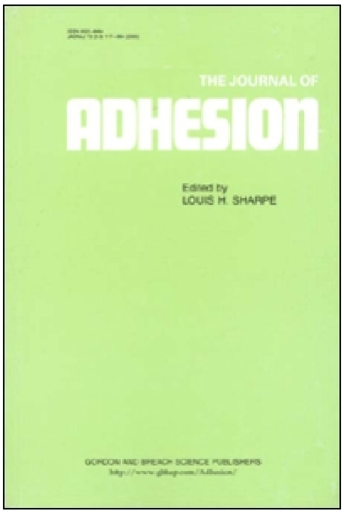

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Fumaric Acid as a Promoter of Adhesion in Vulcanized Synthetic Rubbers*

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The addition of dicarboxylic acids to polyurethane adhesives, to improve their adhesion to vulcanized synthetic rubbers, may cause the degradation over time of the adhesives. To avoid the degradation of polyurethane adhesives, this study proposes a surface treatment on vulcanized synthetic rubbers with carboxylic acid solutions instead of adding them to the adhesives. In all the styrene-butadiene rubbers studied, a great improvement in adhesion to polyurethane adhesives has been obtained. The nature of the solvent used to disperse the fumaric acid over the surface, as well as the nature of the rubber, determined the effectiveness of the surface treatment. The use of fumaric acid solutions provided optimum results when the surface of the rubber was slightly roughened. The increase in the adhesion properties of styrene-butadiene rubbers, treated with fumaric acid, has been attributed to an increase in the degree of the surface roughness and to an enhancement in the surface energy (due to the elimination of abhesive substances on the surface of the rubber and to the formation of C—O groups by surface oxidation). The effectiveness of the surface treatment on rubbers with fumaric acid in the adhesion of styrene-butadiene rubbers has been compared with those produced by other common treatments, such as halogenation and roughening. In general, *T*-peel strengths obtained in the rubbers treated with fumaric acid were similar to those obtained through halogenation and were always higher than those obtained through roughening. Therefore, surface treatment of styrene-butadiene rubbers with fumaric acid can be considered as an alternative method to chemical treatments currently used, especially in the footwear industry.

KEY WORDS: Adhesion; surface treatments; halogenation; polyurethane adhesives; styrene-butadiene rubber; fumaric acid.

INTRODUCTION

Although important progress has been made in the adhesive industry during the last few decades, there still remain problems of compatibility with various substrates. An

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*One of A Collection of papers honoring Lawrence T. Drzal, the recipient in February 1994 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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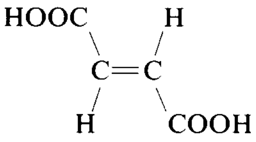
example of this incompatibility can be found in the bonding of synthetic rubbers using polyurethane (PU) adhesives. Even when the adhesive formulations can be adapted to different substrates, it is advisable, and often necessary, to carry out a surface treatment (roughening, solvent wiping, halogenation) to increase the adhesion between the rubbers and the PU adhesive.[1-3]

Roughening is an effective physical treatment to eliminate abhesive substances from the surface of the rubber, although its effectiveness is time-limited because these substances can migrate back again to the surface of the rubber creating a weak boundary layer that lessens the strength of the adhesive joints. For this reason, more aggressive chemical treatments are required to achieve adequate adhesion. The use of agents that release chlorine onto the surface is currently the most used chemical treatment to improve the adhesion of synthetic elastomers with PU adhesives.[4,5] This chemical treatment is effective as it increases both the degree of surface roughness and the surface energy of the rubber eliminating, at the same time, abhesive substances from the surface and creating C—Cl and C—O groups. However, the halogenation of elastomers presents some limitations: *i*) Careful handling is required due to the oxidizing character of the halogenating solutions and their toxicity (chlorine emissions can be produced), *ii*) The reaction takes at least 6 hours for the optimum effectiveness of the surface treatment to be reached, *iii*) The stability of the halogenating solutions is limited, and *iv*) An excess of the halogenating agent can produce weak boundary layers.[6,7] These drawbacks of halogenation show the necessity of finding new surface treatments of elastomers that, being as effective as chlorination in the improvement of the adhesion properties, do not present the disadvantages that chlorination does.

Carboxylic acids have been used, in the past, as additives in formulations of PU adhesives, acting generally as promoters of adhesion on vulcanized synthetic rubbers.[8-10] As has been shown in a previous study,[11] the addition of these acids modifies various physical properties of PU (viscosity, glass transition temperature, molecular weight distribution), the changes being more marked the longer the time elapsed after the addition of carboxylic acid to the PU. The modification of the PU properties is due to specific molecular interactions with the carboxylic acid, producing a reduction of the "pot life" of the adhesive even though, in spite of this, the *T*-peel strengths apparently do not vary. In this way, the usefulness of the addition of carboxylic acids to PU adhesives as promoters of rubber adhesion is offset. However, according to previous studies,[12,13] when the PU adhesive containing a carboxylic acid as additive contacts the surface of a rubber, the carboxylic acid molecules are oriented and, by a diffusion mechanism through the interphase, interact with specific groups on the surface of the rubber. Since the effectiveness of carboxylic acids as adhesion promoters can be justified in this way, the application of carboxylic acid to the surface of vulcanized synthetic rubbers (avoiding the modification of the physical properties of the polyurethane adhesive) is proposed in this work.

The usefulness of the new surface treatment with fumaric acid (FA) (*trans*-1,2-ethylenedicarboxylic acid) on vulcanized styrene-butadiene synthetic rubbers (SBR) will be shown in this study. On the other hand, a comparative study will be carried out on the effectiveness of this new procedure against the more usual surface treatments (roughening, halogenation) for the improvement of adhesion properties of these rubbers. In addition, the surface modifications, produced by treating the SBR with FA solutions, and accounting for the noticeable enhancement in the adhesion properties, will be analysed.



fumaric acid

EXPERIMENTAL

Materials

The greater part of this study has been carried out with two SBRs (R1, R2) of different Shore A hardness (93° and 72°, respectively) and with different oils and plasticizer contents (7 phr (parts per hundred of rubber) for R1 and 12 phr for R2). Formulations for both rubbers are given in Table I. In addition, other commercial SBRs, whose formulations differed in the content and nature of their oils and plasticizers, as well as in their type of mineral filler, have been used. The SBRs were surface-treated by roughening, halogenation and addition of FA solutions to improve their adhesion properties. The surface treatment with FA solutions containing 0.5, 1 and 2 wt% in different mixtures of organic solvents, was carried out by rubbing the surface with a brush. In some cases, a roughening of the surface was carried out before the treatment with FA, a surface layer of 0.5 mm thickness being eliminated. The time elapsed between the consecutive applications of FA and the PU adhesive to the surface of the rubber (treatment time) was varied between 30 minutes and 48 hours. In Figure 1 the *T*-peel strengths for R1 and R2 rubbers treated with 2 wt% FA, as a function of the

TABLE I
Composition of R1 and R2 vulcanized synthetic rubbers

Component	R1	R2
SBR 1620	71	—
SBR 1502	18	100
Carbon black HSR 1904	35	—
Precipitated silica	25	42
Hydrocarbon resin	3.5	5.0
Sulphur	1.8	2.0
N-cyclohexyl-2-benzothiazole-sulphenamide	1.1	2.0
Tetramethylthiuram disulfide	0.2	—
Stearic acid	0.8	2.4
Zinc oxide	3.8	1.5
Polyethyleneglycol	1.1	—
Phenolic antioxidant	0.8	0.5
2-mercaptobenzothiazole-disulphide	—	2.5
Microcrystalline paraffin wax	—	0.8
Hexamethylene tetramine	—	1.0
Fatty acid zinc salts	—	5.4

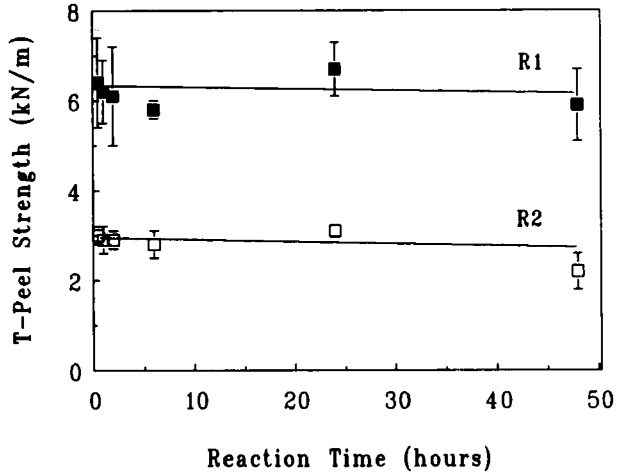


FIGURE 1 *T*-peel strengths (kN/m) of PU adhesive joints of R1 and R2 rubbers roughened and treated with 2 wt% FA in 2-butanone/ethanol (1:1). Influence of the treatment time.

treatment time are given. As there were no variations in the *T*-peel strengths between 30 minutes and 48 hours, one hour was considered to be a suitable treatment time in this study.

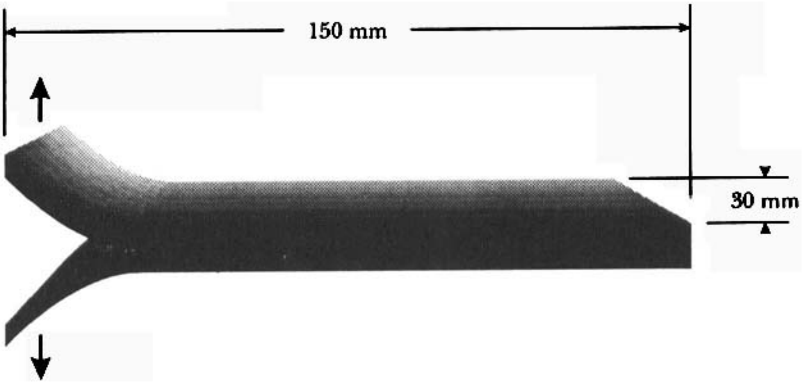
Halogenation of the SBRs was carried out with solutions of 2 wt% trichloroisocyanuric acid (TCI) in 2-butanone, the time used for the treatment being 20 hours to achieve the optimum adhesion of the rubbers. The halogenating agent was not effective when dissolved in a mixture (1:1) of 2-butanone/ethanol (mixture used to apply the FA on the rubber surface), therefore, only 2-butanone was used as solvent.[2]

To determine the *T*-peel strength a ε-polycaprolactone based polyester-urethane adhesive manufactured by Merquinsa (Barcelona, Spain) was used. This polyester-urethane has a medium thermoplasticity, very high crystallization rate and short open time. The adhesive was prepared by dissolving 18 wt% PU in 2-butanone, a Brookfield viscosity of 3.0 Pa·s (23°C) being obtained.

The adhesive joints were prepared by applying approximately 100 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 60°C, putting them into contact immediately under a pressure of 10 Kg/cm^2. The adhesive joints were conditioned for 72 hours at 23°C and 50% relative humidity before undergoing the *T*-peel test.

Experimental Techniques

T-peel strengths 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. The experimental error obtained was less than 5%.



T-peel test

Measurement of contact angles SBR test pieces were immersed for 30 seconds in 2-butanone/ethanol (1:1) solutions containing 0, 0.5, 1 and 2 wt% FA. The test pieces were allowed to react for 24 hours after the treatment and then were introduced into the thermostatized 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 5 μl drops of bidistilled water, *n*-hexadecane and ethylene glycol; the time required to reach the equilibrium was 10 minutes in every case. The experimental error was ± 2 degrees.

The surface energy components for the surface-treated rubbers were calculated from the measured contact angles (θ) of three suitable liquids (one non-polar and two polar) by using the Good equation,[14,15] obtaining separately the dispersive and acid-base components of the surface energy:

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

where the subscripts "L" and "S" refers to the liquid and solid, respectively, and

γ_L = surface tension of liquid.
$\gamma^{\oplus}$ = electron acceptor component of surface energy.
$\gamma^{\ominus}$ = electron donor component of surface energy.
γ^{LW} = dispersive component (Lifshitz-van der Waals) of surface energy.

Scanning Electron Microscopy (SEM) The surface of R1 and R2 rubbers treated with FA were analyzed under a scanning electron microscope JEOL SEM JSM 840.

Fourier Transform Infrared Spectroscopy (FTIR) The IR spectra of R1 and R2 rubbers treated with 0 and 1 wt% of FA in 2-butanone/ethanol (1:1) were obtained in order to determine the nature of the chemical modifications produced by the surface treatment of the rubbers. The attenuated total multiple reflection method (ATR) employing either bromideiodide crystal (KRS-5) (for R2 rubber) or a germanium crystal (for R1 rubber) was used; in this case, the germanium crystal reduces the absorption caused by carbon black. More details on this technique have been given earlier.[6]

RESULTS AND DISCUSSION

Peel Strength

Material roughening Figure 2a shows the *T*-peel strengths measured in adhesive joints between PU adhesives and R1 and R2 rubbers (without previous roughening) after the surface treatment with solutions containing different amounts of FA in 2-butanone/ethanol (1:1). Surface treatment with FA improves rubber adhesion,

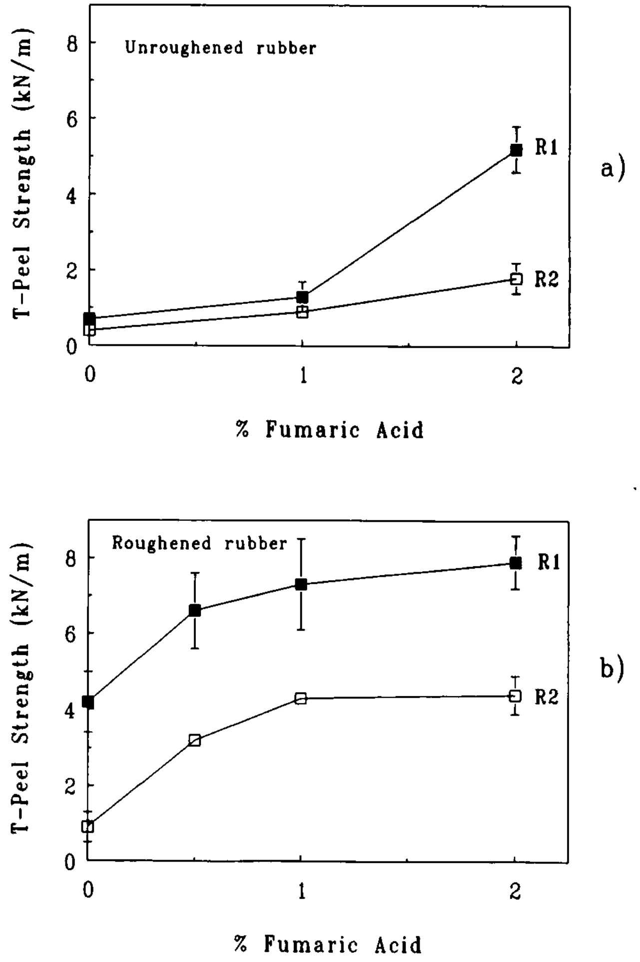


FIGURE 2 *T*-peel strengths (kN/m) of PU adhesive joints of R1 and R2 rubbers treated with fumaric acid solutions in 2-butanone/ethanol (1:1). a) Unroughened rubbers. b) Roughened rubbers.

although its effectiveness depends on the nature of the rubber (more effective in R1), and at least 2 wt% FA is required in order to obtain suitable results. In this way, R1 rubber was found to increase the *T*-peel strength between 0.7 and 5.2 kN/m, whilst for R2 rubber the increase was less marked (0.5 to 1.8 kN/m), possibly due to its higher content of abhesive substances (principally paraffin wax and zinc stearate).

During the vulcanization process of the rubbers, the overheated mould deteriorates the surface of the rubber in contact with it, producing a "vulcanization layer" whose properties differ from the bulk often making adhesion difficult. This vulcanization layer is resistant to many otherwise effective surface treatments in the improvement of the elastomer adhesion. It is, therefore, advisable to eliminate the vulcanization layer before applying a surface treatment and, for this reason, roughening of the vulcanized rubbers was carried out as a step preceding FA treatment. In Figure 2b the *T*-peel strengths obtained when R1 and R2 rubbers were roughened before FA treatment are shown. A new increase in the adhesion of the rubbers is produced by FA treatment and for roughened rubbers the quantity of FA necessary to appreciate this increase in adhesion is only 0.5 wt%, in contrast with the 2 wt% needed for unroughened rubbers. Comparing Figures 2a and 2b we can conclude that the *T*-peel strengths are higher when the rubber is roughened before the FA treatment, reaching values close to the cohesive failure of the R1 rubber (10–11 kN/m). The greater effectiveness of the FA treatment when the rubber is roughened is probably due to the elimination of the vulcanization layer and the creation of surface roughness (enhancing the mechanical adhesion mechanism) during the roughening process. In this way, the application of FA to rubber is more effective with smaller quantities than those which would be specified for unroughened rubber.

Effect of solvents Since FA needs a carrier to be applied on the surface of the rubber, the solvent used could determine the effectiveness of the treatment. Therefore, different solvents were used for the FA, and the *T*-peel strengths obtained for R1 and R2 rubbers treated with FA in 2-butanone/ethanol in different proportions (by volume), are shown in Table II. When using only ethanol as solvent, there results an increase in adhesion more noticeable than when 2-butanone/ethanol mixtures are used. There was no

TABLE II
Influence of the proportion of 2-butanone/ethanol in fumaric acid solutions on the *T*-peel strengths of R1 and R2 surface treated rubbers

Fumaric acid (wt%)	*T*-peel strengths (kN/m)[a]					
	R1			R2		
	(0:1)	(1:1)	(3:1)	(0:1)	(1:1)	(3:1)
0	0.4	2.9	2.7	0.4	0.9	0.3
0.5	5.4	5.7	6.5	2.6	3.2	4.3
1	5.3	6.7	6.5	3.1	4.3	4.6
2	5.3	6.7	—	3.4	4.4	—

(a) An adhesion failure is always produced.

TABLE III
Influence of the nature of the fumaric acid solvent on the *T*-peel strengths of R1 and R2 rubbers

	T-peel strengths (kN/m)[a]			
	R1		R2	
Solvent mixture (1:1)	0wt% FA	2wt% FA	0wt% FA	2wt% FA
2-butanone/ethanol	5.4	9.3	0.5	5.7
ethyl acetate/ethanol	5.4	9.5	0.7	5.5
2-butanone/isoamyl alcohol*	6.2	10.0	1.4	6.7
ethyl acetate/isoamyl alcohol*	5.8	8.9	1.2	6.1
ethyl acetate/isopropyl alcohol	5.0	10.5	1.4	4.4

* 0.85 wt% fumaric acid.
[a] An adhesion failure is always produced.

significant variation in *T*-peel strengths when the proportion of 2-butanone/ethanol is modified, thus, a 1: 1 mixture of 2-butanone/ethanol was considered the most suitable.

Alcohols of a different nature were also used for the application of FA to the surface of the rubbers. These alcohols were chosen paying attention to their higher molecular weight and lower evaporation rate compared with ethanol, favouring a longer contact time between the FA and the rubber, which should allow a greater degree of reaction to be produced. However, due to the lower solubility of FA in isoamyl alcohol than in ethanol, isoamyl alcohol solutions only contained 0.85 wt% FA. Table III includes the *T*-peel strengths for the rubbers treated with 0 and 2 wt% FA in various solvent mixtures (2-butanone, ethyl acetate, ethanol, isoamyl alcohol, isopropyl alcohol) in (1: 1) proportion. According to Table III alcohols with higher molecular weight produce a more noticeable increase in the adhesion of R1 and R2 rubbers treated with FA, so it does not seem relevant to use 2-butanone or ethyl acetate in the mixtures.

Physical/Chemical Changes

Wettability The improvement in adhesion exhibited by the rubbers treated with FA can be attributed to an increase in wettability, so that the advancing contact angles were determined with three liquids of different acid-base characteristics (water, ethylene glycol, *n*-hexadecane), whose surface tension components are given in Table IV. Drops of these liquids were deposited on R1 and R2 rubbers treated with FA. The acidic (electron acceptor component of the surface energy), basic (electron donor component of the surface energy) and dispersive components of the surface energy calculated for the rubbers by using the Good equation are given in Figure 3. Both rubbers behave in a similar way when treated with FA solutions. A noticeable increase in the electron donor component of the rubber is found when it is treated with FA, an increase in the FA concentration having no influence. However, no important increase can be seen in the dispersive component of the surface energy of the rubber, nor does there seem to exist any modification in the electron acceptor component. For R1 rubber the increase in the electron donor component of the surface energy is far more obvious than for R2 rubber, corresponding to a greater *T*-peel strength (Figures 2a and

TABLE IV

Total (γ_L), dispersive (γ_L^{LW}), electron donor ($\gamma_L^{\ominus}$) and electron acceptor ($\gamma_L^{\oplus}$) components of the surface tension (25°C) of water, ethylene glycol and *n*-hexadecane

Liquid	γ_L	γ_L^{LW}	$\gamma_L^{\oplus}$	$\gamma_L^{\ominus}$
Water	72.8	21.8	25.5	25.5
Ethylene glycol	48.0	29.0	1.9	47.0
n-hexadecane	27.5	27.5	0.0	0.0

(a) Values taken from reference 15.

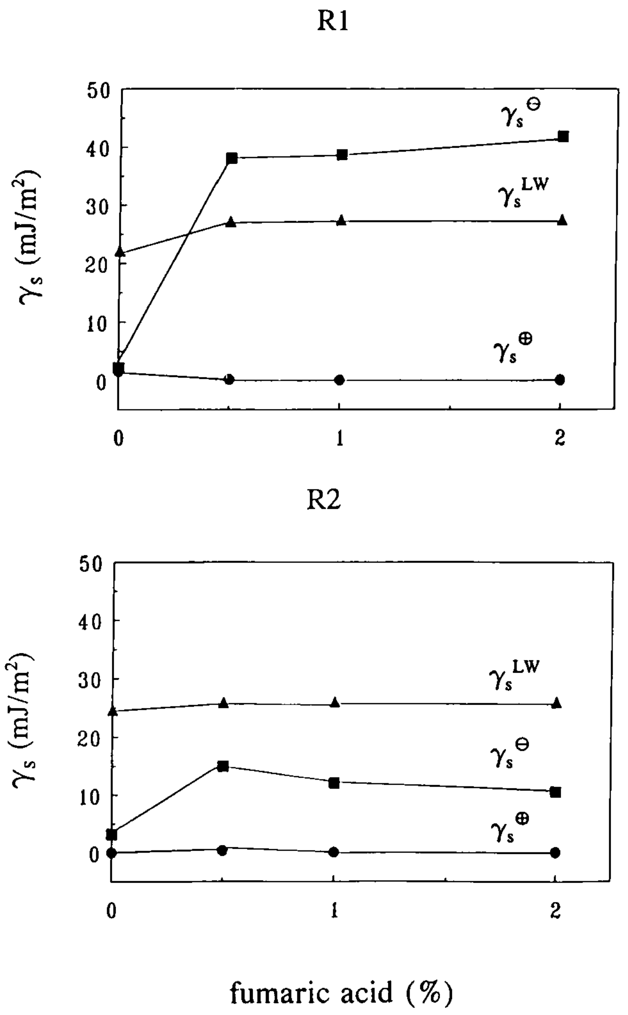


FIGURE 3 Surface energy components (mJ/m^2) of R1 and R2 rubbers treated with fumaric acid solutions in 2-butanone/ethanol (1:1). $\gamma_S^{\oplus}$ = electron acceptor component of surface energy; $\gamma_S^{\ominus}$ = electron donor component of surface energy; γ_S^{LW} = dispersive component (Lifshitz-van der Waals) of surface energy.

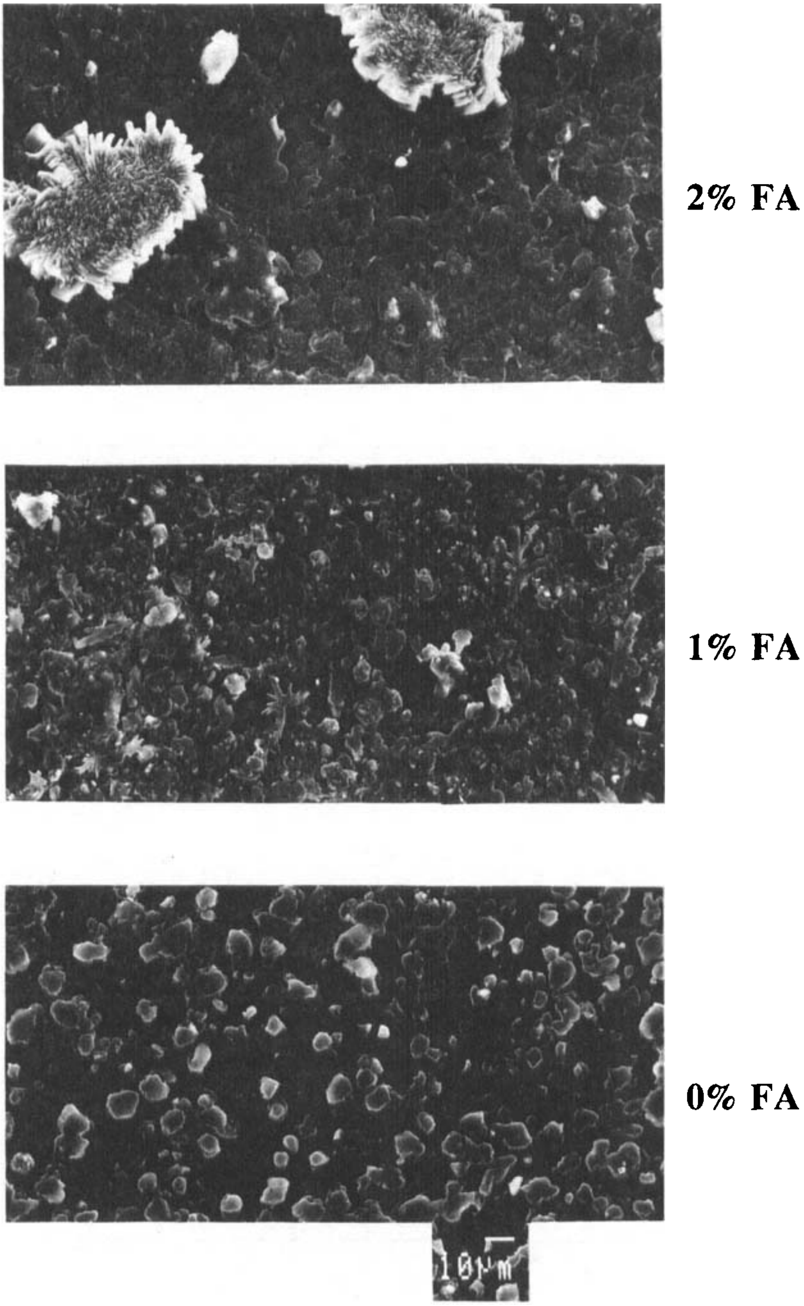


FIGURE 4 SEM microphotographs (*x*500) of R2 rubber surfaces treated with 0 wt%, 1 wt% and 2 wt% fumaric acid in 2-butanone/ethanol (1:1).

2b). Therefore, the nature of the rubber determines the effectiveness of the treatment with FA, as this varies the wettability of the rubber.

Surface treatment with FA improves rubber wettability, be it by the creation of a certain roughness on the surface and/or by the presence of chemical groups which contribute to specific interactions. The measurements of contact angles show that 0.5 wt% FA on the surface of the rubber would be enough to provoke an increase in adhesion, but in some cases a greater concentration of FA is required to reach the maximum *T*-peel strength (Figures 2a and 2b). Therefore, there must be other factors which also contribute to the increase in adhesion of rubbers treated with FA.

Surface morphology To determine the influence of surface roughness in adhesion, the surfaces of the rubbers treated with FA were analyzed by SEM. In Figure 4, the microphotographs of R2 rubber treated with 0, 1 and 2 wt% FA in 2-butanone/ethanol (1: 1) can be seen. Treatment with only the mixture of solvents (0% FA) provokes an attack on the rubber surface, with small rounded particles of rubber, not formerly present, appearing. The treatment with FA produces on the rubber surface a more forceful attack creating roughness and cracks. On increasing the concentration of FA (2 wt%) the attack is deeper and, moreover, discrete needle-shaped particles of about 20 μm of FA, unreacted with the rubber surface, appear. All these modifications to the external topography of the rubber indicate that the surface treatment with FA induces an increase in the mechanical adhesion which must contribute to the increase in the *T*-peel strengths and to the improvement in wettability of the rubbers.

As the surface treatment of R1 and R2 rubbers with FA solutions produces a certain surface roughness, the increase in surface energy in the treated rubbers shown in Figure 3 could be greatly influenced by that topography. Table V contains the advancing contact angles of H_2O and diiodomethane obtained on a thin film (0.1 mm) of polyurethane adhesive deposited on the R2 rubber previously treated with FA (the thin film was used to eliminate the effect that the surface roughness may produce). When R2 rubber is treated with FA, a drop in advancing contact angles for the two solvents is produced, in agreement with the trend showed in Figure 3. Moreover, these results show that the modification in the PU/rubber adhesive interphase is transmitted through the adhesive thin layer, the surface energy enhancement provoked by the treatment of the rubber with FA probably having a chemical origin (short range interactions seem to be produced at the interface).

TABLE V
Advancing contact angles (25°C) of H_2O and diiodomethane of R2 rubber treated with fumaric acid on which a polyurethane adhesive film was deposited

	Contact angles (degrees)	
Fumaric acid (wt%)	H_2O	CH_2I_2
0	92	49
0.5	79	35
1	79	38
2	78	39

IR spectra The chemical modification produced on the rubber surface by FA treatment has been followed by IR spectroscopy. In Figures 5 and 6 the IR spectra of R1 and R2 rubbers treated with FA are shown. The IR spectra of the two treated rubbers are very similar. Examined in this way, the treatment of the rubber surface with FA solutions produces various effects:

— Appearance of bands at 1275, 1410, 1429 and 1669 cm^{-1}, corresponding to the fumaric acid.[6] A new band also appears at 1576 cm^{-1} probably from C=O groups in a less electronegative chemical environment than the carboxylic groups of fumaric acid.

— The band at 1535 cm^{-1} is absent and the relative intensity of the 1398 cm^{-1} band is reduced, both corresponding to zinc stearate (abhesive substance in the formulation of the rubber).

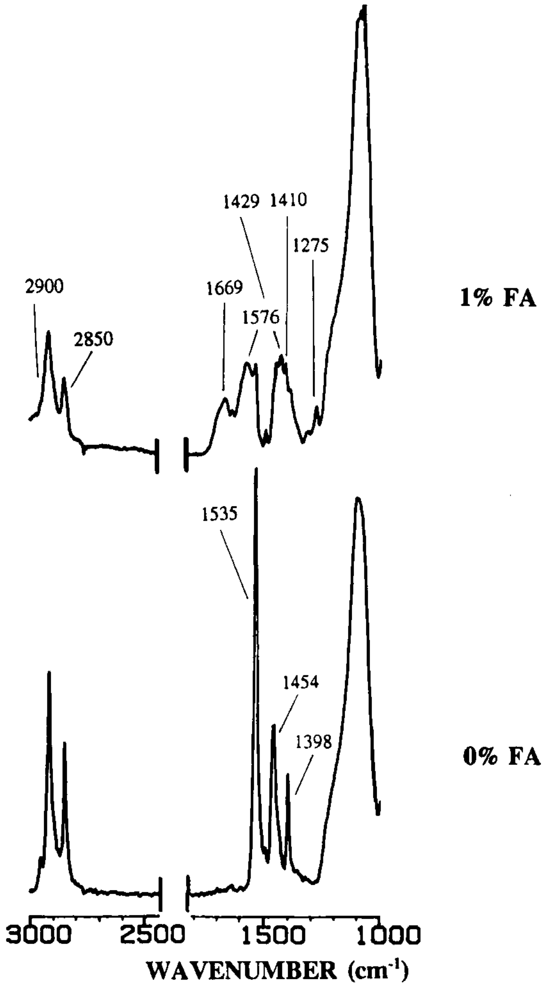


FIGURE 5 IR spectra of R1 rubber treated with fumaric acid solutions in 2-butanone/ethanol (1:1).

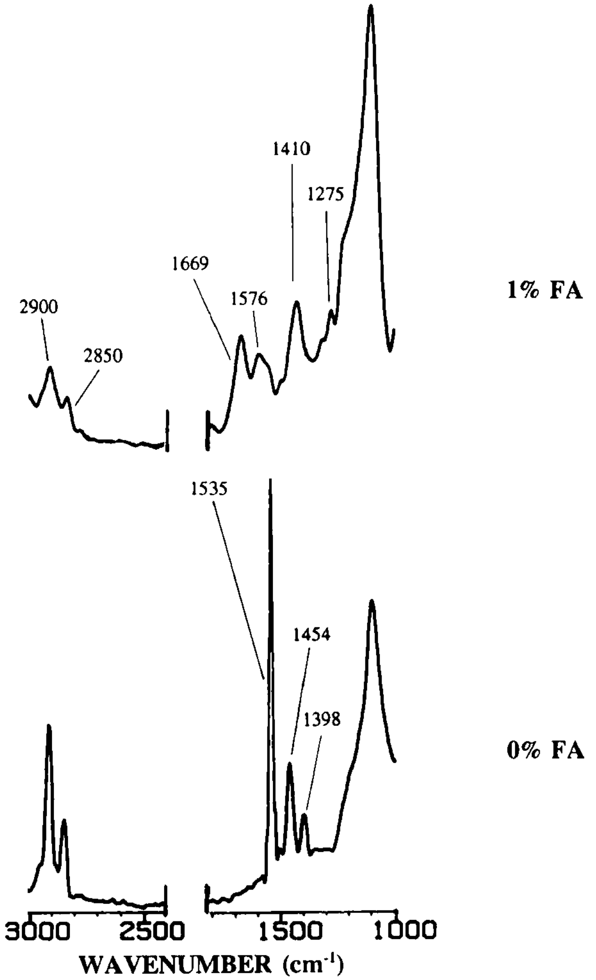


FIGURE 6 IR spectra of R2 rubber treated with fumaric acid solutions in 2-butanone/ethanol (1:1).

- Decrease in the intensity of bands at 1454, 2850 and 2900 cm^{-1} corresponding to CH_2 and CH_3 groups from aliphatic chains. In R2 rubber these lower intensities could be caused by removal of the paraffin wax used as an antioxidant in its formulation (it creates a film on the rubber surface which avoids its oxidation, but it also provides abhesive characteristics). However, R1 rubber does not contain paraffin wax in its formulation but a hydrocarbon resin may be eliminated with the resulting decrease in intensity of the CH_2 and CH_3 bands.
- Badly-defined bands between 1500 and 1700 cm^{-1} appear, corresponding to C—O groups, which can be attributed to a certain surface oxidation of the rubber and to the fumaric acid itself.

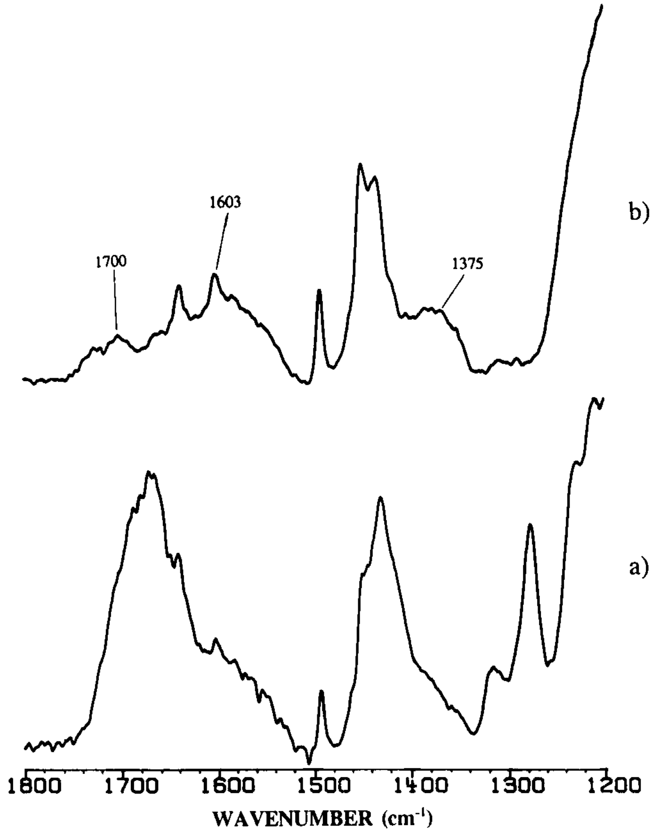


FIGURE 7 IR spectra of R2 rubber treated with fumaric acid solutions in 2-butanone-ethanol (1:1). a) 2 wt% fumaric acid; b) 2 wt% fumaric acid + wiping with ethanol.

In order to determine the nature of the bands appearing in the IR spectra (Figures 5 and 6) between 1500 and 1700 cm^{-1}, IR spectra were obtained for the R2 rubber treated with FA after wiping with ethanol (in order to eliminate any FA remaining free on the surface) (Figure 7). Wiping the R2 rubber with ethanol does not affect some of the bands due to C—O groups (1603 and 1700 cm^{-1}), so that the treatment of the vulcanized rubbers with FA seems to provoke a chemical modification on the surface of the rubber, giving rise to the appearance of C—O groups, possibly through a surface oxidation mechanism.

Effects of Accelerated Ageing

Complementarily, a study on accelerated ageing of rubbers treated with FA solutions has been carried out to determine the time that the effects of FA persist on the rubber surface before forming the adhesive joint. Industrially, this aspect is important to determine the duration and stability of the surface preparation of rubbers treated with FA. As an example, the *T*-peel strength of R2 rubber treated with 0 and 2 wt% FA, after

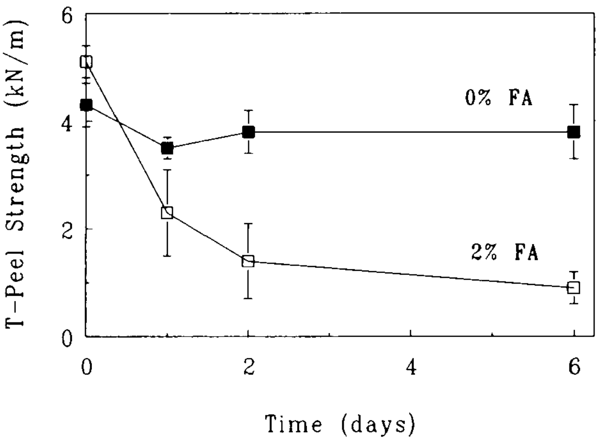


FIGURE 8 *T*-peel strengths of R2 rubber heat-treated at 70°C as a function of the treatment time.

an ageing treatment at 70°C between 1 hour and 6 days, can be seen in Figure 8. Heat treatment produces a decrease in the *T*-peel strength of the adhesive joint which is more noticeable for the rubber treated with FA. The longer the ageing time, the more marked the decrease in *T*-peel strength. This is explained in Figure 9, where the IR spectra of the R2 rubber before and after ageing at 70°C for 6 days are shown together. For the untreated rubber (Figure 9a), the temperature favours the migration of zinc stearate to the surface (bands appearing at 1395 and 1538 cm^{-1}), whilst for the rubber treated with FA (Figure 9b) all the bands corresponding to FA disappear and moreover the bands corresponding to the zinc stearate reappear. These results explain the drop in the *T*-peel strengths experienced after the heat treatment, although they do not clarify the reasons why a much more noticeable drop is produced in rubbers treated with FA. In any case, at a practical level, it is advisable to treat the rubbers with FA immediately before forming the adhesive joints, to ensure the optimum effect of the treatment on the adhesion properties.

Summary

To sum up, it can be indicated that treatment of styrene-butadiene vulcanized rubbers with fumaric acid solutions in 2-butanone/ethanol (1:1) improves adhesion with polyurethane adhesives through three adhesion mechanisms: *i*) Mechanical (creation of surface roughness); *ii*) Thermodynamical (increase in surface energy); and *iii*) Chemical (elimination of abhesive substances, creation of C—O groups). These adhesion mechanisms are also those which contribute to the enhanced adhesion obtained in the halogenation of styrene-butadiene vulcanized rubbers[3] but with the fumaric acid treatment, in addition, the reaction is quick (30 minutes), the solutions are stable for a long period of time and there is no risk of toxicity. Consequently, it is feasible to consider the possibility of replacing the halogenation of styrene-butadiene vulcanized rubbers with the FA treatment. For this reason, the effectiveness of both treatments have been compared through the determination of the *T*-peel strengths for several

TABLE VI

T-peel strengths (kN/m) of PU adhesive joints of several commercial styrene-butadiene vulcanized rubbers treated with solutions of 2 wt% fumaric acid in 2-butanone/ethanol (1:1) or with solutions of 2 wt% trichloroisocyanuric acid (TCI) in 2-butanone

Styrene-butadiene rubber	Wiping with 2-butanone/ethanol (1:1)	2wt% FA in 2-butanone/ethanol (1:1)	2wt% TCI in 2-butanone
R1	5.6-A	9.0-A	11.5-M
R2	5.0-A	6.0A	12.0-A
R3	3.4-A	4.8-S/A	5.2-S
R4	3.4-A	4.9-S/A	4.8-M/S
R5	4.6-A	6.7-S/A	6.2-S/A
R6	3.4-A	5.5-S/A	6.4-M
R7	6-A	7.1-A	8.7-A
R8	2.7-A	4.3-S/A	4.9-S/A
R9	4.2-A	6.4-S/A	6.4-S/A
R10	4.6-S/A	5.1-M/A	5.3-M/S/A
R11	4.1-M/A	3.7-M/N/A	5.0-M/N/A
R12	3.6-A	5.0-A	5.3-A/S

(a) Kind of failures in the adhesive joint:
A = Adhesion failure
S = Exfoliation of a very superficial layer of rubber
M = Cohesive failure of rubber
N = Cohesive failure of adhesive

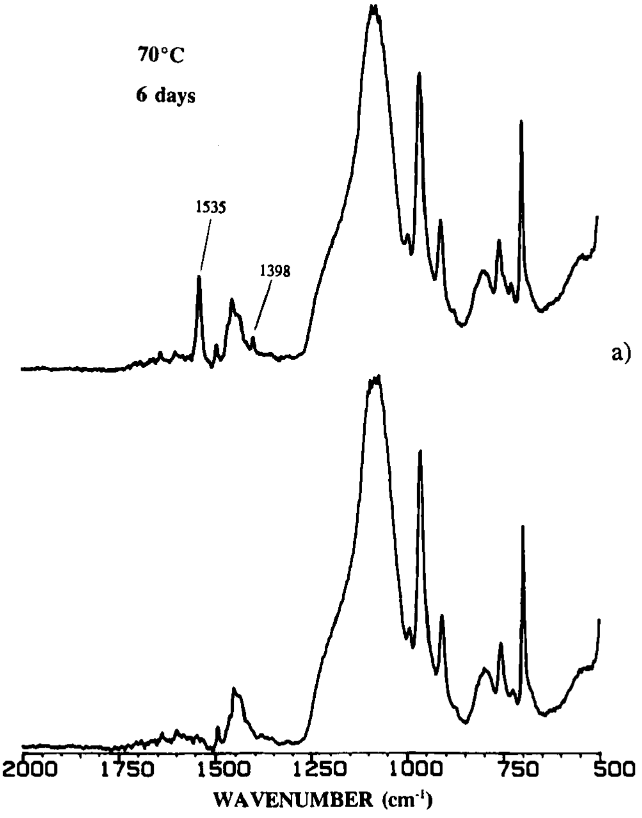


FIGURE 9 IR spectra of R2 rubber before and after heat treatment at 70°C for 6 days with a) 0 wt% fumaric acid, and b) 2 wt% fumaric acid.

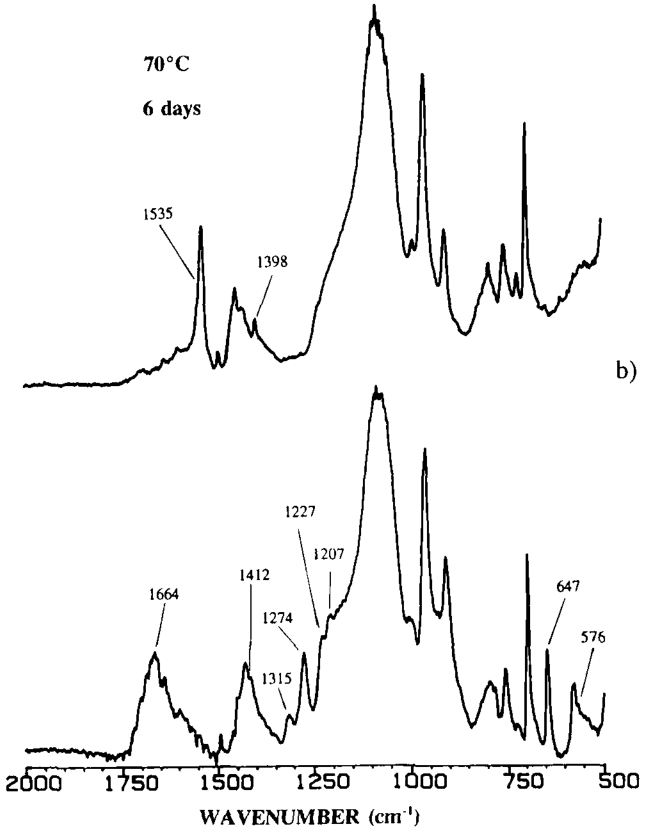


FIGURE 9 (*Continued*)

different commercial SBRs treated with fumaric acid or trichloroisocyanuric acid under the conditions described in the experimental section of this paper. The results obtained are gathered in Table VI, showing that both halogenation and fumaric acid treatments improve the adhesion of SBRs. Even though the halogenation treatment of some rubbers gives greater *T*-peel strengths than treatment with fumaric acid, with both treatments high values are reached (close to those corresponding to the cohesive failure of the material). Consequently, the surface treatment with FA solutions can be considered as an alternative to halogenation for styrene-butadiene vulcanized rubbers.

CONCLUSIONS

Surface treatment of styrene-butadiene vulcanized rubbers with FA solutions is effective, due to the creation of surface roughness, an increase in surface energy, the elimination of abhesive substances, and the creation of chemical groups on the surface. These modifications contribute to the improvement of adhesion in these rubbers. The nature of the solvent mixture used to apply the FA to the rubber surface, as well as the nature of the rubber itself, determines the effectiveness of the surface treatment. The use of FA solutions leads to optimum results when the surface of the rubber has been previously roughened. In all cases, improvement in the adhesion of styrene-butadiene vulcanized rubbers comparable to that obtained through halogenation is produced and, moreover, the FA treatment lacks some of the disadvantages of halogenation. For this reason, it could be an alternative surface treatment for these rubbers in the footwear industry where halogenation is a customary treatment.

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