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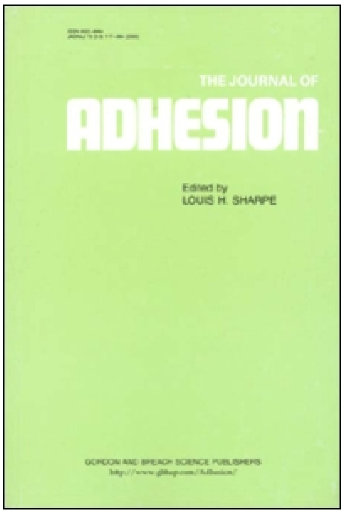

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Adhesion of Styrene-Butadiene Rubbers with Different Silica Content*

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The influence of silica content of four styrene-butadiene rubbers on their adhesion to polyurethane adhesives was studied. Untreated rubber shows no adhesion due to a weak boundary layer of zinc stearate. Roughening removed zinc stearate from the rubber surface, increased the surface energy and produced surface roughness, so improved adhesion was obtained. The adhesion increased as the silica content in rubber increased, due to an improvement in intrinsic adhesion, and mechanical and physical properties of the rubbers. Chemical surface treatments (halogenation with trichloroisocyanuric acid, treatment with fumaric acid) provided higher adhesion than roughening. In general, chlorination was somewhat more effective than the treatment with fumaric acid, especially in roughened rubbers. Improved adhesion of chemically surface-treated rubbers was due to enhanced mechanical, thermodynamic and chemical adhesion, and to the improved physical, mechanical and viscoelastic properties of rubbers.

KEY WORDS: styrene-butadiene; surface treatments; roughening; halogenation; fumaric acid; silica; solvent based polyurethane adhesives

1. INTRODUCTION

The nature and formulation of synthetic vulcanized rubber determines its adhesion with different adhesives. Some adhesion problems in styrene-butadiene rubbers are due to mould release agents, low-molecular weight substances able to migrate to the rubber surface (*i.e.* zinc stearate) and to incompatibility with some adhesives.[1,2] A noticeable improvement in adhesion is obtained by applying surface treatments to rubber. Physical (*i.e.* roughening) and/or chemical (*i.e.* sulphuric acid, halogenation, carboxylic acid) surface treatments have been proposed to develop adhesion in several styrene-butadiene, natural or nitrile rubber compounds.[3-7] In some studies[6,7] it was suggested that the nature of the rubber and the compounding affect the effectiveness of chemical surface treatments.

Silica is generally added in rubber compounding to provide improved mechanical properties and to decrease production costs.[8] The role of silica in rubber adhesion has

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* One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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not yet been clearly stated. Therefore, the main objective of this study is to determine the influence of the silica content of styrene-butadiene rubber formulations on their adhesion to polyurethane adhesives. The effectiveness of physical (roughening), chemical (halogenation, fumaric acid) and physical + chemical surface treatments to promote the adhesion of rubber will be discussed.

2. EXPERIMENTAL

2.1. Styrene-butadiene Rubbers (SBR)

Four synthetic sulphur-vulcanized SBR rubbers were used. The rubbers have the same formulation (Table I) except for different amounts of Ultrasil VN3 precipitated silica (15–47 parts by weight in respect to rubber). The nomenclature used corresponds to the capital letter **R** followed by the amount of silica in the rubber. Several physical properties of rubbers were measured, including hardness (ISO 868–85), density (ISO 2781–88), abrasion resistance (ISO 4649–85), and tensile strength at different degrees of elongation (ISO 37–77. A type I dumbbell test pieces were used).

Surface treatments of SBR rubbers Roughening was carried out to remove nearly 0.5 mm of the external surface of the rubber. Additionally, halogenation and a treatment with fumaric acid (*trans*-1,2-ethylene dicarboxylic acid) were applied to the untreated and roughened rubber surface. Halogenation was carried out with 2-butanone solutions containing 2 wt% of trichloroiscyanuric acid (TCI); the time of halogenation was 18 hours. 2 wt% fumaric acid (FA) solutions in 2-butanone: ethanol (1:1 by wt) were applied to the rubber surface; the treatment time was 18 hours. More experimental details were given elsewhere.[6,7]

2.2. Experimental Methods

Surface-treated rubbers were characterized by IR spectroscopy, contact angle measurments (ethylene glycol, 25°C), and Scanning Electron Microscopy (SEM).

TABLE I
Formulation of styrene-butadiene rubbers

Component	Rubber			
	R15	R23	R36	R47
Styrene resin	31.5	31.5	31.5	31.5
SBR 1712	31.5	31.5	31.5	31.5
SBR 1502	37.0	37.0	37.0	37.0
Silica	14.5	22.5	36.0	46.6
Stearic acid	0.9	0.9	0.9	0.9
Paraffinic wax	2.4	1.8	2.4	2.4
Benzoic acid	0.5	0.5	0.5	0.5
Zinc oxide	2.7	2.7	2.7	2.7
N-Cyclohexyl-2-benzothiazole sulphenamide	1.4	1.4	1.4	1.4
Tetramethyl thiuram disulphide	0.4	0.4	0.4	0.4
Sulfur 80%	2.7	2.7	2.7	2.7

IR studies A Nicolet 510 FTIR spectrophotometer was used with a signal/noise ratio of 0.04 %T (at 2000 cm^{-1}). IR spectra were obtained by using the attenuated total multiple reflection method (ATR); a thallium bromoiodide crystal (KRS-5) was used. More details on this technique have been given earlier.[2]

Contact angle measurements Contact angles of surface-treated rubbers were measured in a Ramé-Hart 100 goniometer. Single sessile drops (2 μl) of etane diol (99% minimum purity) were placed on the rubber surface in a hermetic, isothermal (25°C) and solvent-saturated chamber, and the contact angles on both sides of the drops were measured. The measurements were taken 10 minutes after the drops were placed on the surface. Average values of at least three drops on three different batches of the same surface-treated rubber were taken and the standard deviation was always less than 2°.

SEM Micrographs of surface-treated rubbers were taken in a Jeol SEM JSM 840 microscope. The samples were gold-coated to give sufficient contrast in the micrographs.

Peel strength measurements Adhesion was measured by means of T-peel tests of joints between identically surface-treated rubbers. A solvent based polyurethane adhesive (18 wt% of *Pearlstick* 45–40/15 polyurethane-Merquinsa S.A., Barcelona-in 2-butanone), with a Brookfield viscosity of 2.6 Pa.s, was used to join the rubber test pieces. The following detailed experimental procedure was used. Strips (150 × 30 mm) of vulcanized styrene-butadiene rubber (SBR)-about 3 mm thick-were used to prepare the adhesive joints. After surface treatment (roughening, halogenation, fumaric acid), the PU adhesive was applied to the rubber surface and left to dry for 40 min (weight of dried adhesive film = 100 mg). The PU adhesive film was heated to 80°C using infrared radiation in order to facilitate contact of the adhesive applied to the two identically surface treated SBR strips. The strips were then placed in contact and a pressure of 3 atm was immediately applied for 10 seconds to achieve a suitable joint. The adhesion was determined between 30 seconds and 72 hours after two strips were joined. The T-peel strength was measured on an Instron 1121 (peel rate: 0.1 m/min). The values obtained were the average of three tests (standard deviation was less than 5%). More details were given elsewhere.[6]

3. RESULTS AND DISCUSSION

3.1. Characterization of SBR Rubbers

Table II shows the experimental values of some physical properties of SBR rubbers, including the hardness, density, abrasion resistance, and tensile strength at different degrees of elongation (100%, 200%, at break). According to these values, the addition of silica to SBR rubber improves its physical properties, and there is a more marked increase of each physical property when the amount of silica in the rubber increases. Tensile strengh at 100% and 200% changes more noticeably for silica amounts of 23–36 wt%, for which it is expected to find the most important differences in mechanical properties. In fact, considering that in T-peel the tensile stresses at the interface are caused by bending with a significantly lower strain (and therefore stress) at the adhesive interface depending on the angle of the fracturing interface at a steady-state peel

TABLE II
Some physical properties of rubbers

Rubber	Hardness (Shore °A)	Density (g/cm^3)	Abrasion Resistance (mm^3)	Tensile strength at break (MPa)	Tensile strength at 100% (MPa)	Tensile strength at 200% (MPa)	Elongation at break (%)
R15	79	1.08	154	8.6	3.0	4.9	330
R23	80	1.11	164	10.6	2.6	4.4	431
R36	85	1.15	164	15.3	4.3	6.8	420
R47	91	1.19	168	17.5	4.4	6.8	480

configuration, an influence of the physical and mechanical properties on adhesion (measured from T-peel experiments) of the four rubbers is expected.

A more complete description of the behaviour of the rubbers under tensile loading may be obtained from stress-strain curves (Figure 1) Actually, the curves are of load/original cross-sectional area *versus* deformation, *i.e.*, they are "engineering" stress-strain curves) All show a non-linear stress-strain curve, as is usual in filled amorphous rubber,[9] the deviation from the linearity becoming more marked in the rubbers with higher amounts of silica. R36 and R47 rubbers show the highest stress values for a given strain and exhibit the more pronounced rubber-like behaviour, *i.e.* an interfacial failure would be observed in the rubbers with high amounts of silica.

3.2. Roughening of SBR Rubber

All untreated SBR rubbers studied show lack of adhesion (Figure 2) (The experimental points, left to right, correspond to the four rubbers, R15–R47) because they contain zinc stearate, an abhesive component of rubber compounding.[6] Roughening of SBR

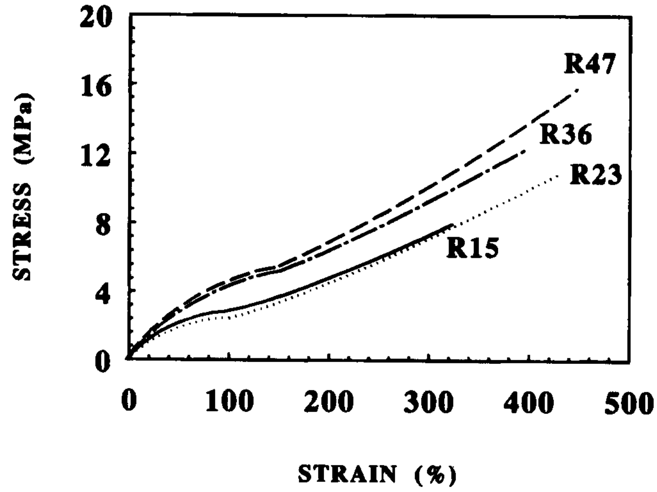


FIGURE 1 Stress *versus* strain relationships for styrene-butadiene rubbers containing different amounts of silica.

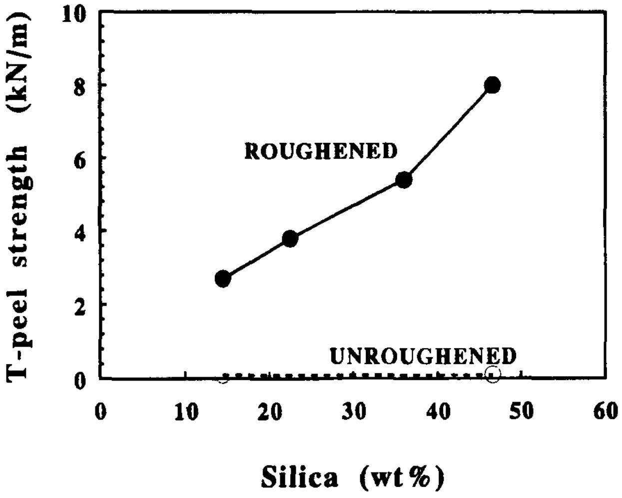


FIGURE 2 *T*-peel strength of SBR rubber/polyurethane adhesive/SBR rubber joints as a function of silica content of rubbers. An adhesion failure is always produced. The experimental points, left to right, correspond to the four rubbers, R15–R47.

produces a noticeable increase of T-peel strengh (Fig. 2), which is more noticeable as the amount of silica in the rubber increases; adhesion values near 8 kN/m were obtained, and an adhesion failure (visually determined) was always found.

The development of T-peel strength was monitored with time after adhesive joint formation (Fig. 3). The T-peel strength for R15 rubber is smaller than for R47, and as the time increases the adhesion increases, more markedly for R47 rubber. This increase

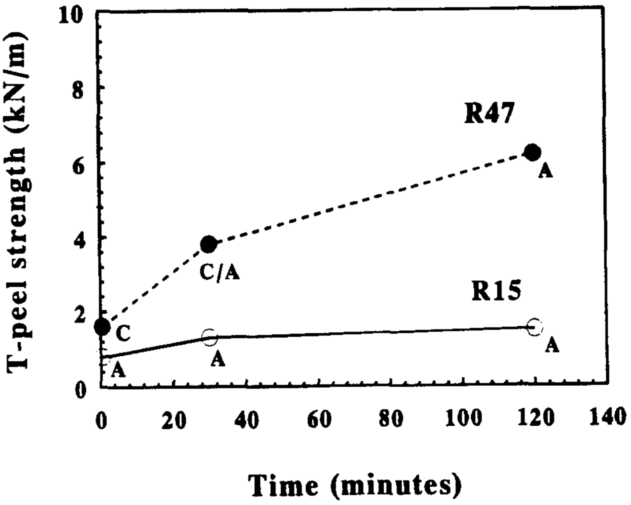


FIGURE 3 Variation of *T*-peel strength with the time after SBR rubber/polyurethane adhesive/SBR rubber joint formation. Type of failure: *C* = adhesive cohesion; *A* = adhesion.

partially influences the kind of failure of joint (from cohesive failure of the adhesive in the first stages of adhesive joint formation, to adhesion failure as the time increases). Thus, the silica content of rubber affects both the T-peel strength and the kind of failure of the joint. The increase of adhesion produced by roughening, which is more pronounced in rubbers with high silica content, can be ascribed to several factors.

IR spectra of unroughened R15 and R47 rubbers (Fig. 4) show the presence of zinc stearate (1540 cm^{-1}). Although the amounts of stearic acid and zinc oxide are similar in

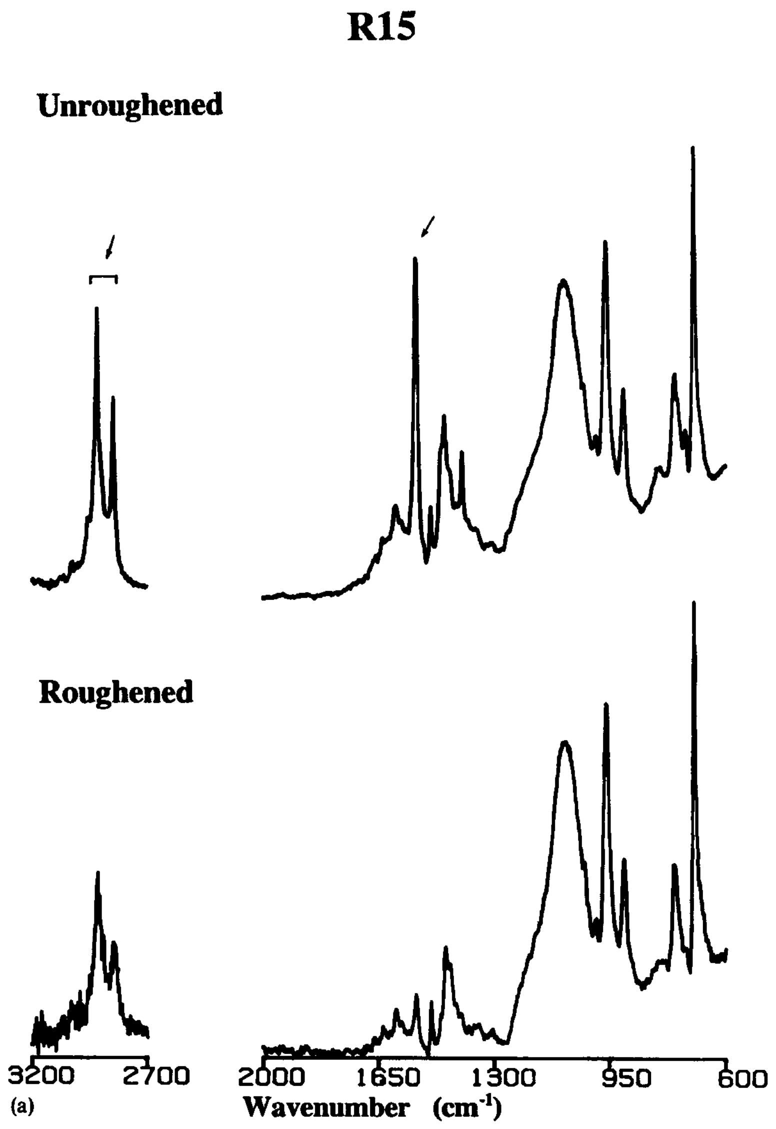
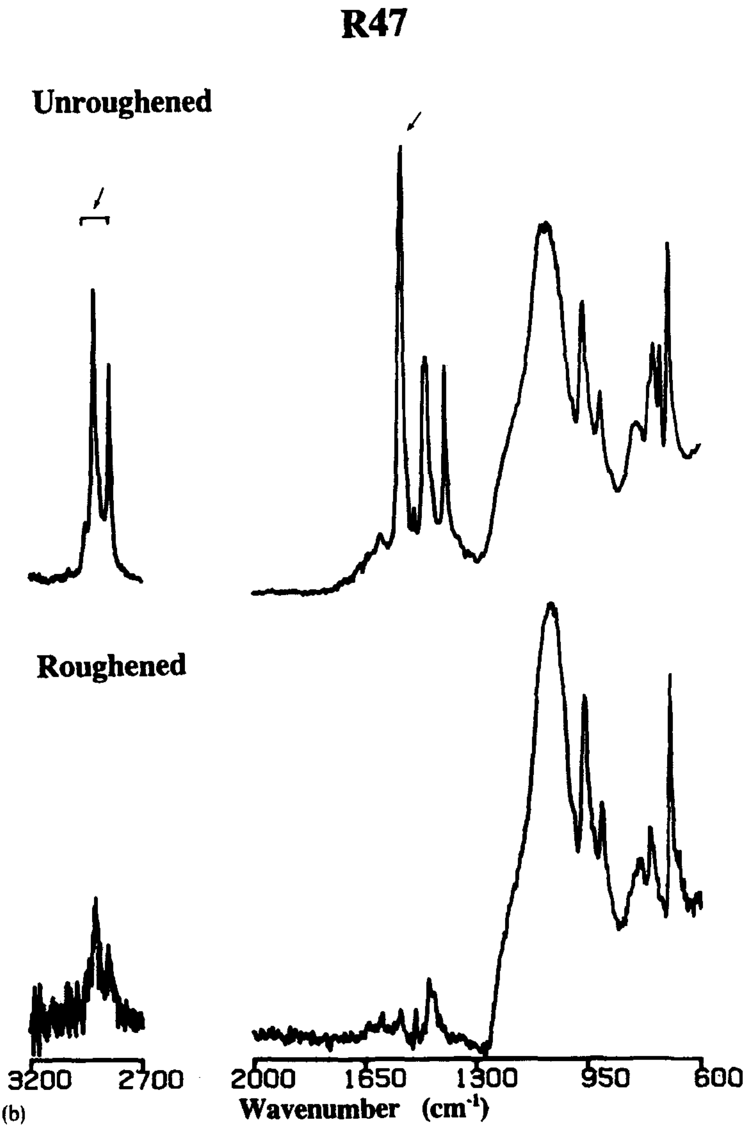


FIGURE 4 IR spectra of untreated and roughened rubbers: a) R15 rubber; b) R47 rubber.


R47

Unroughened

Roughened

FIGURE 4 *(Continued)*.

all rubbers, the surface concentration of zinc stearate is higher in R47 rubber (with high silica content). A definitive explanation has not yet been established but probably a high silica content in rubbers may facilitate the migration of zinc stearate to the surface. The IR spectrum of R47 shows a smaller relative intensity of C=C bands (703, 760, 797, 910, 964 cm^{-1}) in comparison with R15 rubber, due to its higher silica content. Roughening removes zinc stearate from the rubber surface (reduction of intensity of bands at 1540 cm^{-1} and at 2850-CH_2 groups–and 2920 cm^{-1}-CH_3 groups), more efficiently in rubbers with high silica content.

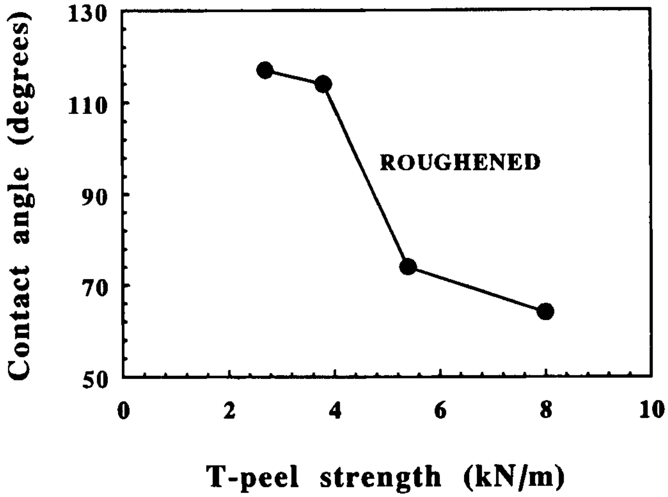


FIGURE 5 Contact angle (ethane diol, 25°C) on roughened rubber with different content of silica as a function of *T*-peel strength of SBR rubber/polyurethane adhesive/SBR rubber joints. The experimental points, left to right, correspond to the four rubbers, R15–R47.

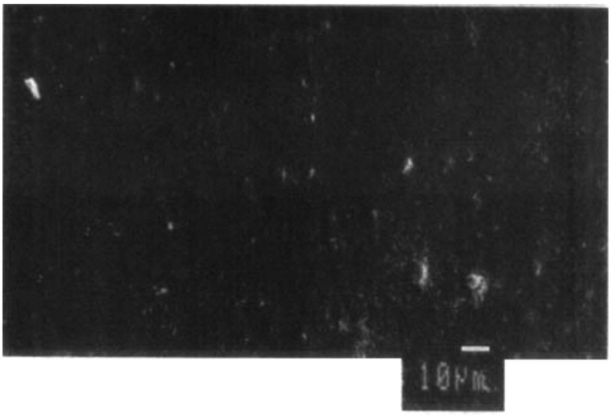
Figure 5 shows a decrease of the contact angle for roughened rubber as the amount of silica increases. The highest T-peel strength corresponds to the smallest contact angle. Thus, the higher the amount of silica, the higher the surface energy of rubber. Furthermore, SEM photographs (Fig. 6) show the creation of roughness on the rubber surface, which should enhance the mechanical adhesion. The effects produced on the surface topography by roughening are very similar in all rubbers, *i.e.* there is an influence of silica content. Thus, an increase of mechanical and thermodynamic adhesion, and the removal of a weak boundary layer (zinc stearate) on the rubber surface, explain the improvement of adhesion for roughened SBR rubbers.

On the other hand, the increase of adhesion as the silica content in roughened rubber increases cannot be explained by only an improvement of intrinsic adhesion. Although the increase of silica content in rubber favoured the removal of zinc stearate and increased its surface energy, the differences in adhesion might also be influenced by the mechanical response of each rubber to the force to peel. Figure 7 shows how the T-peel increased when the tensile strength at break of roughened rubbers is improved, the increase being more noticeable in R47 rubber. Considering that in T-peel the tensile stresses at the interface are caused by bending with a lower strain at the adhesive interface, for all samples the increasing modulus of the filled rubber adherends is more directly related to the increase in peel strength, and thus a curved T-peel *vs* tensile strength plot should be expected. On the other hand, the viscoelastic dissipation of rubbers in T-peel, which is related to the viscous component of mechanical stress response, becomes more important in the rubber with high amount of silica (there will be more numerous silica particle interfaces). Although we do not have viscoelastic data, both the elastic and viscous contributions to the energy of the rubbers will influrence the value measured in peel.

3.3. Chemical Surface Treatments of SBR Rubbers

3.3.1. Chemical surface treatment of unroughened rubbers Surfaces of unroughened rubbers were treated with TCI (halogenation) and with fumaric acid (FA). Figure 8 shows the T-peel strength of joints between surface-treated rubbers. Chemical treatments always increase the adhesion to an extent which is a function of the silica content in the rubber. The effectiveness of FA treatment in R15 rubber is less pronounced than halogenation (a rubber cohesive failure is produced), whereas both halogenation and FA treatment of R47 rubber are similarly effective (an adhesion failure is produced).

R15



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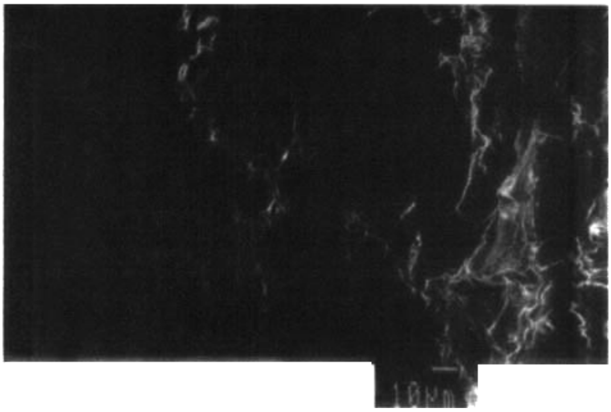
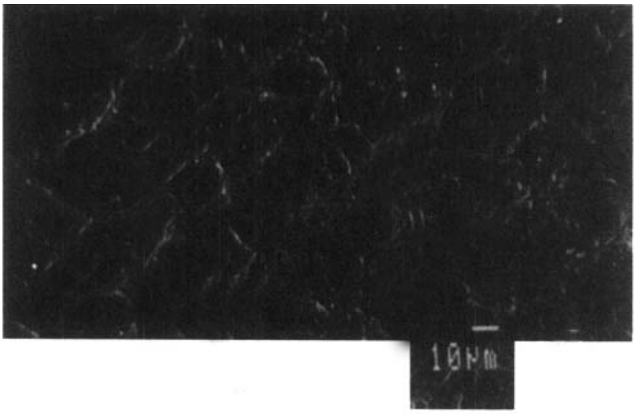


(a) ROUGHENED

FIGURE 6 SEM micrographs of untreated and roughened rubbers: a) R15 rubber; b) R47 rubber.

R47



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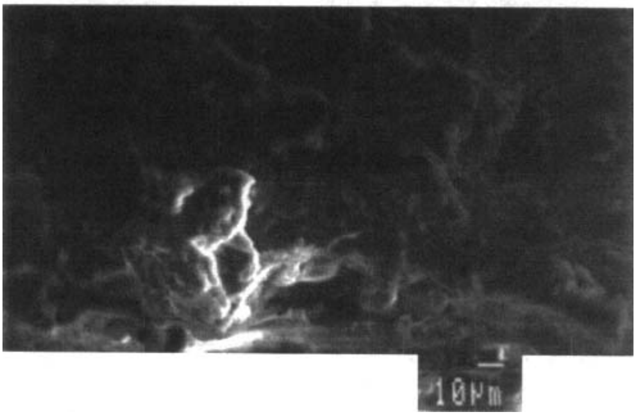


(b) ROUGHENED

FIGURE 6 *(Continued).*

Halogenation treatment provides smaller adhesion in R47 rubber because, accordcing to Table III, the tensile strength at break of halogenated rubbers is greatly reduced, facilitating the rubber cohesive failure when the silica content is small. Furthermore, according to Table IV, there is an influence of the mechanical properties of rubbers in T-peel because a thick rubber layer as a result of cohesive failure remains on chlorinated R15 rubber, whereas a predominant adhesion failure is produced in R47 rubber. On the other hand, according to Figure 4, the rubber with high silica content

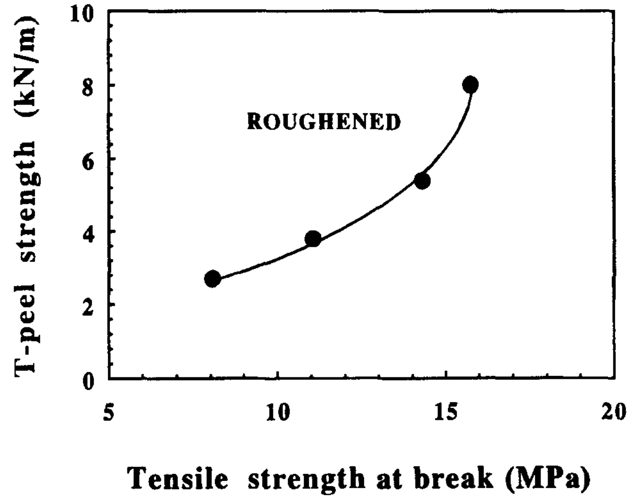


FIGURE 7 Relationship between *T*-peel strength of roughened SBR rubber/polyurethane adhesive/roughened SBR rubber joints and tensile strength at break of rubbers.

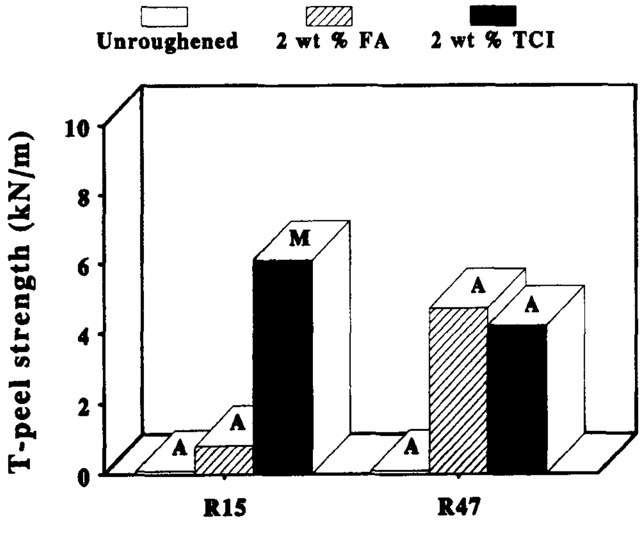


FIGURE 8 *T*-peel strength of unroughened, chemically surface-treated SBR rubber/polyurethane adhesive/unroughened, chemically surface-treated SBR rubber joints for R15 and R47 rubbers. The kind of failure is given by capital letter *A* (adhesion failure) or *M* (rubber cohesive failure).

has a higher surface concentration of zinc stearate which may reduce the effectiveness of the halogenation treatment. IR spectra of chlorinated surface-treated R15 and R47 rubbers are shown in Figure 9. Chlorination of rubbers favours the removal of zinc stearate, decreases the intensity of C=C bands, produces C—Cl groups (759, 1399,

TABLE III
Tensile strength at break of unroughened, chemically surface-treated rubbers

Rubber	Tensile strength (MPa)		
	Unroughened	2 wt% TCI	2 wt% FA
R15	8.3	4.6	7.7
R23	10.6	6.0	10.0
R36	12.9	9.7	13.5
R47	17.6	13.2	14.9

TABLE IV
Remarks on the kind of failure of surface-treated, unroughened rubber/polyurethane adhesive joints

Rubber	Surface treatment	Kind of failure	Remarks
R15	2 wt% TCI	M	Rupture produced at moving clamp side; thick rubber layer (near 0.5 mm) as a result of cohesive rupture
	2 wt% FA	A	100% adhesive in one rubber adherend; stick-slip surface
R47	2 wt% TCI	A	70% adhesive in one rubber adherend
	2 wt% FA	A	100% adhesive in one rubber adherend

1416 cm^{-1}) and forms C—O groups (1704 cm^{-1}) by oxidation of C=C bonds. These chemical surface modifications are more noticeable in R15 rubber.

FA treatment is more effective when the silica content of the rubber is high (Fig. 8). The treatment does not produce significant changes in tensile strength at break of rubber (Table III), and the increase of silica favours the adhesion (100% adhesion failure is always produced, but in R15 rubber a stick-slip adhesive surface is found–Table IV). IR spectra of R15 and R47 rubbers treated with FA are shown in Figure 9. FA treatment favours the removal of zinc stearate (1540 cm^{-1}, decrease in intensity of CH_2 and CH_3 bands at 2849–2919 cm^{-1}), and the formation of C—O groups (1670 cm^{-1}) different from those existing in the IR spectrum of FA. A smaller degree of reaction of FA with R15 rubber is produced in comparison with R47, and although chlorination also produces the removal of zinc sterate, the FA treatment is more effective.

Contact angle measurements (Fig. 10) are very similar in unroughened chemically surface-treated R15 and R47 rubbers. Chemical treatments increase the surface energy of rubbers, independently of their silica content, more noticeably when the FA treatment is used. These trends do not agree with the values of peel strength of Fig. 8.

SEM micrographs provide additional information. Halogenation of rubbers (Fig. 11) does create roughness and small, rounded, well-distributed rubber particles (larger size in R15 rubber) over the surface. Thus, mechanical adhesion should be favoured in chlorinated rubbers independently of their silica content. On the other hand, FA treatment (Fig. 11) does not produce cracks or modification of surface topography of rubbers but solid FA clusters are formed on the surface, as a result of an excess of FA and/or a low degree of reaction with rubber. The size of the FA clusters is

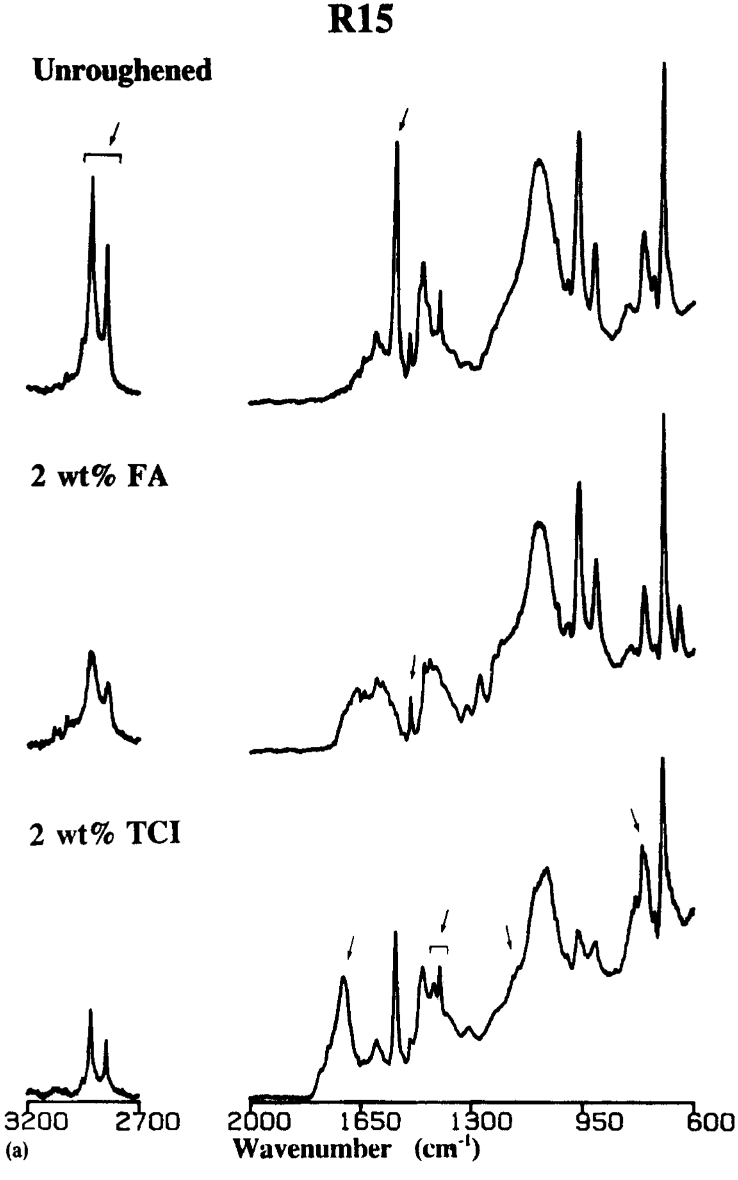


FIGURE 9 IR spectra of unroughened, chemically surface-treated SBR rubbers: a) R15 rubber; b) R47 rubber.

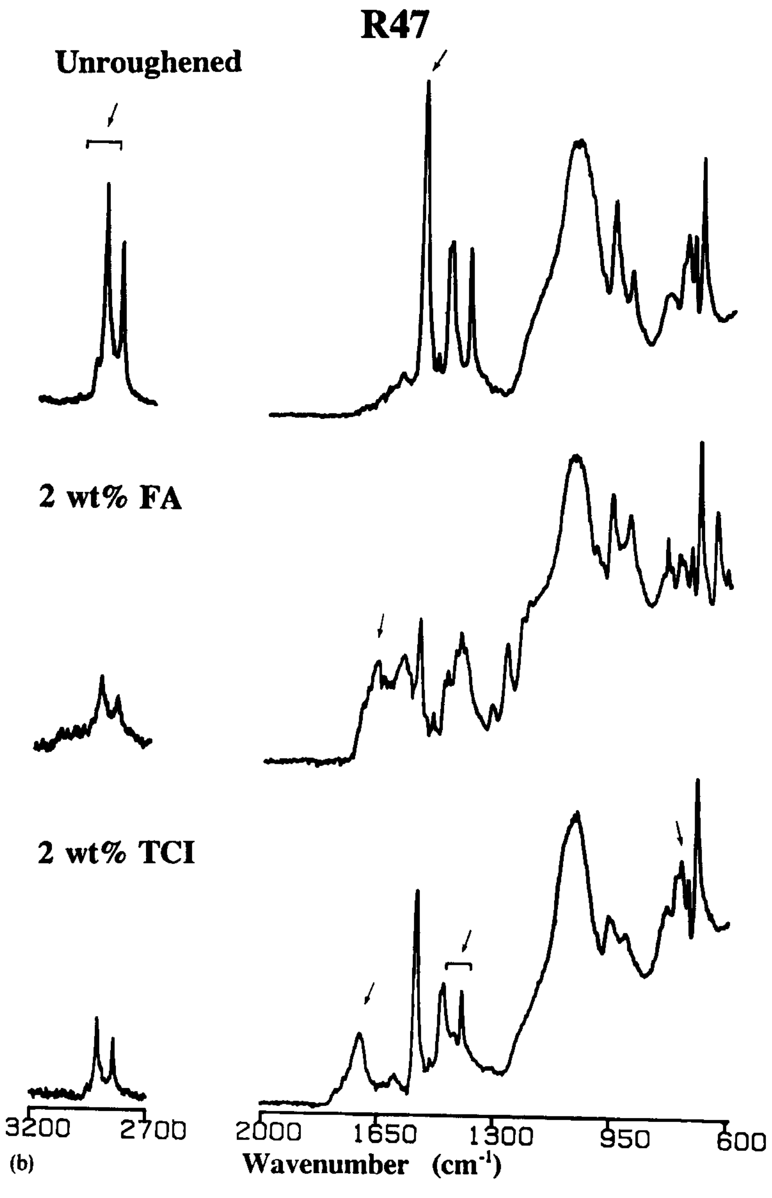


FIGURE 9 *(Continued)*.

much larger in R15 (30–40 μm) than in R47 rubber (10–15 μm). Big particles in R15 rubber might disturb its adhesion.

Therefore, according to the above results, the effect of silica content of chlorinated unroughened rubber on adhesion can be related to differences in chemical adhesion, and in mechanical and physical properties of rubbers: the increase of

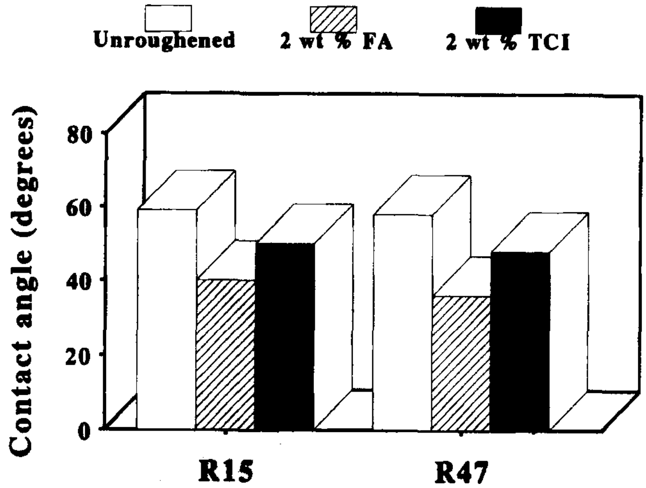


FIGURE 10 Contact angle measurements (ethane diol, 25°C) on unroughened, chemically surface-treated SBR rubbers.

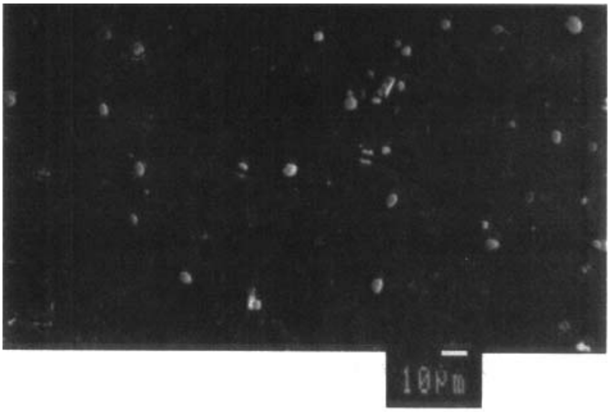
silica content in rubber does not favour a high effectiveness of the chlorination. In the case of FA treatment, the increase of silica content of rubbers enhances the adhesion.

3.3.2. Chemical surface treatment of roughened rubbers Figures 12 and 13 show T-peel strength values of joints between roughened rubber treated with TCI (halogenation) or FA. Green adhesion (monitored from 30 seconds until two hours after adhesive joint formation) increases as the silica content of rubber increases (Fig. 12), and the halogenation provides higher peel strength than FA treatment. Two hours after joint formation, an adhesion failure is obtained in joints with R47 rubber whereas a rubber cohesive failure is produced in R15 rubber, because its physical properties are reduced. T-peel strength (72 hours after adhesive joint formation) also increases as the amount of silica in roughened rubber increases (Figure 13). Halogenation is more effective than FA treatment, the differences in T-peel strength being greater as the amount of silica in rubber increases. Although a rubber cohesive failure is found in chlorinated and FA surface-treated roughened R15 rubber, the increasing silica content in rubber gradually favours an adhesion failure or a rubber surface failure. In contrast, a smaller T-peel strength is obtained in unroughened chemically treated rubbers and the increase in adhesion produced by halogenation is more marked than that for the FA treatment in roughened rubbers.

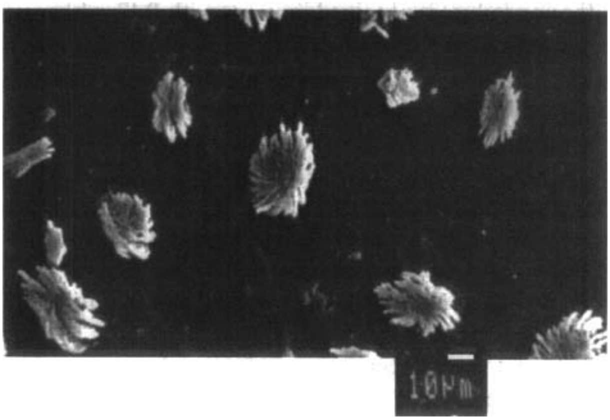
According to Table III the halogenation produces a decrease in the tensile strength at break of rubbers, whereas no differences in rubber treated with FA are found. Because the tensile strength at break of halogenated roughened rubber is drastically reduced, the cohesive failure of the rubber may be facilitated. In the rubber treated with FA there are no important changes in mechanical properties, and thus cohesive failure will not be facilitated. In fact, according to Table V, there is an evolution from a thick layer of halogenated R15 rubber produced as a result of cohesive rupture, to a predominantly adhesion failure homogeneously distributed in both adherends (from 70% in R23 rubber to 90% in R47) shared with a thin surface layer for halogenated R47 rubber. For rubbers treated with FA a similar trend is obtained, although the adhesion failure is mainly produced in one rubber adherend (90% of adhesion failure in R23 rubber to 100% in R47 rubber).

The effectiveness of chemical treatments of roughened rubbers can be explained by using different experimental techniques. Contact angles are drastically reduced when

R15



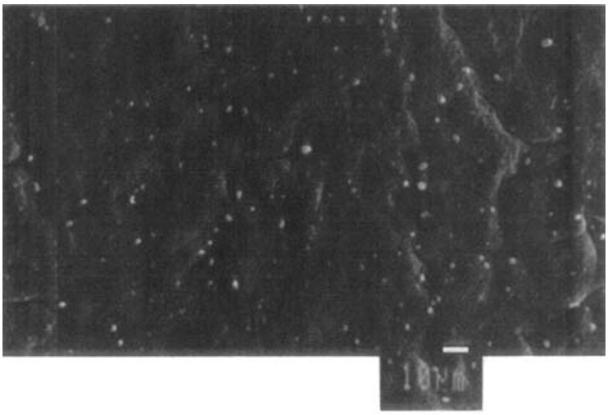
2 wt % TCI



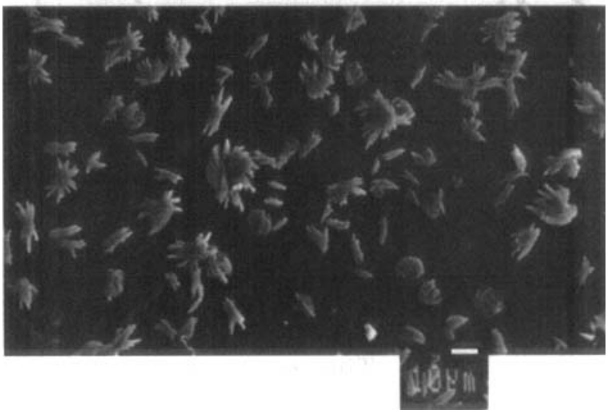
(a) **2 wt% FA**

FIGURE 11 SEM micrographs of unroughened, chemically treated rubbers: a) R15 rubber; b) R47 rubber.

R47



2 wt % TCI

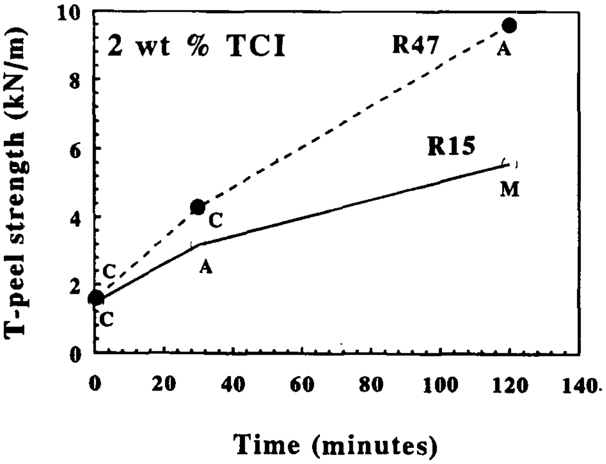


(b) 2 wt % FA

FIGURE 11 *(Continued)*.

roughened rubbers are chemically treated (Fig. 14), due to a noticeable increase of surface energy (much more than in unroughened, chemically-treated rubbers). Similar surface energies are found for TCI and FA treatments, and no influence of silica content of rubber can be observed.

IR spectra of treated, roughened rubbers (Fig. 15) show similar noticeable effects (independent of the silica content in the rubber) when a treatment with FA (creation of C—O groups, reduction of intensity of CH_2 and CH_3 bands) or a treatment with TCI



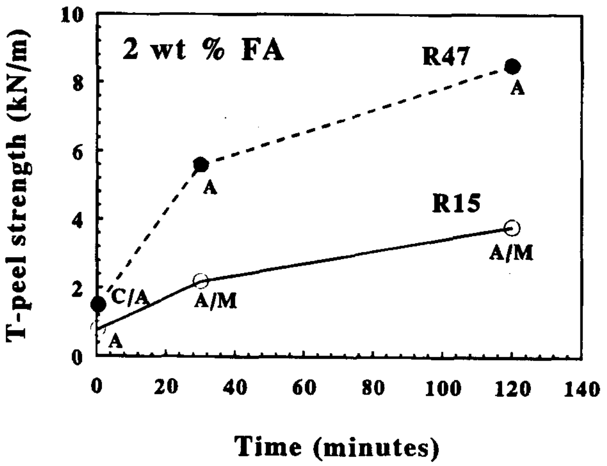


FIGURE 12 Green *T*-peel strength of roughened, chemically surface-treated SBR rubber/polyurethane adhesive/roughened, chemically surface-treated SBR rubber joints for R15 and R47 rubbers. The kind of failure is given by capital letters *A* (adhesion failure), *C* (cohesive failure of adhesive) or *M* (cohesive failure of rubber).

(creation of C—Cl and C=O groups, reduction of intensity of CH_2 and CH_3 bands) are carried out. On the other hand, the degree of surface modification obtained by halogenation of rubber is more marked than by treatment with FA. Consequently, chemical adhesion is more enhanced in chlorinated rubbers (Fig. 13). On the other hand, a comparison between IR spectra of unroughened and roughened, chemically-treated rubbers (Fig. 9 and 15) show a more extended degree of reaction of TCI and FA with roughened rubber than with unroughened; except for the removal of zinc stearate

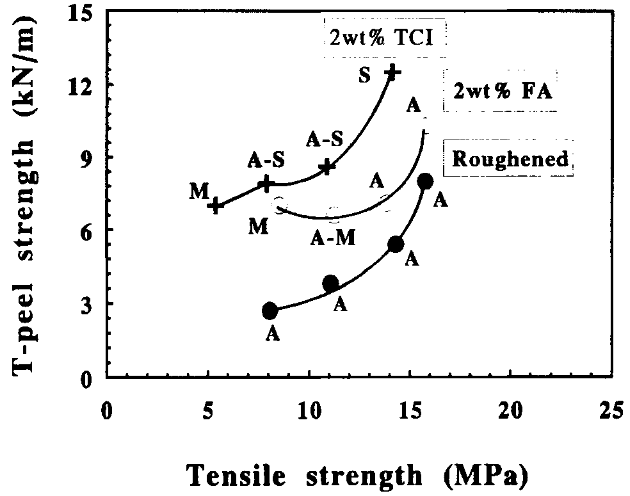


FIGURE 13 Relationship between *T*-peel strength of roughened, chemically surface-treated SBR rubber/polyurethane adhesive/roughened, chemically surface-treated SBR rubber joints (72 hours after adhesive joint formation) and tensile strength at break of roughened, chemically surface-treated SBR rubbers. The kind of failure is given by capital letter *A* (adhesion failure), *M* (cohesive failure of rubber) or *S* (rubber surface failure). The four experimental points on each curve, from left to right, correspond to the four rubbers, R15–R47.

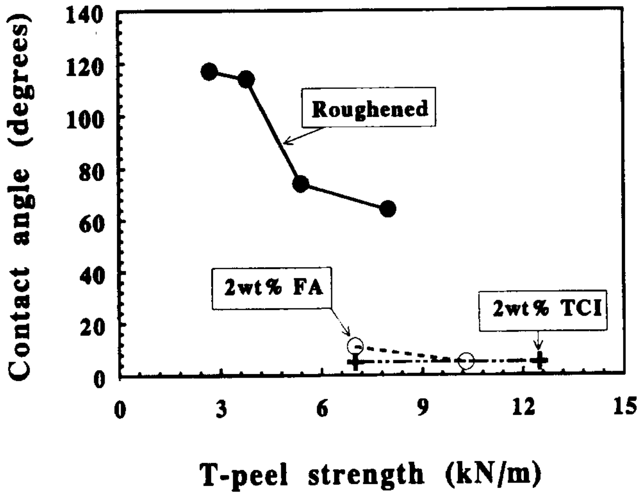


FIGURE 14 Contact angles (ethane diol, 25°C) on roughened, chemically-treated rubbers with different silica content as a function of *T*-peel strengh of roughened, chemically surface-treated SBR rubber/polyurethane adhesive/roughened, chemically surface-treated SBR rubber joints. The experimental points, left to right, correspond to the four rubbers, R15–R47.

by roughening, similar modifications are produced on the rubber surface of unroughened and roughened rubber. Thus, the presence of zinc stearate on the rubber surface greatly determines the effectiveness of chemical surface treatments.

Enhanced adhesion of roughened SBR rubber treated with TCI or FA might be, therefore, ascribed to an improvement of mechanical, thermodynamic and chemical adhesion. Furthermore, TCI treatment is somewhat more effective

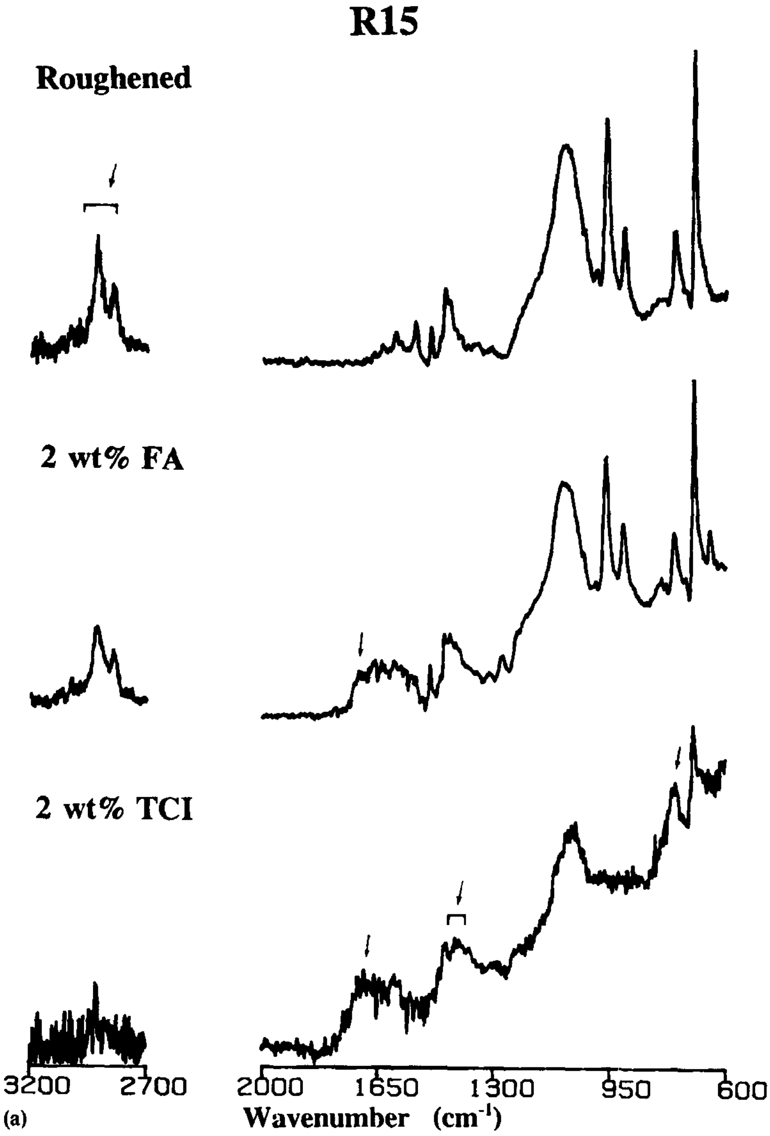


FIGURE 15 IR spectra of roughened, chemically surface-treated SBR rubbers: a) R15 rubber; b) R47 rubber.

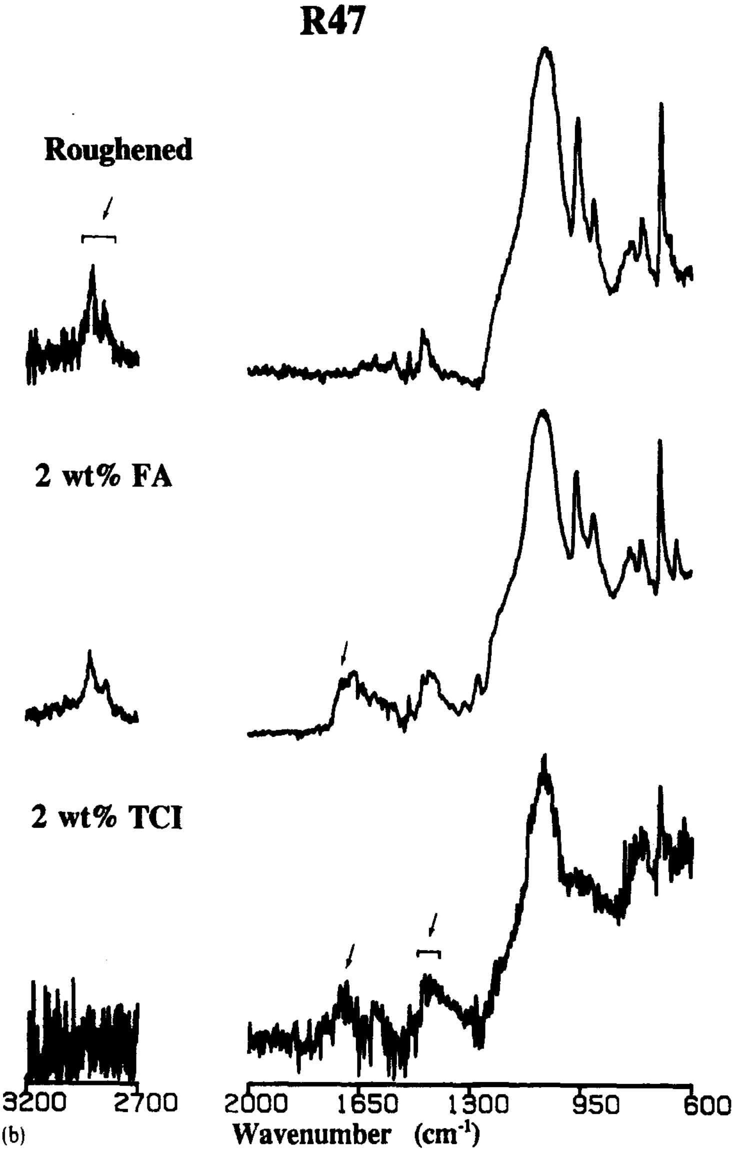


FIGURE 15 (*Continued*).

than FA treatment, due to improved chemical and mechanical adhesion (higher degree of roughness and more marked cracks can be noticed in SEM pictures–not given in this paper). Silica content of rubber does not modify the extent of these mechanisms of adhesion, although *T*-peel strength increases as the silica content in rubber increases.

TABLE V
Remarks on the kind of failure of surface-treated, roughened rubber/polyurethane adhesive joints

Rubber	Surface treatment	Kind of failure	Remarks
R15	2 wt%TCI	M	Rupture produced at moving clamp side; thick rubber layer (near 0.5 mm) as a result of cohesive rupture
	2 wt% FA	M	Rupture produced at moving clamp side; a thicker rubber layer is produced as peel progresses
R23	2 wt% TCI	A-S	70% adhesive + 30% thin rubber layer in one rubber adherend
	2 wt% FA	A-M	90% adhesive + 10% very thin rubber layer in one rubber adherend
R36	2 wt% TCI	A-S	90% adhesive homogeneously distributed in both rubber adherends + 10% very thin rubber layer in one rubber adherend
	2 wt% FA	A	100% adhesive in one rubber adherend
R47	2 wt% TCI	S	90% adhesive homogeneously distributed in both rubber adherends + 10% very thin rubber layer in one rubber adherend
	2 wt% FA	A	100% adhesive in one rubber adherend

4. CONCLUSIONS

1. The increase of silica content in SBR rubbers produced improved physical, mechanical and adhesion properties.
2. Roughening of SBR rubber increases its adhesion to polyurethane adhesives,this increase being more important as the silica content increases. The improvement is due to removal of zinc stearate, to an increase of surface energy and to mechanical adhesion. The increase of mechanical properties of rubber by adding silica also determines its adhesion.
3. Chemical surface treatments of unroughened rubbers enhance their adhesion. Different degrees of effectiveness are reached by halogenation and FA treatments, depending on silica content of the rubbers. Chlorination is somewhat more effective than treatment with FA in R15 rubber, but both treatments are similarly effective in R47 rubber. Improved intrinsic adhesion and physical properties of rubbers with different silica contents also determine the effectiveness of the treatment.
4. Chemical surface treatments are more effective in roughened than in unroughened rubbers, probably due to the different surface concentration of zinc stearate in rubbers with different amounts of silica. *T*-peel strength increases as the silica content of rubber increases, the chlorination treatment being somewhat more effective than the FA treatment. However, no differences in mechanical, thermodynamic and chemical adhesion have been found between the rubbers with different silica contents, although the mechanical properties of rubber might be responsible for the improved *T*-peel strengths.

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