface tension of liquid, γ^P = polar component of the surface energy, and γ^{LW} = dispersive component (Lifshitz–van der Waals) of the surface energy.

Two polar liquids (water, ethanediol) were used in the study because zero contact angles were obtained using hydrocarbons (*i.e.*, *n*-hexadecane), 1-bromo-naphthalene or CH_2I_2.

Attenuated Total Multiple Reflection – Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra of treated samples were obtained using a Nicolet FTIR 205 spectrometer. To avoid deep penetration of the IR radiation into the sample, the attenuated total reflection method was employed (ATR-IR spectroscopy), using a germanium crystal. Two hundred scans were obtained and averaged at a resolution of 4 cm^{-1}. The chemical nature of the modifications was determined for about the most external 5 μm of the treated rubber surface.

SEM

Scanning Electron Microscopy (SEM) allowed the external surface modifications on the rubber to be analyzed (a *JEOL SEM JSM 840* system was used). The samples were secured on copper mounts using silver paint and coated with gold to obtain enough contrast in the SEM photomicrographs.

Stress–Strain Measurements

The mechanical properties of treated rubber samples were measured in an *Adamel L'Homargy DY-32* test instrument. All experiments were carried out using dog-bone test pieces 6 ± 0.5 mm thick and 2 ± 0.5 mm wide (in the center of the test sample) and following the test procedure given in the ISO 37-77 standard; a rate of 0.1 m/min was used. The tensile strength and the elongation-at-break were measured. The values obtained were the average of at least three experimental determinations.

T-peel Strength Measurements

T-peel strength measurements were carried out for adhesive joints produced with strip test pieces (150 mm × 30 mm) which were treated in the same way. Before applying the adhesive, the treated rubber pieces were flexed to develop cracks and facilitate the mechanical interlocking with the adhesive. The polyurethane adhesive solution was applied on the treated rubber surface with a brush and the solvent was allowed to evaporate for one hour. The dried PU adhesive film was heated to 100°C under infrared radiation in order to facilitate the interlocking of the chains of the two polyurethane films applied to the two identically surface-treated rubber strips. The strips were then placed in contact and a pressure of 0.8 MPa was immediately applied for 10 s to achieve a suitable joint. The *T*-peel strength was measured in an *Adamel L'Homargy DY-32* test instrument (peel rate 0.1 m/min). The values obtained were the average of three tests (standard deviation was less than 10%). The adhesive joints were conditioned at 25°C and 50% relative humidity before undergoing the *T*-peel test. The evolution in *T*-peel strength was followed for different times (15 min and 72 h) after joint formation.

Aging Test

The durability of the adhesive joint was studied under temperature and humidity conditions. The most successful adhesive joints obtained with rubber samples treated with sulfuric acid were aged for 1 day at ambient conditions, 3 days at 50°C + 95% relative humidity, followed by 1 day at ambient conditions prior to *T*-peel testing. Three replicates were tested for each experimental variable.

RESULTS AND DISCUSSION

This section will be divided into two parts. First, the effects of the treatment with sulfuric acid on R1 rubber will be considered. In the second part, the influence of the different experimental variables on the effectiveness of the treatment will be considered.

Surface Modifications Produced by Treatment of R1 Rubber with Sulfuric Acid

Two different concentrations of H_2SO_4 (50 and 95 wt%) were considered. The immersion time (*ti*) in H_2SO_4 solution was varied and a reaction time in air (*tr*) of 1 minute was always used.

The wettability of the rubber surface was characterized by contact angle measurement. Table II shows the contact angle values obtained after placing drops of water and ethanediol as test liquids on the R1 rubber surface. The untreated R1 rubber shows a high contact angle due to the poor wettability of this non-polar rubber. The surface energy (mainly the polar component) is increased only when the R1 rubber is treated with 95 wt% H_2SO_4 (Tab. II).

TABLE II Contact angle values (degrees, 25°C) and surface energy (mJ/m^2) of H_2SO_4 treated R1 rubber. *tr* = 1 min.; NH_4OH 15%

	Contact angle (degree)				
Treatment	*Water*	*Ethane diol*	γ_S^{LW} *(mJ/m^2)*	γ_S^{P} *(mJ/m^2)*	γ_S *(mJ/m)^2*
None	94	80	8.6	7.9	16.6
50 wt% H_2SO_4 *ti* = 5 min.	99	81	3.6	9.3	12.9
95 wt% H_2SO_4 *ti* = 0.5 min.	45	40	3.1	57.2	60.3
95 wt% H_2SO_4 *ti* = 5 min.	30	23	3.3	69.4	72.3

The treatment of R1 rubber with 95 wt% H_2SO_4 for just 30 seconds produces a noticeable decrease in both contact angle values (45 degrees for water and 40 degrees for ethanediol) due to an increase in the wettability of the rubber surface.

The increase in surface energy of R1 rubber after treatment with 95 wt% H_2SO_4 can be ascribed to severe modifications in its surface chemistry and morphology (Fig. 1). The ATR-IR spectrum of untreated R1 rubber shows the presence of a broad Si—O stretching band (1089 cm^{-1}) due to silica (a filler in the rubber composition) and also shows the presence of zinc stearate (typical band of C=O stretching at 1539 cm^{-1}, C—H stretching (2850, 2920 cm^{-1}), —CH_2 scissoring (1452 cm^{-1}), and —CH_2 twisting (1380 cm^{-1})). There are also bands corresponding to butadiene (=CH stretching (~3000 cm^{-1}), and *trans*-1,4-C=C (913 and 968 cm^{-1}), and styrene (703 and 760 cm^{-1} due to C—H out-of-plane deformation of the vinyl group, aromatic C—C at 1601 cm^{-1} and aromatic C—H stretching at 3034 cm^{-1})).

The ATR-IR spectrum of the surface treated with 50 wt% H_2SO_4 is similar to that of the untreated R1, indicating a lack of chemical modifications when the lower concentration of H_2SO_4 is used. Consequently, no increase in adhesion is obtained by treating R1 rubber with 50 wt% H_2SO_4 (Tab. III). However, the treatment with 95 wt% sulfuric acid (Fig. 1) produced a noticeable removal of hydrocarbon moieties and zinc stearate from the rubber surface (there is an increase in the intensity of the Si—O stretching band at 1089 cm^{-1}, and the intensity of bands at 2850, 2920, 1539, 1452 and 1380 cm^{-1} are reduced). Furthermore, the treatment creates sulfonic

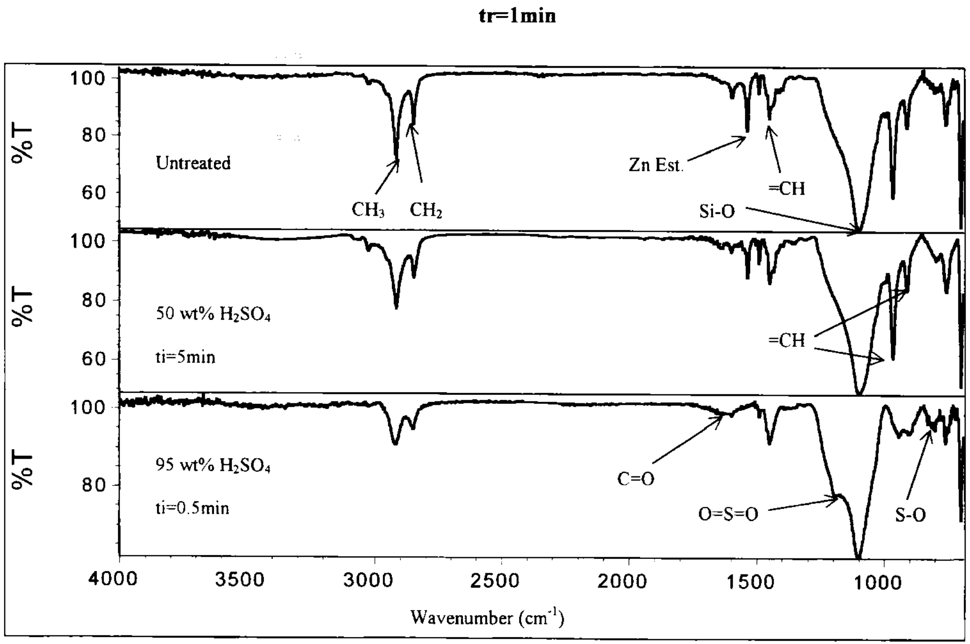


FIGURE 1 IR-ATR spectra of untreated and sulfuric acid treated R1 rubber. Influence of the concentration of H_2SO_4 solution; $ti = 0.5$ and $ti = 5$ min.; $tr = 1$ min.; NH_4OH 15%.

TABLE III *T*-peel strength values (kN/m) of H_2SO_4 treated R1 rubber/polyurethane adhesive joints. *tr* = 1 min.; NH_4OH 15%

Treatment	15 *min.*	*Failure*	72 *h*	*Failure*	*Aging* (72 *h*; 95% *h.r*; 50°C)	*Failure*
None	1.2	A	0.2	A	0.3	A
50 wt% H_2SO_4 *ti* = 5 min.	2.9	A	0.5	A	–	–
95 wt% H_2SO_4 *ti* = 0.5 min.	6.6	A	6.1	(A, R)	5.7	R
95 wt% H_2SO_4 *ti* = 5 min.	7.9	R	7.6	R	6.9	R

A = adhesional failure; R = cohesive failure in the rubber.

acid moieties (S=O stretching at 1167 cm^{-1} and S—O stretching at 870 cm^{-1}) some degree of oxidation (C=O stretching at 1600–1700 cm^{-1}), and a reduction of *trans*-1,4-C=C bonds in the butadiene (913 and 968 cm^{-1}) is also produced.

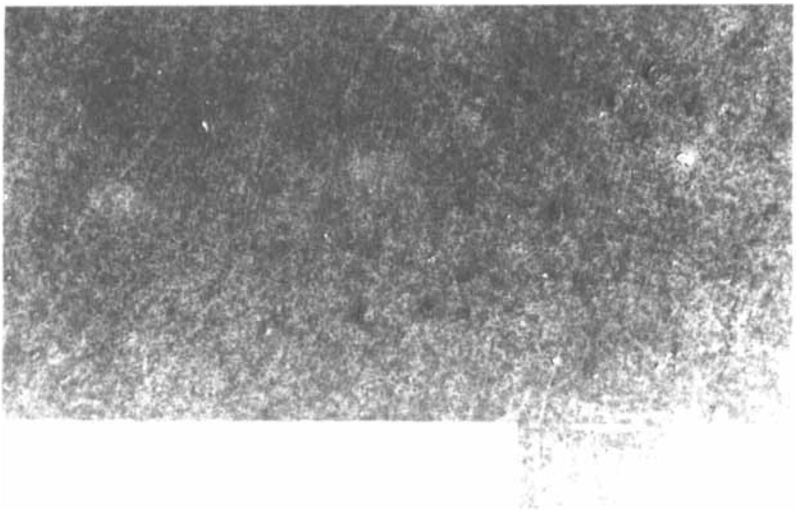
The topography of the rubber surface is also affected by the treatment. SEM micrographs (Fig. 2) show the homogeneous surface of untreated R1 rubber. The treatment with 95 wt% H_2SO_4 removes rubber particles from the surface and produces swelling.

The mechanical properties of the treated R1 rubber samples were obtained using stress–strain measurements. Table IV shows the decrease in tensile strength and elongation-at-break of R1 rubber after the treatment with H_2SO_4, due to a hardening of the rubber surface. Therefore, the treatment affects not only the outermost surface but produces a surface layer modification, *i.e.*, the presence of the surface defects causes a reduction in both maximum tensile strength and the elongation-at-break.

Adhesion was obtained from *T*-peel tests of H_2SO_4-treated R1 rubber/polyurethane adhesive joints. The peel tests were conducted 15 minutes and 72 hours after making the joint to investigate the effects of the crystallization of the thermoplastic polyurethane adhesive with time once the joint is produced. Immersion of R1 rubber in 95 wt% H_2SO_4 for 30 seconds (Tab. III) produced a noticeable increase in immediate strength (15 minutes after the joint is produced) and final strength (72 hours after joint formation); the failure of the joint changes from adhesional (non-treated rubber/adhesive joint) to a mixed failure mode (adhesional + cohesive failure in the rubber).

Durability of the joints was studied by performing an aging test. Table III shows that the aging does not produce a decrease in peel strength values and a cohesive failure in the rubber is obtained. Thus,

Untreated R1



H_2SO_4 95%; ti=0.5min.; tr=1min.; NH_4OH 15%

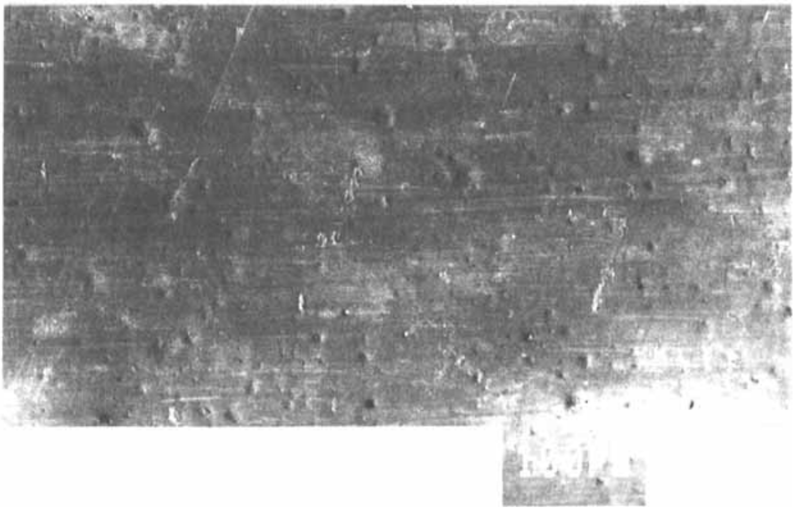


FIGURE 2 SEM micrographs of untreated and sulfuric acid treated R1 rubber. H_2SO_4 95%; *ti* = 0.5 min.; *tr* = 1 min.; NH_4OH 15%.

TABLE IV Tensile strength (MPa) and elongation-at-break (%) of H_2SO_4 treated R1 rubber

Treatment	*Tensile strength (MPa)*	*Elongation-at-break (%)*
Untreated	17.6	338
95 wt% H_2SO_4 $ti = 0.5$ min., $tr = 1$ min.	10.9	225

the treatment is effective not only in improving the immediate and final adhesion but, also, in producing durable joints.

Therefore, the treatment with sulfuric acid modifies the surface chemistry of R1 rubber by removing zinc stearate and creating $C=O$ and sulfonic acid moieties. Furthermore, a noticeable increase in surface energy (mainly due to the polar component) is obtained. The treatment also produced a decrease in tensile strength and elongation-at-break of R1 rubber. In addition, it increases the immediate and final peel strength of adhesive joints, producing a mixed failure or a cohesive failure in the rubber depending on the immersion time in H_2SO_4 solution.

Influence of Different Experimental Variables in the Treatment of R1 Rubber with Sulfuric Acid

In this study, the time of immersion in sulfuric acid solution, the time elapsing between the removal of the rubber from the acid and the neutralization stage (reaction time in air), and the neutralization with and without ammonium hydroxide were considered. The influence of these parameters on the effectiveness of the treatment with H_2SO_4 will be discussed.

Immersion Time in H_2SO_4 Solution

The influence of the immersion time in acid solution on the surface energy of R1 rubber is shown in Figure 3a. A short time of immersion in sulfuric acid (30 seconds) is enough to increase the total surface energy of R1 rubber, the increase being mainly due to an increase in the polar component of the surface energy. After 5 minutes immersion in sulfuric acid solution, the surface energy values remain almost constant and no longer depend on immersion time.

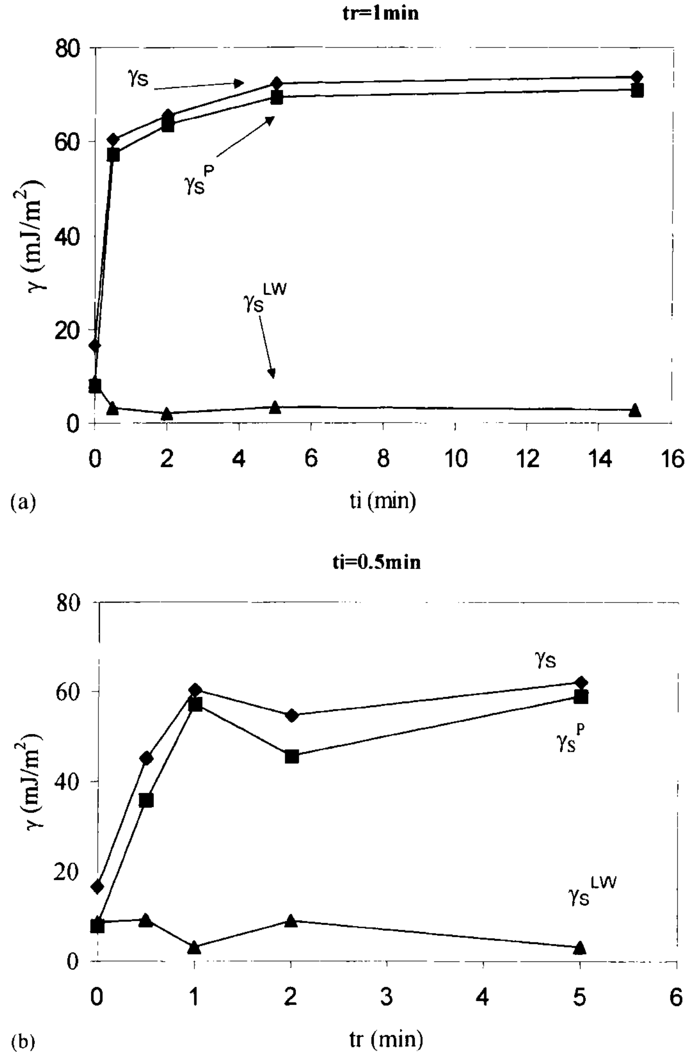


FIGURE 3 Variation of polar (γ_s^P) and dispersive (γ_s^{LW}) components of the total surface energy (γ_s) of H_2SO_4 treated R1 rubber as a function of (a) immersion time in H_2SO_4 95% solution; *tr* = 1 min.; NH_4OH 15%. (b) reaction time in air. H_2SO_4 95%; *ti* = 0.5 min.; NH_4OH 15%.

According to the ATR-IR spectra of the treated R1 rubber immersed for different times (Fig. 4a), similar chemical modifications are produced: creation of sulfonic acid moieties (O=S=O

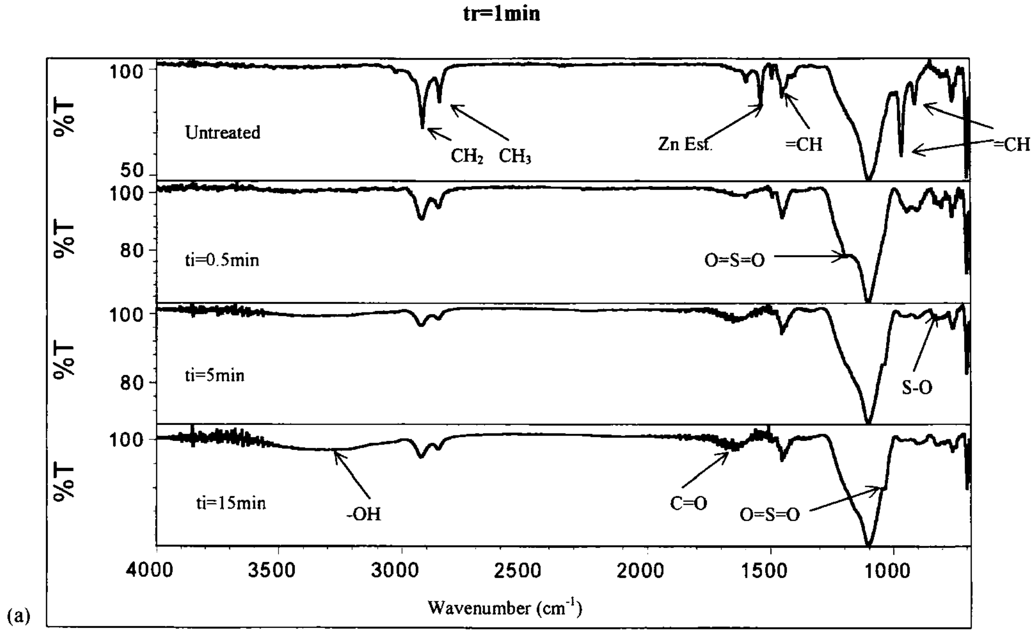


FIGURE 4 ATR-IR spectra of untreated and sulfuric acid treated R1 rubber. (a) Influence of the immersion time in H_2SO_4 95% solution (*ti*); *tr* = 1 min.; NH_4OH 15%. (b) Influence of the reaction time in air (*tr*). H_2SO_4 95%; *ti* = 0.5 min.; NH_4OH 15%.

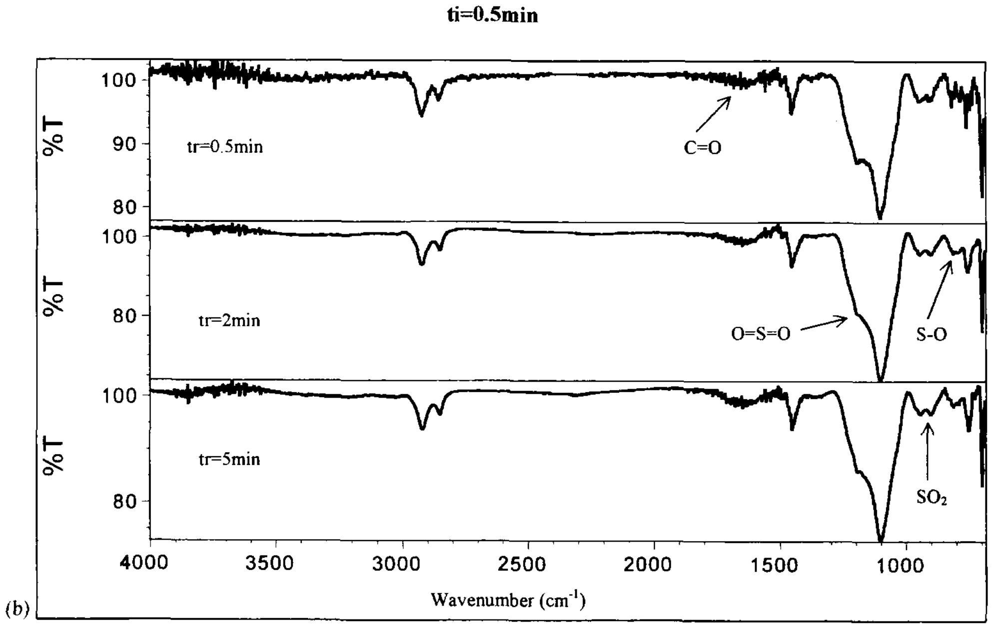


FIGURE 4 (Continued).

stretching bands at 1167 and 1050 cm^{-1}, S—O stretching at 870 cm^{-1}, and —S—OH stretching broad band at 3100–3400 cm^{-1}); and formation of C=C double bonds (=CH_2 in plane deformation at 1450 cm^{-1}, C=C stretching at 1650 cm^{-1}) due to the cyclization process. Increasing the immersion time in sulfuric acid enhances these effects and, thus, the intensities of the O=S=O and S—OH bands increase.

The SEM photomicrographs (Fig. 5) show the formation of cracks along the treated R1 rubber surface. An extended immersion time in sulfuric acid solution enhances the degree of swelling, and the rubber surface is modified. Additionally, the increase in the immersion time in sulfuric acid produces a noticeable decrease in mechanical properties (tensile strength and elongation-at-break) (data not shown). The treatment with sulfuric acid for extended immersion time produces the degradation of the rubber surface, the cohesive strength of the surface layer being a limiting factor in the adhesion to polyurethane adhesives.

Since a cohesive failure in the rubber was always obtained (both for immediate and final joint strength) (Fig. 6a), the increase of the immersion time in the acid solution did not produce variation in peel strength values, as the actual cohesive strength of the rubber was measured during the test. These results indicate that although the adhesion is enhanced by the treatment with H_2SO_4, an excessive modification of the outermost surface layer may not be appropriate as the failure is directed within this damaged surface. Therefore, an immersion time in sulfuric acid shorter than 2 minutes is optimal to produce an adequate performance in the adhesive joints and a negligible mechanical degradation of the rubber.

Reaction Time in Air

After immersion in H_2SO_4, the rubber was allowed to continue to react at room temperature. During this stage, reaction between the residual sulfuric acid on the rubber surface and the rubber itself may take place. Thus, the influence of the time elapsed between the removal of the rubber from the acid and the neutralization was considered.

The R1 rubber was immersed in sulfuric acid for 30 seconds and the neutralization with ammonium hydroxide was performed between 30 seconds and 5 minutes after treatment. A noticeable increase in

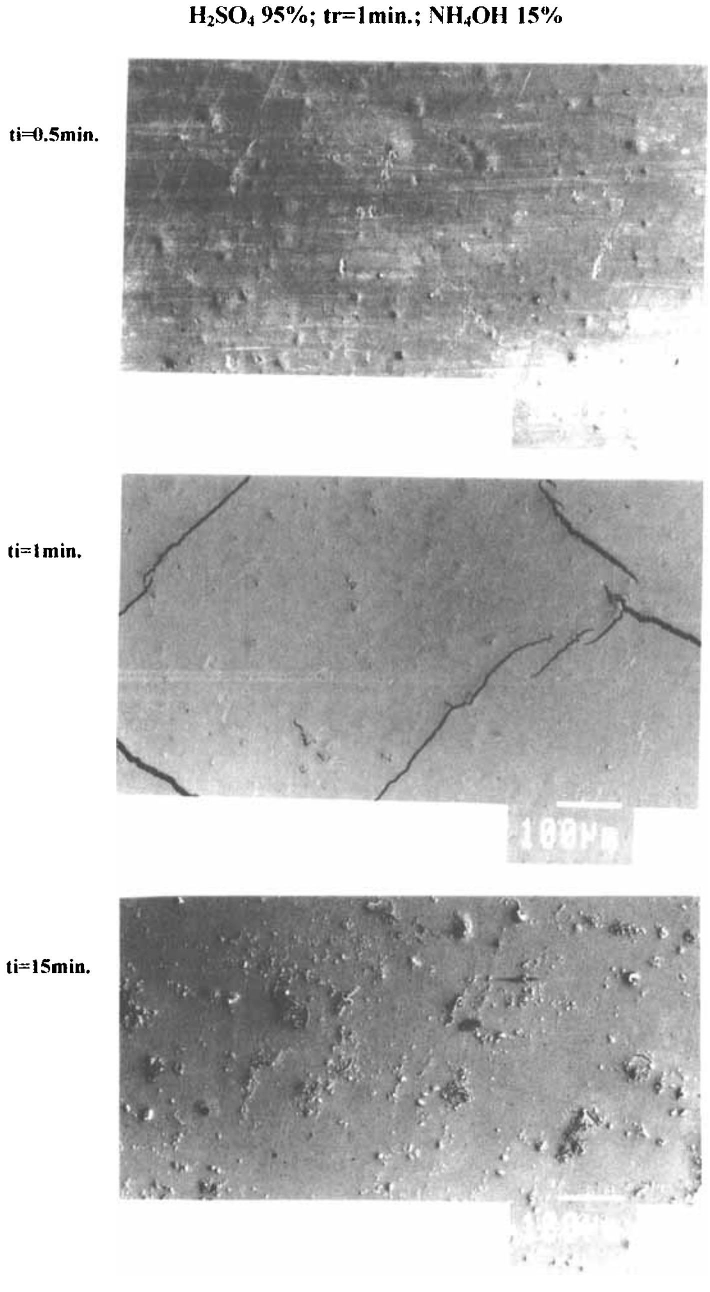


FIGURE 5 SEM micrographs of R1 rubber treated with sulfuric acid. Influence of the immersion time in H_2SO_4 95% solution (*ti*); *tr* = 1 min.; NH_4OH 15%.

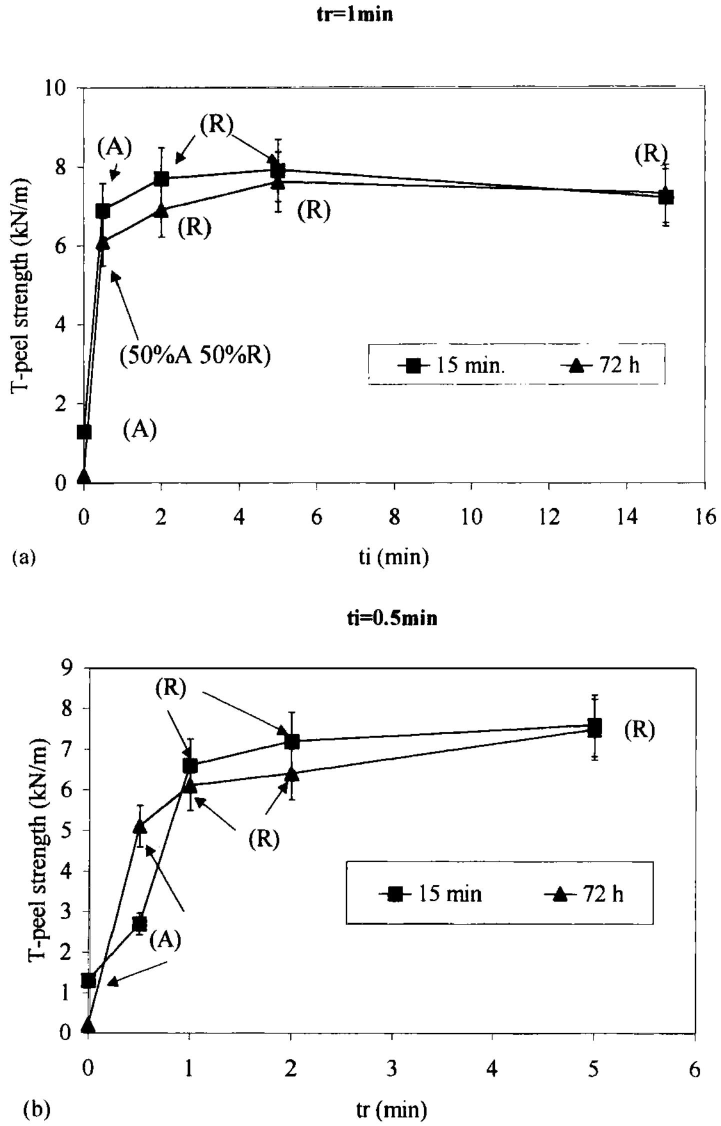


FIGURE 6 *T*-peel strength values of H_2SO_4 treated R1 rubber/polyurethane adhesive joints as a function of (a) immersion time in H_2SO_4 95% solution; $tr = 1$ min.; NH_4OH 15%. (b) reaction time in air. H_2SO_4 95%; $ti = 0.5$min.; NH_4OH 15%.

surface energy (Fig. 3b) is obtained for a reaction time in air of 1 minute; however, the increase in the reaction time in air does not greatly affect the surface energy values.

ATR-IR spectra of R1 rubber treated for different reaction times in air (Fig. 4b) show similar chemical modifications. These chemical modifications are affected by an increase in the reaction time in air, although these modifications are less marked than when the immersion time in sulfuric acid is increased (Fig. 4a). Additionally, after an initial decrease in tensile strength, mechanical properties are similarly affected for reaction times in air longer than 30 seconds (data not shown). There is a noticeable increase in immediate *T*-peel strength up to 1 minute reaction time in air, and the failure mode changes from adhesional to cohesive in the rubber (Fig. 6b). The failure mode obtained 72 hours after joint formation was always cohesive in the rubber. Reaction times in air higher than 1 minute did not improve adhesion.

Therefore, the reaction time with sulfuric acid in air influences to a lesser extent the properties and the adhesion of R1 rubber than does the immersion time, and a 1-minute reaction time is sufficient to produce an adequate performance. These findings suggest that after 1 minute no further reaction between the sulfuric acid on the surface and the rubber occurs. Furthermore, as the experiment was performed at ambient conditions, the residual sulfuric acid on the rubber surface may absorb water from the atmosphere, which will decrease its concentration and reduce the effectiveness of the treatment.

Neutralization with and without Ammonium Hydroxide

Neutralization of the treated R1 rubber surface using a base is a key step in the treatment with sulfuric acid, as a highly acidic surface might produce degradation of the adhesive once the joint is made.

Neutralization of the rubber treated with H_2SO_4 was carried out in two different ways: (i) Immersion in hot water followed by extensive washing with distilled water until neutral pH in the rubber surface was obtained; (ii) Immersion in hot water + neutralization with a solution of 15 wt% NH_4OH + extensive washing in distilled water. These two processes will be referenced as "without" and "with" NH_4OH, respectively.

Figure 7 shows the variation in surface energy of R1 rubber treated with H_2SO_4 with and without NH_4OH as a function of the immersion time in acid solution. A similar trend is obtained for both neutralization conditions, although the surface energy is higher in the R1 rubber treated with H_2SO_4 followed by neutralization with

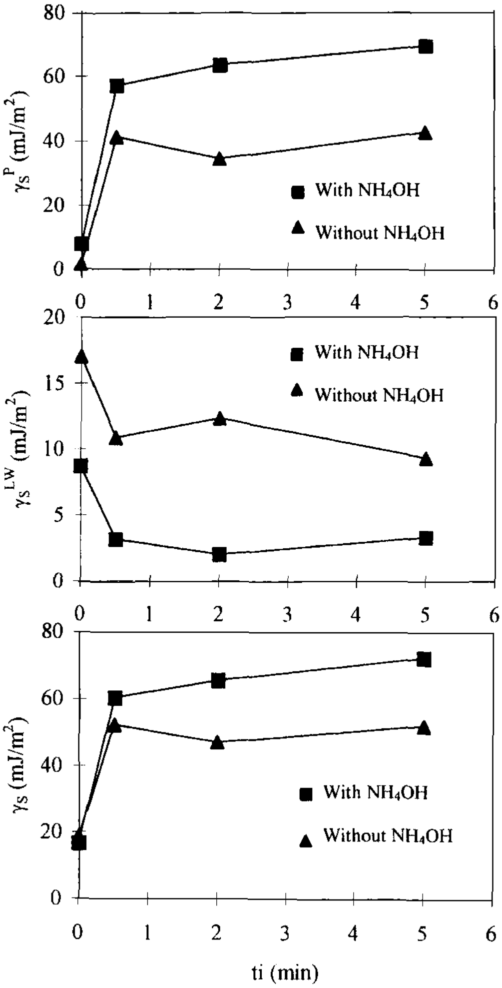


FIGURE 7 Variation of polar (γ_s^P) and dispersive (γ_s^{LW}) components of the total surface energy (γ_s) of H_2SO_4 treated R1 rubber as a function of the immersion time in acid solution. Influence of the neutralization with and without NH_4OH 15%. H_2SO_4 95%; *tr* = 1 min.

ammonium hydroxide. In this case, an increase in the polar component of the surface energy is produced.

A comparison of the ATR-IR spectra (Fig. 8) shows similar surface modifications regardless of the neutralization procedure for immersion times in sulfuric acid solution of 30 seconds and 2 min. On

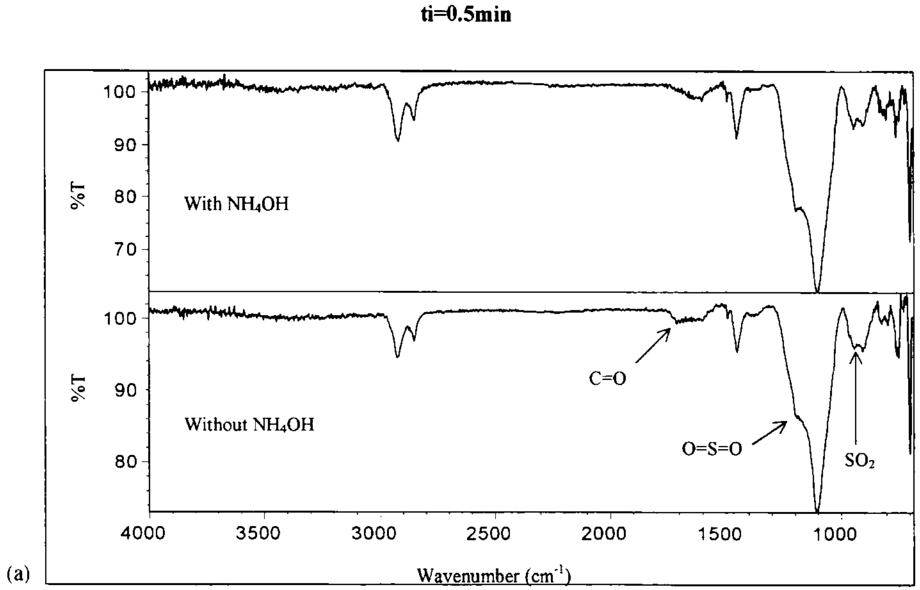


FIGURE 8 IR-ATR spectra of R1 rubber treated with sulfuric acid. Influence of the neutralization with and without NH_4OH 15%. H_2SO_4 95%; *tr* = 1 min. (a) *ti* = 0.5 min. (b) *ti* = 2 min.

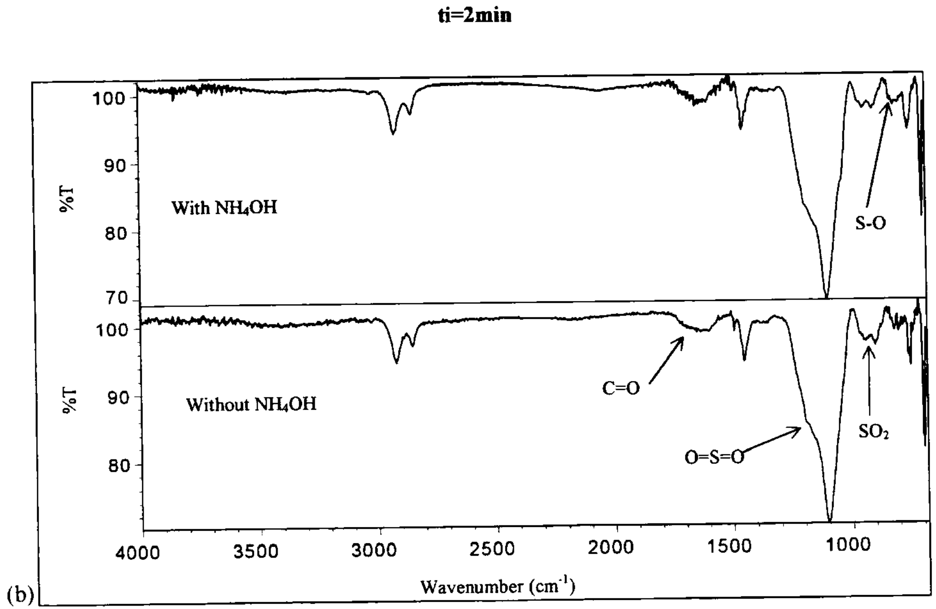
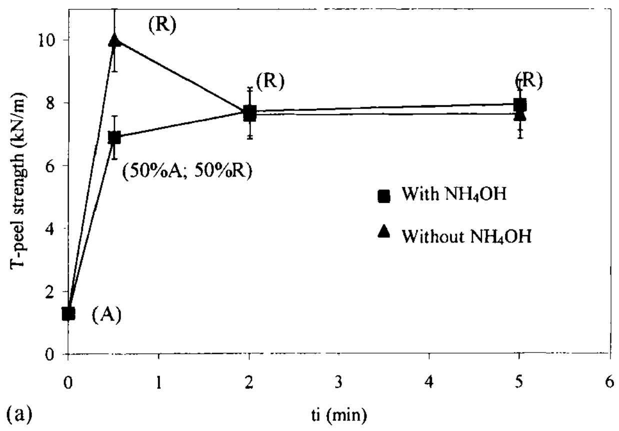


FIGURE 8 (Continued).

15 min after joint formation



72 h after joint formation

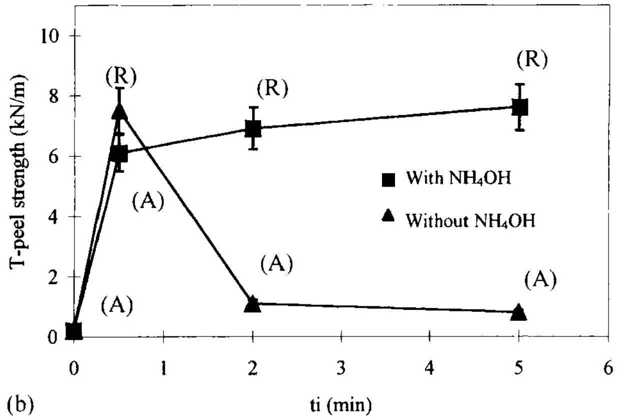


FIGURE 9 *T*-peel strength values of H_2SO_4 treated R1 rubber/polyurethane adhesive joints as a function of the immersion time in acid solution (*ti*). Influence of the neutralization with and without NH_4OH 15%. H_2SO_4 95%; *tr* = 1 min. (a) 15 min. after joint formation. (b) 72 h after joint formation.

the other hand, similar trends and values in mechanical properties (tensile strength and elongation-at-break), are obtained by neutralization with and without NH_4OH (data not shown).

Treated R1/PU joint

Failed surfaces

H_2SO_4 95%; ti=5min.; tr=1min.; Without NH_4OH

72 h after joint formation

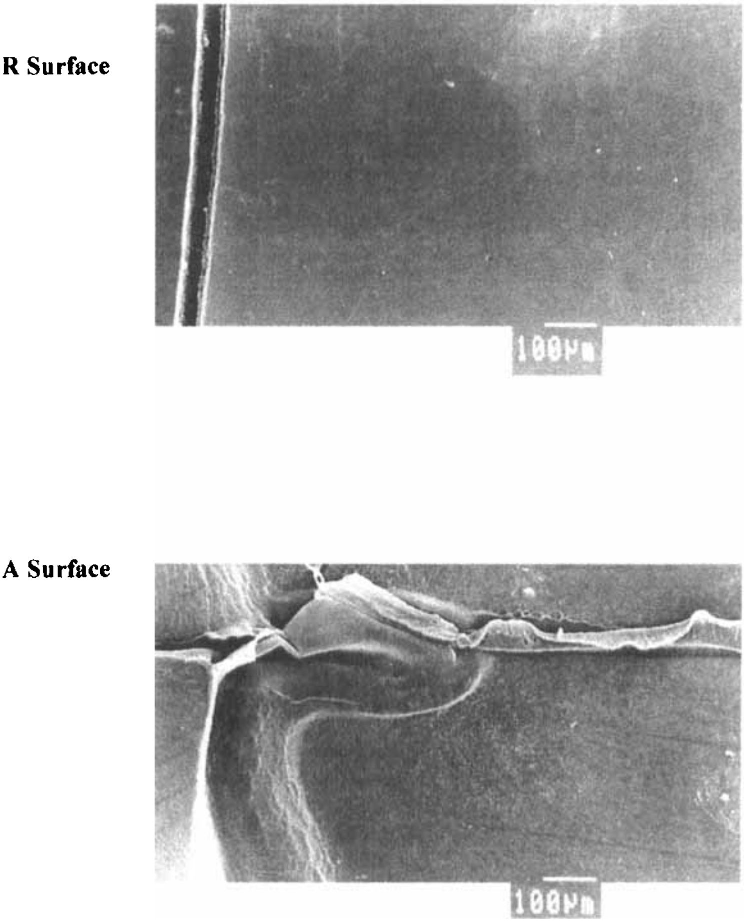


FIGURE 10 SEM micrographs of failed H_2SO_4 treated R1 rubber/polyurethane adhesive joints. H_2SO_4 95%; $ti = 5$ min.; $tr = 1$ min.; without NH_4OH 15%; 72 h after joint formation.

The *T*-peel strengths of H_2SO_4-treated R1/polyurethane-adhesive joints are given in Figure 9. For short immersion times in the acid solution, the immediate adhesion (15 minutes after joint formation) (Fig. 9a) is higher if the neutralization is produced without NH_4OH and a cohesive failure (instead of adhesional) is obtained. For a longer immersion time in H_2SO_4 solution, the peel strength is not affected by the neutralization procedure. However, a marked decrease in final adhesion (72 hours after joint formation) (Fig. 9b) is produced when the neutralization is performed without NH_4OH (this can be mainly noticed for immersion times in sulfuric acid solution higher than 2 minutes). This decrease in peel strength can be ascribed to a degradation of the adhesive by the remaining acidic moieties on the treated R1 rubber surface. In fact, SEM photomicrographs of the failed surfaces corresponding to the joint produced with R1 rubber treated with sulfuric acid followed by neutralization without NH_4OH (Fig. 10) show a highly degraded adhesive surface (A surface).

Consequently, the removal of acidic moieties from the rubber surface with ammonium hydroxide after the treatment is essential to prevent degradation of the polyurethane after joint formation and to produce an adequate adhesive joint.

CONCLUSIONS

Treatment with sulfuric acid modifies the surface chemistry of R1 rubber by removal of zinc stearate and creation of $C=O$ and sulfonic acid moieties. Furthermore, a noticeable increase in surface energy (mainly due to an increase in polar component) is produced and some cracks are created on the surface. The treatment also produced a decrease in tensile strength and a reduction in elongation-at-break of R1 rubber. Therefore, the treatment with H_2SO_4 is not restricted to the most external surface but modifies a surface layer of a considerable depth, affecting the mechanical properties of the rubber. The treatment with sulfuric acid increases the immediate and final peel strength of adhesive joints producing a cohesive failure in the rubber. The joints are also resistant to aging. The increase in adhesion strength is the result of the increase in mechanically-produced cracks, and also of chemical oxidation and of creation of sulfonic acid moieties (chemical adhesion), as well as of thermodynamic adhesion (increase in the polar component of the surface energy).

The optimum immersion time in sulfuric acid solution is less than 1 minute, and the reaction time in air is not found to be critical (longer than 1 min.). The use of concentrated sulfuric acid (95 wt%) and neutralization with ammonium hydroxide are essential to produce an adequate treatment.

Acknowledgement

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