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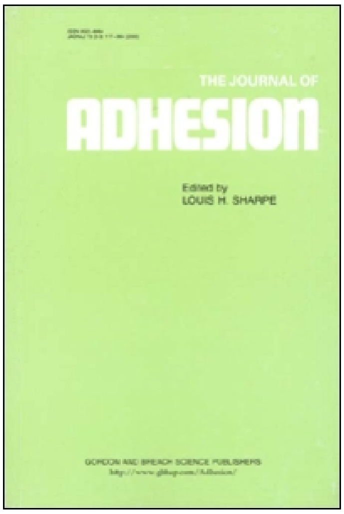

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Addition of Silica to Polyurethane Adhesives

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Addition of Silica to Polyurethane Adhesives

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The influence of the addition of silica (Aerosil-200) (5–25 wt%) to polyurethane adhesives on their adhesion properties with non-chlorinated and surface-chlorinated rubbers has been studied. The chlorinating agent was Trichloroisocyanuric acid (TIC) in 2-butanone solution at a concentration of between 1 and 9 wt%. In general, silica produced an increase in the adhesive viscosity and an improvement of green (immediate) peel strength (especially with chlorinated rubber). The best results were obtained for a silica content of 10–20 wt%. However, the addition of silica did not improve the peel strength after a thermal ageing process. Polyurethane adhesives containing silica undergo an improvement in their resistance to degradation by chlorine on the rubber surface. On the other hand, the chlorination of silica produces the rupture of Si—O bonds and the formation of Si—H and Si—Cl groups. Furthermore, the stirring speed (directly related to the dispersion) of silica into the adhesive is an important parameter which affects the viscosity and peel strength. A stirring speed of 1000 rpm gives the best silica dispersion.

KEY WORDS Adhesion; silica; polyurethane adhesives; chlorination of rubber; green peel strength; contact angle measurements.

I INTRODUCTION

Mineral additives (talc, kaolin, silica)[1] have been shown to improve wet tack, bond reinforcement and viscosity control of adhesives.[2,3] It has been established that highly dispersed amorphous hydrophilic silica contributes useful thixotropic effects on non-polar or slightly viscous but not thixotropic liquids.[4] On the other hand, high surface area silicas also enhance the long term stability of adhesive joints. Nowadays, fumed silicas with specific surface areas from 50 to 400 m^2/g are often used as a component in the formulation of polyurethane adhesives.

Polyurethane adhesives (PU) are often employed to join styrene-butadiene rubbers (SBR) in the footwear industry due to their advantageous properties with respect to polychloroprene adhesives.[5] In order to solve some adhesion problems with PU and SBR materials, some years ago a chlorination of the rubber surface was proposed.[6–8] The chlorination of synthetic rubber is a quite complex process, which involves substitution and addition reactions.[9] TIC is an active halogenating and a strong oxidizing agent, able to produce a direct convertion of ethers into esters.[10] An ionic mechanism has been proposed to explain the reaction of TIC with 1,4 butadiene groups of the rubber, an electrophilic addition being the initial step to create cyclic species (probably a charge-transfer intermediate[10]) which afterwards results in the chlorinated product.[11]

There are a few papers dealing with the adhesion of polyurethane adhesives to chlorinated rubbers,[7,8,12,13] especially when the addition of silica to adhesives is considered. However, a systematic study has not yet been carried out. The main objective of this paper will be to study the influence of the addition of silica on the formulation of PU-adhesives and on their adhesion properties to non-chlorinated and surface-chlorinated styrene-butadiene-rubbers.

II EXPERIMENTAL

II.1 Materials

Vulcanized styrene-butadiene rubber (SBR) sheets about 3 mm thick were used. This rubber is commonly used in the footwear industry as a reference material to test the peel strength of adhesive joints. Table I includes the SBR formulation.

Trichloroisocyanuric acid (1,3,5-trichloro-1,3,5-triazine-2,4,6-trione) was the halogenating agent applied to the rubber surface. The effectiveness of this organic chlorine donor to improve the adhesion of styrene-butadiene rubber and the ability of TIC to oxidize the rubber surface has been previously shown.[11,14]

Aerosil-200 silica was used as an additive to the polyurethane adhesives. It is a fumed silica comprised of spherical particles with an average diameter of between 10 and 20 nm. This silica is hydrophilic (Figure 1), because of the silanol groups on the surface. Some physical and chemical properties of this silica are given in Table II.

TABLE I
Formulation of SBR rubber

Component	Percentage
SBR 1502	65
SBR 1904	35
Carbon Black (N330)	23
Silica	25
Sulphur	1.76
Cumarone-indene resin (85°C)	3.52
Zinc oxide	3.81
Stearic acid	0.76
N-cyclohexyl-2-benzothiazole sulphenamide	1.14
Phenolic antioxidant	0.78
Dibenzothiazyl disulphide	0.16
Polyethylene glycol	1.13

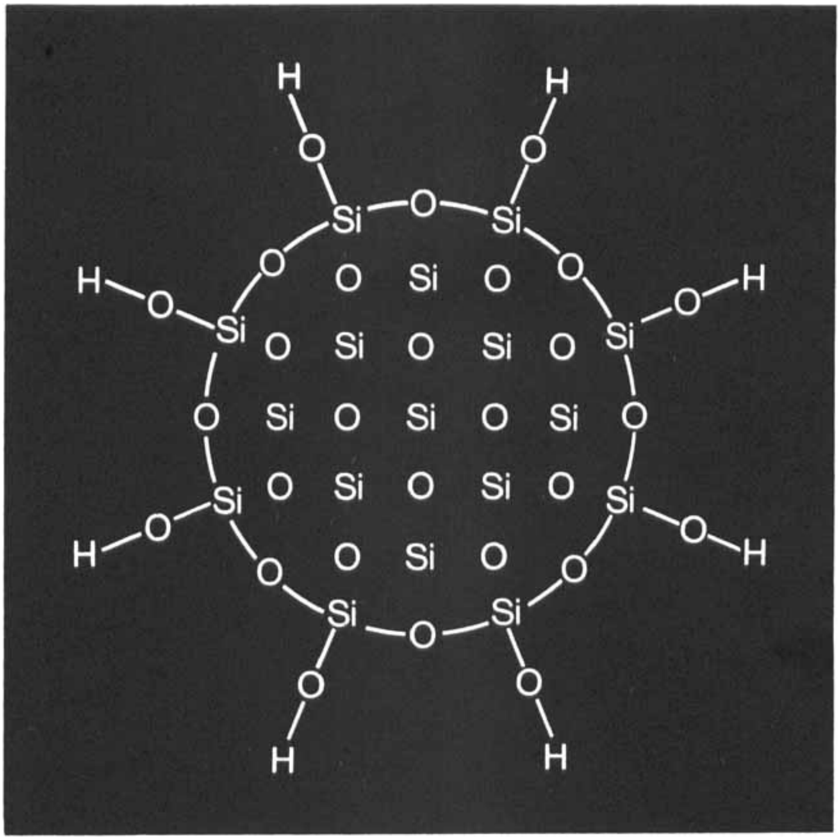

FIGURE 1 Schematic representation of an Aerosil-200 silica particle.

A polyurethane adhesive (PU) based on fully-reacted polycaprolactone supplied by Merquinsa SA (Barcelona, Spain) was used.

Adhesive solutions were prepared by adding 18 wt% of solid polyurethane to 2-butanone, silica being also added (5–25 wt%). Two series of adhesives were obtained:

- Series A. Solid content (polyurethane + silica) was always maintained constant (18 wt%).

TABLE II
Some properties of Aerosil-200

Average primary particle size	12 nm
Tap density standard material	0.05 g/cm^3
Moisture	< 1.5 %
Ignition loss (2 hours 105°C)	< 1.0 %
pH-value (4% aqueous dispersion)	3.6–4.3
SiO_2	>99.8 %
Al_2O_3	< 0.05 %
Fe_2O_3	< 0.003 %

TABLE III
Some characteristics of the PU adhesives

Adhesive	% Sol.	PU/total (%)	Brookfield viscosity (Pa·s, 25°C)	
			1 Week	1 Month
A-0	18.2	18.2	4.0	4.3
Series A				
A-5	18.3	17.1	3.8	4.1
A-10	18.4	16.2	3.6	4.2
A-15	18.1	15.3	4.2	4.4
A-20	18.2	14.4	4.1	4.0
A-25	17.9	13.5	5.5	5.6
Series B				
B-5	19.4	18.0	6.1	7.2
B-10	19.8	18.0	8.3	8.8
B-15	20.8	18.0	11.2	10.6
B-20	21.4	18.0	14.7	15.8

- Series B. Silica was added to an 18 wt% solution of the polyurethane, so that a solid content greater than 18 wt% was obtained.

Adhesives of Series A will be expressed as the capital letter "A" followed by the amount of silica added; Series B maintains the same nomenclature, except that the letter "B" will be used instead of "A." Table III includes some characteristics of the adhesives.

A laboratory mixer (1000 rpm, approximately) provided with a Baird and Tatlock motor with controlled speed was used to prepare the adhesive solutions. An aluminum helicoidal spindle 30 cm long was used to stir the solutions, which were placed in a 2 l glass container (Figure 2). The mixture was stirred for three hours

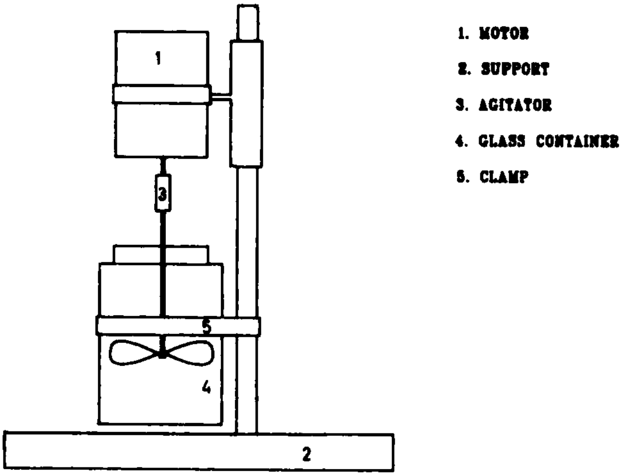

FIGURE 2 Diagram showing the experimental device used to manufacture the adhesive solutions.

at room temperature. Silica was always added (to the mixture) at the beginning of the process. The adhesive solutions were kept in an hermetic container until used.

Eventually, the speed of the laboratory mixer was varied between 400 and 1500 rpm in order to study its influence on peel strength of polyurethane adhesives to rubber.

Adhesives were characterized by using contact angle measurements and infrared spectroscopy. In addition, the Brookfield viscosity of adhesive solutions (at 25°C) over time (1 day, 1 week, 2 weeks, 1 month or more) was measured. Three spindles (no. 3, 4 and 5) and several speeds (5, 10, 20 and 50 rpm) were selected in an RVT Brookfield Synchro-Lectric Viscometer. The measurements were taken after 1 min under each experimental condition.

II.2 Experimental Methods

II.2.1 $N_2/77K$ adsorption isotherm of silica The specific surface area and porosity of Aerosil-200 were calculated from its $N_2/77K$ adsorption-desorption isotherm determined in a Carlo Erba Sorptomatic 1800 instrument. The BET equation was applied to the adsorption isotherms to calculate the specific surface area.[15]

II.2.2 Contact angle measurements Adhesive films were prepared by placing the adhesive solutions in a rectangular mould and allowing the solvent to evaporate slowly to prevent the formation of solvent bubbles.

Contact angles were determined with a Ramé-Hart 100 goniometer. Single sessile drops (2 μl) of water (doubly distilled) and 1-bromonaphtalene (Merck, 98% minimum purity) were placed on the surface of the above mentioned adhesive films or on SBR test samples in an hermetic, isothermal (25°C) and solvent-saturated chamber, and the contact angle on both sides of the drops were measured. Although a constant contact angle was obtained after 5 minutes, the measurements were taken 15 minutes after the drops were placed on the adhesive film. Average values of at least three drops on three different batches of the same SBR rubber or adhesive film were taken and the standard deviation was always less than 2°.

II.2.2 FTIR Studies

A Nicolet 510 FTIR spectrophotometer with a signal/noise ratio of 0.04 % transmittance (at 2000 cm^{-1}) was used. Samples were prepared in three different ways:

- A thin adhesive film was obtained by spreading a drop of the adhesive solutions with a glass rod on a smooth glass surface and allowing the solvent to evaporate. This film was analysed by transmission[16] and 10 scans per experiment were done.
- A KBr:silica (300:1) mix was pressed to prepare a pastille and then was analysed by transmission.
- The non-chlorinated and chlorinated SBR surfaces were analysed using an ATR technique, Multiple Attenuated Total Reflectance.[17] A germanium crystal was

used because of the presence of carbon black in the rubber formulation. The incident angle was 45° and 80 scans per experiment were carried out.[16]

II.2.3 Peel Strength Measurements

Peel strength of adhesive joints created between SBR strips (150 × 30 mm) was measured by a standard peeling test at 180°, which is described in detail in other papers.[18] SBR samples were cleaned in an ultrasonic bath of doubly-distilled water for 15 min and stored in vacuum for 60 minutes to remove any retained water. In some cases, after the cleaning process, SBR was halogenated by brushing its surface with 2-butanone solutions containing TIC between 1 and 9 wt%. A brush was impregnated with the halogenating solutions and the SBR surface was rubbed with it. After 6 hours, the reaction of chlorine with the rubber was complete.[19] Subsequently, 100 mg of the adhesive was applied to the rubber surface and left to dry for 30 minutes. This adhesive film was heated to 80°C using infrared radiation in order to facilitate contact of the adhesive applied to the two SBR strips. The strips were then placed in contact and a pressure of 3 atm. (1 atm. = 101325 Pa) was immediately applied for 10 seconds to achieve a suitable joint.

The green (immediate) peel strength was measured 30 seconds after the two strips were joined. Other test samples were kept at 23°C and 50% relative humidity for 72 hours before the peel strength was measured on an Instron Model 1121 (peel rate: 0.1 m/min). The values obtained were the average of three tests (standard deviation $\sigma<5\%$) for both the green and 72-hour peel strength tests. In order to analyse the stability of the adhesive/rubber interfaces, the test pieces were kept in an air oven at 50°C for one week (thermal ageing test) and then the peel strength was measured (standard deviation $\sigma<5\%$).

III RESULTS AND DISCUSSION

III.1 Silica Characterization

Figure 3 shows the N_2/77K adsorption-desorption isotherm obtained for Aerosil-200 silica. It corresponds to Type IV in the BDDT classification,[20] indicating the mesoporous nature of this silica. There is a hysteresis loop closing at a relative pressure (P/P_o; P_o is the saturation pressure of N_2 at 77K) of approximately 0.8 due to the presence of relatively large mesopores (mean pore size of around 10 nm, according to the Dollimore and Heal method[21,22]). The shape of the hysteresis loop corresponds to Type H1 of the IUPAC classification,[23] which is characteristic of pores between packed spheres. Therefore, it can be assumed that the capillary condensation in mesopores corresponds to the spaces between the silica particles.

On the other hand, the BET equation[23] was applied to the N_2/77K adsorption isotherm in order to obtain the monolayer capacity (n_m). According to this equation:

$$\frac{P}{n(P_o-P)}=\frac{C-1}{n_mC}\cdot\frac{P}{P_o}+\frac{1}{n_mC}$$

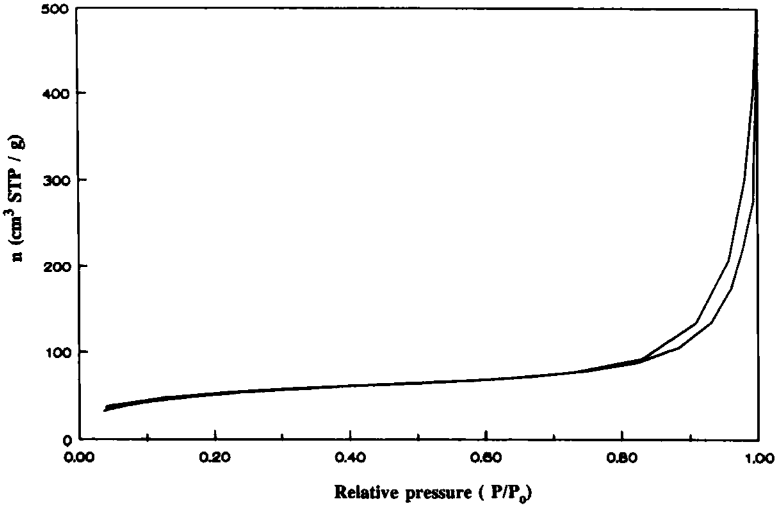

FIGURE 3 N_2/77K adsorption-desorption isotherm of Aerosil-200 silica.

a plot of $P/n(P_o - P)$ *versus* P/P_o should be a straight line, from which n_m and C can be obtained. C is an indirect measurement of the adsorbent-adsorbate interaction. In the case of Aerosil-200 silica a straight line was obtained between P/P_o values of 0.05 and 0.35 and the monolayer capacity was 43 cm³ STP/g and the C value was 132. Considering the relatively low C value, the presence of micropores is not expected in the silica. Specific surface area (S) can easily be calculated from the monolayer capacity (n_m):

$$S = n_m \cdot A \cdot a_m$$

where A is the Avogadro's constant and a_m the cross-sectional area of the adsorbate (0.162 nm²/molecule of N_2 at 77K). The application of the above equation gives a specific surface area of 188 m²/g for Aerosil-200 silica, in accordance with previous results.[24]

Other properties of Aerosil-200 silica are given in Table II. Considering the preparation procedure, an acidic character ($pH<7$), a small particle size and a high purity (greater than 99.8% SiO_2) are expected.

III.2 Characterization of Adhesives

III.2.1 Viscosity Series A This series was prepared by adding different amounts of silica (5–25 wt%) to the polyurethane solutions in 2-butanone but always maintaining the solid content near 18 wt%. Therefore, the larger the amount of silica added, the smaller the PU content in the adhesive. In this series there are two effects which can contribute to a change in the viscosity. An increase in the amount of silica should produce an increase in the adhesive viscosity, because of the thixotropy imparted by the silica.[25] On the other hand, a reduced amount of polyurethane in the adhesive tends to reduce the adhesive viscosity. Consequently, these two factors will have a totally different effect, at constant percentage of solids, on the adhesive viscosity according to the PU/SiO_2 ratio. Table III shows no significant changes in adhesive viscosities with the increasing amount of silica, except for adhesive A-25 which presents a greater value. Viscosities are in the range of 3.6 to 4.2 Pa·s, the value for A-25 adhesive being 5.5 Pa·s.

Figure 4 shows the variation of the SiO_2/PU ratio as a function of the silica content of the adhesives. There is an exponential increase of this ratio with the silica content which is very important for adhesive A-25. Therefore, it is not surprising that the effect of the addition of silica on the viscosity is very noticeable for this adhesive.

The viscosity of the SiO_2/PU solutions remained unchanged 1 month after the preparation of the adhesive, indicating that the presence of silica in the adhesive does not seem to change the viscosity or thixotropic behaviour of the solutions with time, even in the case of composition A-25.

Series B This series was prepared by keeping the amount of polyurethane constant and adding different percentages of silica (from 5 to 20 wt%). Therefore, the larger the amount of silica added, the larger the solid content in the adhesive solution (from 18% to 21.5%). Sample B-25 was prepared but its viscosity was too high and there were problems of adhesion to rubber because of its poor wettability by the adhesive.

In series B, both the elastomer and the silica contributed to an increase in the viscosity of the adhesives, although it is difficult to determine which had a greater influence. According to Table III, there is an increase in viscosity from 6.1 to 14.7 Pa·s, so series B always presents larger viscosities than series A. Figure 4 also shows greater SiO_2/PU ratios in series A with respect to series B, the difference being greater with increasing amount of silica (and solids content). There was also an increase in the viscosity of the adhesives containing silica of about 1.0 Pa·s one month after adhesive preparation.

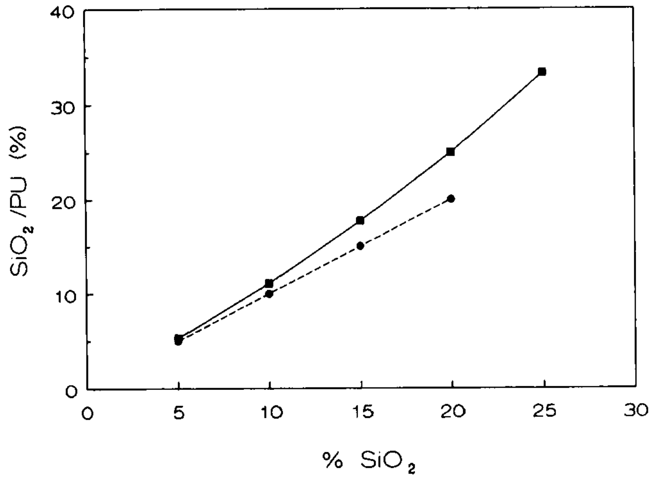

FIGURE 4 Silica/Elastomer ratio as a function of silica content of adhesives. (■) Series A; (●) Series B.

III.2.2 Contact Angle Measurements In order to characterize the adhesive film surfaces, some contact angle measurements were carried out. Figure 5 shows the contact angles obtained by dropping water (an essentially polar liquid) and 1-bromonaphtalene (a non-polar liquid) on the adhesive films. The addition of silica to polyurethane adhesives generally results in a slight decrease in the contact angle (always less than 10° with the increase of silica content in the adhesives). This trend is the same for the polar and non-polar liquids, although differences are more pronounced with water and especially with series B. Therefore, there is an improvement in wettability by the adhesive with the addition of silica, and adhesion will be favoured.

On the other hand, series A generally has greater water contact angles than series

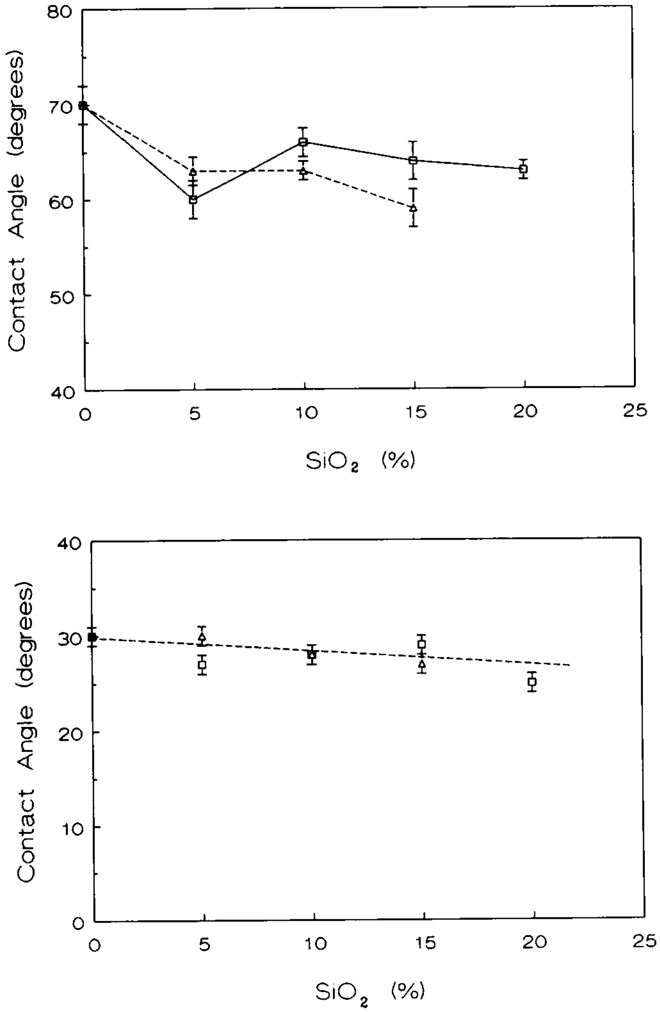

FIGURE 5 Contact angle on adhesive films. a) Water b) 1-bromonaphthalene (□) Series A; (△) Series B.

B, indicating poorer wettability of the adhesives of series A which have a smaller amount of polymer in their formulation.

III.2.3 Adhesive FTIR spectra In order to find out the chemical modifications, if any, produced by adding silica to polyurethane solutions, FTIR transmission spectra were obtained on the adhesive films.

The IR spectrum of silica Aerosil-200 showed typical bands due to the —Si—O—group (3346, 1638, 1075, 1026, 808 cm^{-1}), those at 3346 and 1075 cm^{-1} being quite broad. Additionally a band at 470 cm^{-1} was obtained.

Figure 6 shows the IR spectra of some adhesive films of series A. Series B did not present significant differences in respect to series A, so their IR spectra will not be included in this paper. The IR spectrum of the A-0 adhesive (Figure 6) exhibits some typical bands:

- Urethane group (1730, 1540 cm^{-1})
- Polycaprolactone polyurethane group (1107, 1066, 1049 cm^{-1})

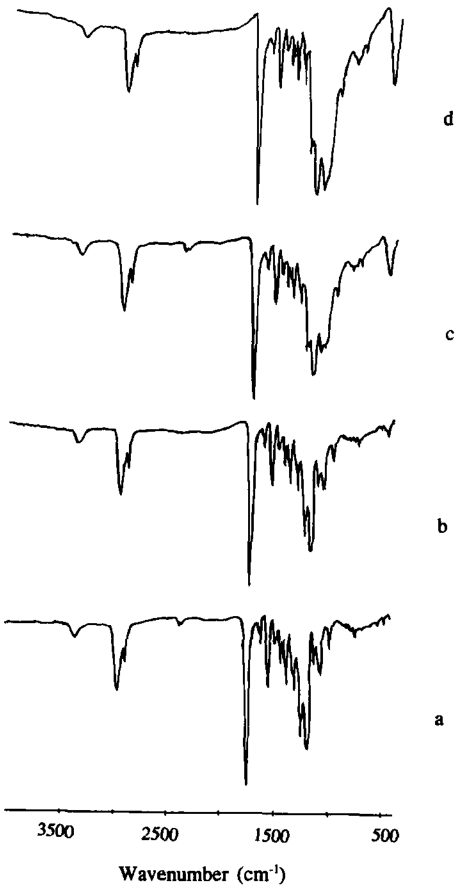

FIGURE 6 FTIR spectra of series A. a) A-0; b) A-5; c) A-15; d) A-25.

- —CH_2—groups (2945, 2866, 1189, 962 cm^{-1})
- Benzene ring (1598, 818, 771 cm^{-1})

It is clear that the silica and the adhesive have two quite close bands, near 1100 and 800 cm^{-1}, but the remainder are easily differentiated. In fact, the IR spectra of series A (Figure 6) reveals an increase in bands due to silica, mainly at 1075 and 1026 cm^{-1}, so that the addition of the silica to the adhesive does not seem to introduce any new bands into the spectra. The greater the silica content in the adhesive, the greater the intensity of bands in the IR spectrum that correspond to silica. However, there is no evidence of chemical changes in the spectra of the adhesives. The intensity of the band at 1730 cm^{-1} (C=O in urethane group) increases with the amount of silica. This band is not present in the silica spectrum, but it is in the adhesive one, so it should indicate any kind of interaction between silica and polyurethane. In fact, a previous paper[26] describes typical $O{=}C{=}(Si_KC_{2-K})$ IR bands between 1735 and 1725 cm^{-1}. This could be an indication of a chemical interaction between silica and elastomer. However, further research will be necessary to corroborate this hypothesis.

III.3 SBR/Adhesive/SBR System

III.3.1 Peel Strength It has previously been stated[27] that the addition of silica to adhesives enhances the green or immediate adhesion to different adherends.

Figure 7a shows green peel strength for series A and series B adhesives. The two series greatly resemble each other. The addition of silica produces a slight increase

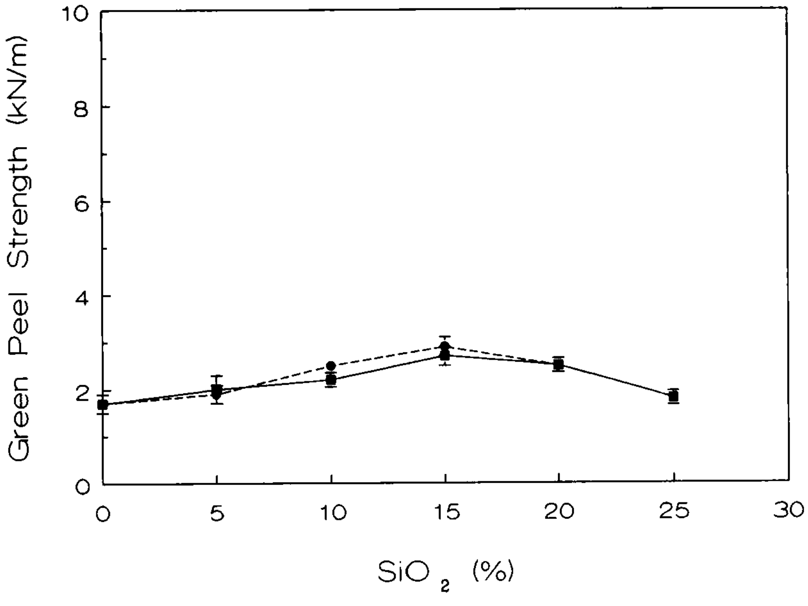

FIGURE 7a Green peel strength for SBR/adhesive/SBR system. (■) Series A; (●) Series B.

in green peel strength (always smaller than 1 kN/m) until the A-15 adhesive, and then a decrease occurs; in fact, the green peel strength of the A-25 adhesive is the same as for A-0. Series B follows the same trend, with B-15 adhesive giving the greatest green peel strength. In all tests carried out there was an adhesion failure of the polyurethane film. The increase of green peel strength is due to the silica added to the polyurethane. However, the decrease found in Figure 7a for high silica content can be explained in a different way for series A and B. In series B, adhesives with a large amount of silica are too viscous to wet the rubber properly. However, in series A there is no change of viscosity with the amount of silica but there is a continuous increase of the SiO_2/PU ratio (see Figure 4), so a noticeable decrease in polyurethane content and an increase in silica content is produced. For adhesives having more silica than A-15 the influence of the silica on green peel strength is less pronounced than that of the polyurethane and a decrease of such green peel strength is produced.

In order to study the influence of the addition of silica to polyurethanes on their final adhesion properties, some peel strength tests (after 72 hours of curing time) were also carried out. Results obtained are given in Figure 7b. The silica content does not influence the peel strength of adhesives with amounts of silica that are smaller than those of A-15 and B-15; however, a large amount of silica produces a decrease in peel strength. In general, peel strength (72 h) values are larger than green peel strength. Therefore, the addition of silica does not improve the final adhesion of the polyurethane adhesive to the rubber.

Thermal ageing tests of adhesive joints were also carried out. Figure 7c shows the peel strength obtained, and the trend is the same as in Figure 7b. However, there is a small increase in peel strength (around 1 kN/m) after the thermal ageing process which is independent of the amount of silica.

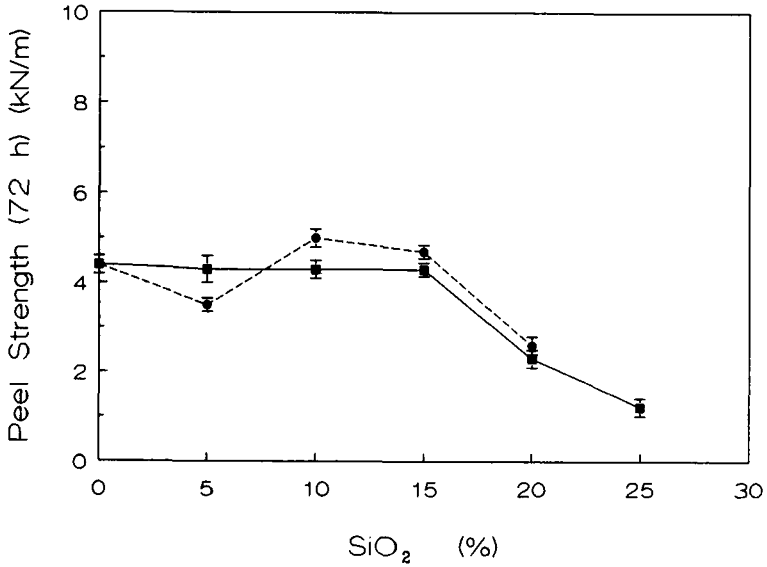

FIGURE 7b Peel strength (72 h) for SBR/adhesive/SBR system. (■) Series A; (●) Series B.

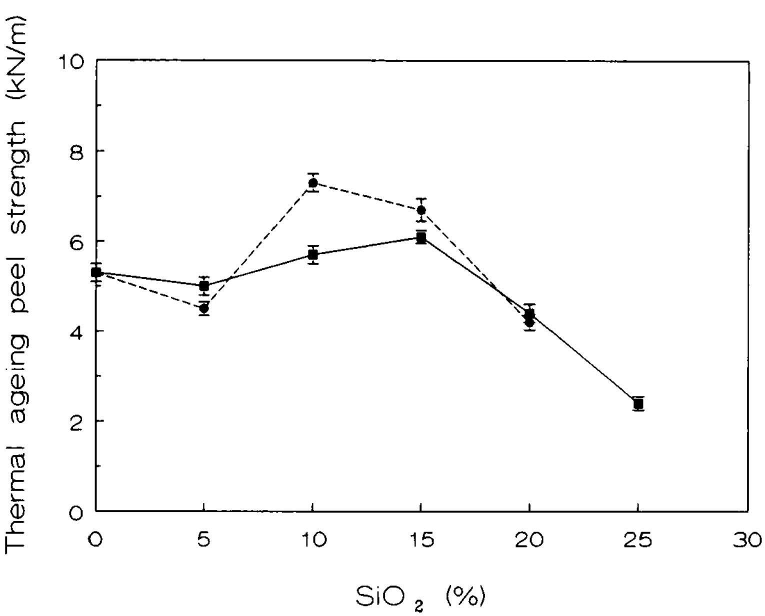

FIGURE 7c Peel strength for SBR/adhesive/SBR system after a thermal ageing. (■) Series A; (●) Series B.

III.3.2 Contact Angle Measurements Contact angles were also measured by placing adhesive drops on a SBR surface. Results obtained are given in Figure 8. In general, there is no difference between series A and B. Only adhesives A-20 and B-20 have larger contact angles (44°) than the adhesive without silica (41°). Contact angles in Figure 8 show a slight decrease when a small amount of silica is added to the polyurethane (adhesives A-5 and B-5 (38°)) and the remainder of the contact angles are similar to that for A-0. Therefore, the silica content does not produce important changes in the adhesive wettability and a noticeable improvement of adhesion properties is not to be expected; in fact, it was found that the addition of silica did not produce differences in peel strength.

III.4 SBR (halogenated)/Adhesive/SBR (halogenated) System

Chlorination of the SBR surface has been found[28-30] to enhance the adhesion properties to polyurethane adhesives. Trichloroisocyanuric acid is quite an effective chlorination agent,[30] so we also studied the influence of silica addition to polyurethanes on the adhesion to surface-chlorinated rubber. Peel strength and contact angle measurements were carried out on chlorinated SBR-polyurethane adhesive joints.

III.4.1. Peel strength measurements Figure 9 shows the green peel strength of SBR(1%TIC)/adhesive/SBR(1%TIC) system as a function of the silica content in

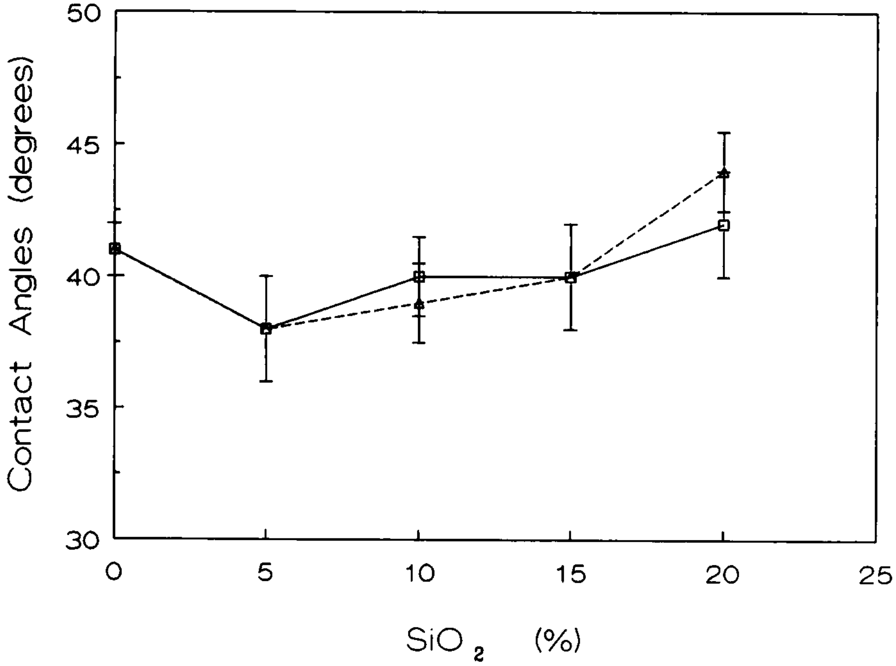

FIGURE 8 Contact angle of adhesive drops placed on a SBR surface. (□) Series A; (△) Series B.

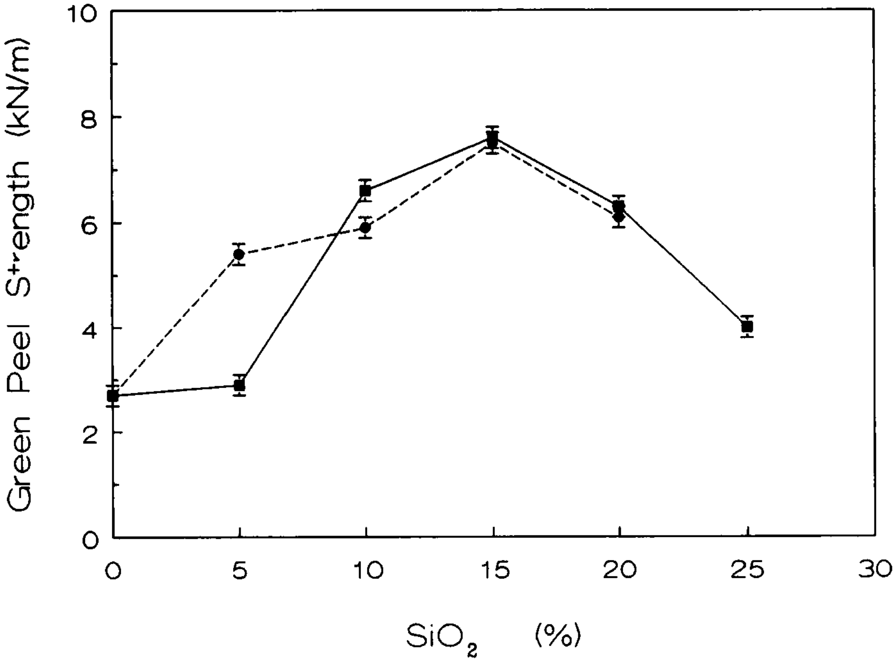

FIGURE 9 Green peel strength of chlorinated (1 wt% TIC in 2-butanone) rubber surfaces. (■) Series A; (●) Series B.

the adhesives. Chlorination treatment of the rubber (1 wt% TIC in 2-butanone) always produces greater green peel strength values than non-chlorinated rubber (Figure 7a). As for non-chlorinated SBR there is an enhancement of the green peel strength with silica until A-15 and B-15, and then a decrease occurs. This decrease is less pronounced than that of non-chlorinated rubber. Therefore, the effect of the addition of silica to polyurethane adhesives is more pronounced in halogenated rubbers. A cohesive failure of the adhesive film was always found.

Figure 10 shows the effect of chlorination (TIC percentages between 1 wt% and 9 wt%) on green peel strength for adhesives without (A-0) and with (A-15 and B-15) silica. An adhesive without silica (A-0) does not show an improvement of green peel strength with the increase of TIC percentage, values around 2 kN/m are always obtained. However, the addition of silica enhances the green peel strength (values near 8 kN/m are obtained). There are no important variations in peel strength until 5 wt% TIC is reached. Percentages of TIC greater than 5 wt% allow a decrease in adhesion that is more significant in series A. This decrease is probably produced by the degradation of the adhesive with the excess of TIC that remains unreacted on the SBR surface, and also there is the possibility of formation of a weak boundary layer of primer contaminating the rubber surface when excessive amounts of TIC are used. The larger the solid content of the adhesive (B-15), the smaller the effect of degradation by reaction of polyurethane with chlorine.

These results show the obvious advantage of using silica as an additive to adhesives for increasing the green peel strength.

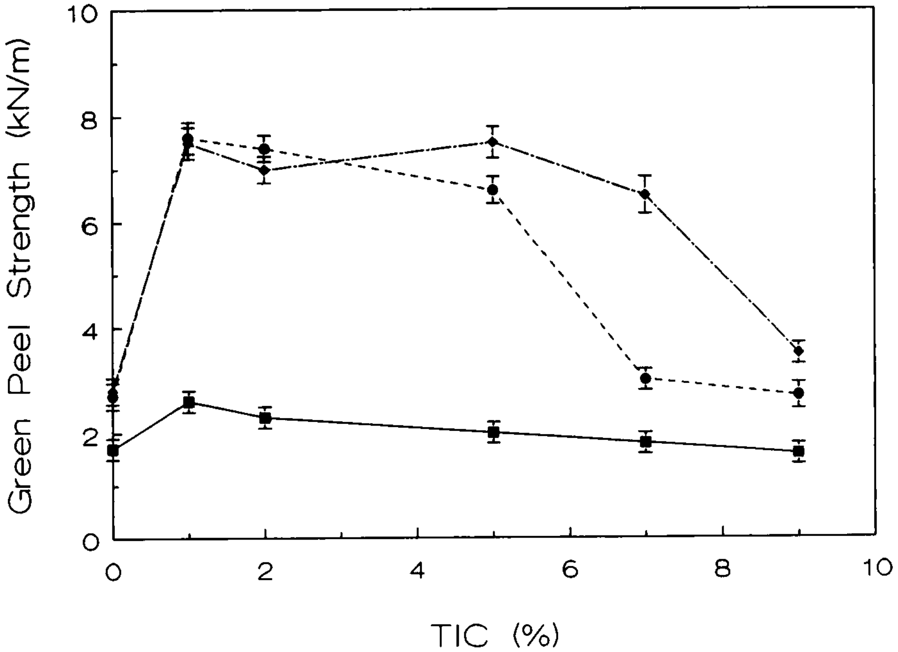

FIGURE 10 Variation of green peel strength of rubbers as a function of the TIC percentage. (■) A-0 adhesive (without silica); (●) A-15 adhesive; (♦) B-15 adhesive.

In relation to peel strength values after 72 hours and following a thermal ageing test, the same trend as for non-chlorinated rubber was found. However, the absolute peel strength values are greater (generally around 12 kN/m) and a cohesive failure of rubber was always produced.

III.4.2 Contact angle measurements Figure 11 shows the contact angles of the adhesive on chlorinated SBR surfaces.

Adhesive A-0 (without silica) shows a decrease in the contact angle which is more noticeable for percentages of TIC larger than 7 wt%, mainly due to the excess of chlorine on the rubber surface.[28] However, adhesives containing silica do not show any change in contact angle, regardless of the percentage of TIC applied to the rubber surface. The increase in the amount of silica in the adhesive produces no change in the contact angle. This lack of change in contact angle might be due to the fact that even small concentrations of silica produce thixotropy in the adhesive, restricting its flow and, thus, its ability to "adjust" the contact angle with the different chemical environments produced on the rubber surface by increasing chlorination. Hence, the silica in the adhesive seems to increase its "resistance" to be degraded by chlorine from the rubber surface, and no decrease of contact angle for TIC percentages greater than 7 wt% is found.

The trend of the contact angles does not agree with that of green peel strength, but it should be considered that the influence of the adhesive joint design is very important in the peeling test, and this is not taken into account in the contact angle measurements.

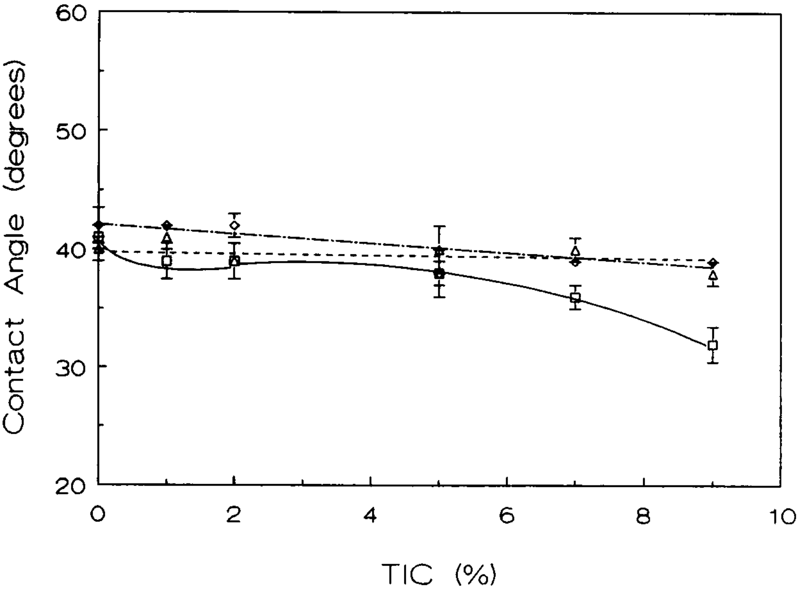

FIGURE 11 Contact angle of adhesive drops placed on TIC-treated rubber surface. (□) A-0; (△) A-10; (◇) A-20.

III.4.3 FTIR Spectra IR spectroscopy was used in order to find out the nature of the interaction between chlorine on the rubber surface and the adhesives containing silica. The adhesive films were immersed in TIC solutions for 10 seconds and, once the solvent was evaporated, the IR spectra were obtained. In relation to the chlorination of SBR (Figure 12), as a result of the addition of chlorine there is a significant reduction in the bands corresponding to the stretch of $—CH_2—$ and trans 1,4 —C=C— groups. Moreover, some new bands appear: 1702 cm^{-1} (carboxylic group created by oxidizing the SBR surface with the chlorination agent), 1420 and 760 cm^{-1} (both corresponding to C—Cl groups). The intensity of these new bands increases depending upon the concentration of trichloroisocyanuric acid applied to the polymer surface and, at the same time, a broad band between 1300 and 1100

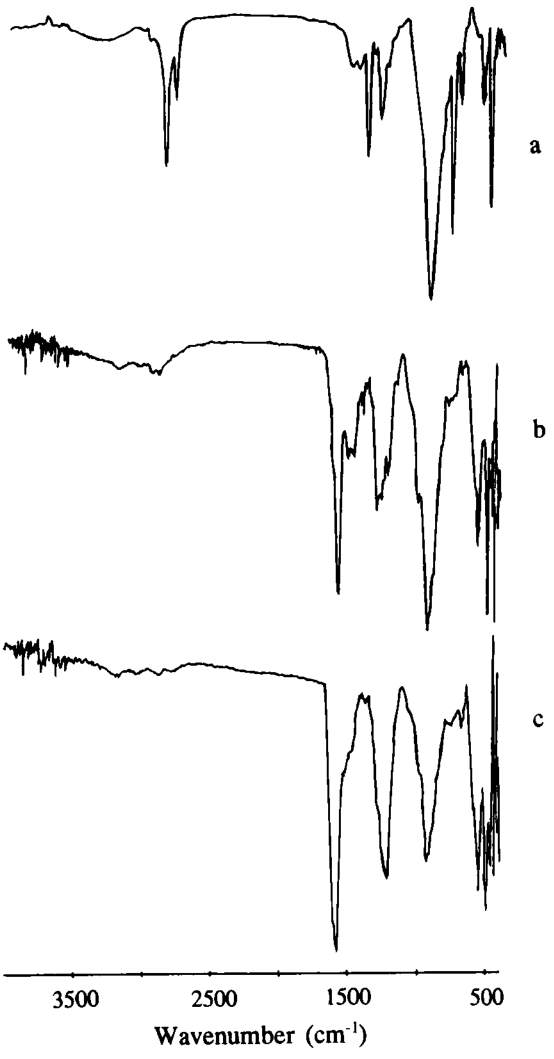

FIGURE 12 FTIR spectra of a) non-chlorinated, b) 2 wt% TIC and c) 5 wt% TIC-treated rubber.

cm^{-1} due to the Si—O group (silica is a filler in SBR) suddenly decreases. Thus, some Si—Cl bonds can be formed on the rubber surface indicating a reaction of the filler with chlorine, which is in agreement with recent results.[12] However, the nature of the reaction has not yet been established and additional work is presently being carried out in our laboratory.

The chlorination of adhesive films with trichloroisocyanuric acid was also carried out and the chemical changes produced were followed by FTIR. Figure 13 includes the FTIR spectra of chlorinated adhesives with (A-10), and without (A-0), silica. In comparison with Figure 6, it is evident that the chlorination of the adhesive without silica produces a decrease in the intensity of the bands corresponding to polyurethane (3300, 1599, 1540 cm^{-1}) and some new C—Cl bands appear (1402, 796, 764, 692, 532 and 535 cm^{-1}). There is also a peak at 1701 cm^{-1} corresponding to an aromatic carboxylic acid. Most of these C—Cl bands are also present in the chlorinated SBR. Thus, it appears that a chlorination of the urethane group is produced. On the other hand, for adhesives containing silica the chlorination

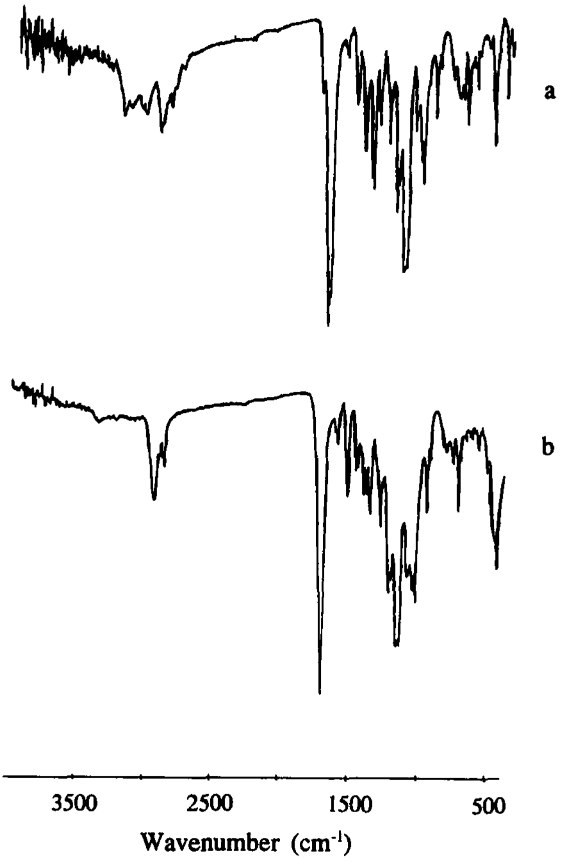

FIGURE 13 FTIR spectra of adhesives treated with a 2 wt% TIC solution in 2-butanone a) A-0 adhesive; b) A-10 adhesive.

process of the urethane group seemed to be inhibited as is also the oxidation by TIC. Some C—Cl bands still remain in the IR spectra, but they are less intense. Therefore, silica could be acting as a scavenger to react with active chlorine.

In order to have a better understanding of the kind of reaction produced in the silica by chlorination, Aerosil-200 silica was immersed for 10 seconds in 2-butanone solutions of a 2 wt% and 5 wt% TIC and, once the solvent was evaporated, the FTIR spectra were obtained (Figure 14). The comparison of non-chlorinated and chlorinated silica shows new bands which appear after halogenation:

a) 2176 cm^{-1}. Si—H bond formed during chlorination.[26]

b) 1472, 1424, 1360 cm^{-1} bands due to chloroketone groups of the TIC/2-butanone solutions.[28]

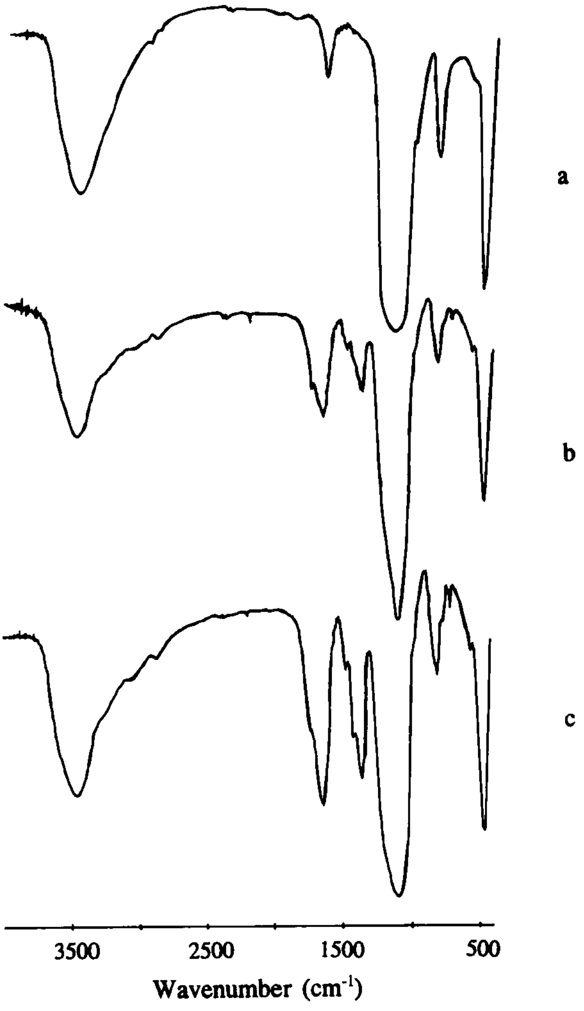

FIGURE 14 FTIR spectra of Aerosil-200 silica a) untreated and b) treated with 2 wt% TIC and c) 5 wt% TIC.

c) 752, 464 cm^{-1}. Bands of C—Cl bond of the chlorinating agent.

d) 560 cm^{-1}. Si—Cl bond formed during chlorination.

Therefore, the chlorination of silica creates new Si—H and Si—Cl groups. The rest of the bands correspond to the chlorination agent.

On the other hand, the intensity of some bands is modified by chlorination:

a) 1640 cm^{-1}. This band is due to C=O and C—Cl groups. There is an increase in intensity of this band with the TIC percentage.

b) 850 cm^{-1}. This band could be assigned to a Si—H bond.[16] It increases in intensity with increases in the TIC percentage.

c) 1000–1100 cm^{-1}. There is a decrease in these bands which correspond to Si—O groups.

Thus, the effects produced by the chlorination of the silica with TIC can be summarized as follows:

a) Some Si—O bonds can be broken due to the reaction of chloroketones (the active chlorination species in TIC solutions) with silica.

b) New Si—H and Si—Cl bonds appear.

Therefore, the addition of silica to polyurethane adhesives gives a positive effect toward adhesion when the rubber is subjected to a chlorination process. This positive effect can be explained by the fact that the chlorine can react with both urethane groups and silica; hence, the amount of bound chlorine on the adhesive surface will be reduced and improved adhesion will be expected for the greatest TIC concentrations.

III.5 Effect of the Dispersion of Silica in the Adhesion Properties of Polyurethane

It is well known that thickening and thixotropic effects produced by silica depend on its dispersion in the liquid considered.[16] In fact, a good dispersion allows better contact between the adhesive and the silica, and a change in the adhesion properties is thus expected. The dispersion of the silica can be altered by the use of a high stirring speed (which will probably produce a high shear mixing) in the laboratory mixer during the manufacture of the adhesive solutions. Thus, silica was added to some adhesives (a solids content of 18 wt% was always maintained) but three different speeds were used: 400 rpm, 1000 rpm and 1500 rpm.

Figure 15 shows the viscosity increase of the adhesives (with and without silica) as a function of the stirring speed employed during its manufacture. A noticeable influence of the stirring speed can be observed: the greater the speed, the greater the viscosity for the same silica content in the adhesive. There is an increase of viscosity with the silica content for a stirring speed of 1500 rpm, the opposite trend being found for 400 rpm. Thus, at low stirring speeds, the dispersion of silica is poor and there is no improvement in viscosity, probably because of the reduced mechanical degradation of the polyurethane produced at such low stirring speeds, which will not favour the reaction of the polymer with the silica. A stirring speed

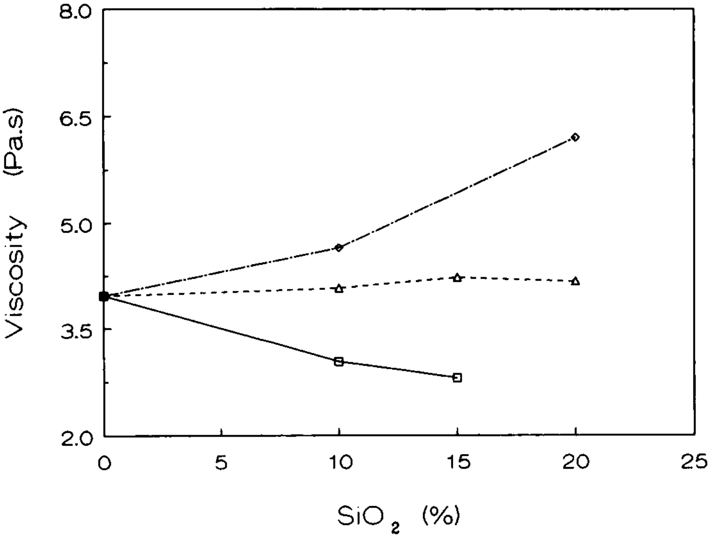

FIGURE 15 Viscosity evolution for adhesives prepared at different stirring speeds. (□) 400 rpm; (△) 1000 rpm; (◇) 1500 rpm.

of 1000 rpm maintains adhesive viscosities at between 3.9 and 4.3 Pa·s, and no change in the silica content is observed.

In order to study the effect of the different dispersions of the silica in the adhesives on the green peel strength, some green peel strength tests were carried out for adhesives A-0 and A-10 prepared with the three different stirring speeds. Figure 16

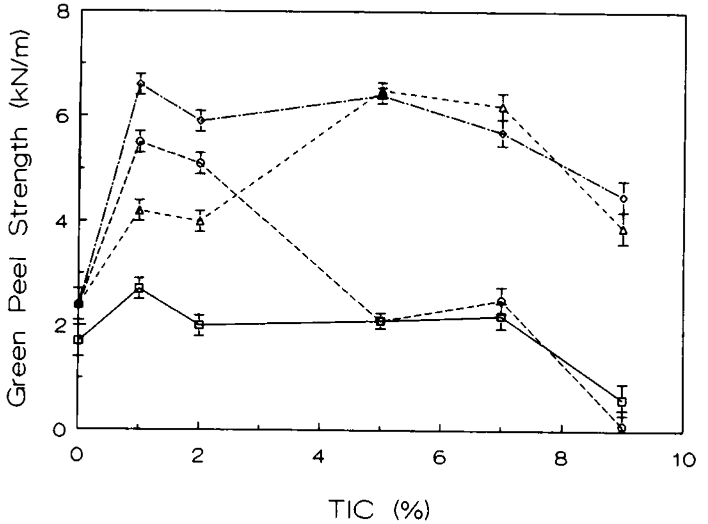

FIGURE 16 Influence on the stirring speed in the adhesive solution manufacture on the green peel strength obtained with chlorinated rubber. a) A-0 adhesive (1000 rpm) (□); b) A-10 adhesive: (△) 400 rpm; (◇) 1000 rpm; (○) 1500 rpm.

shows the results obtained for the SBR(halogenated)/Adhesive/SBR(halogenated) system. The stirring speed does not affect the viscosity and green peel strength of adhesive A-0, so only the value obtained at 1000 rpm was considered. According to this figure, the silica dispersion (and/or the adhesive viscosity) affects the green peel strength. TIC percentages smaller than 2 wt% show the greatest peel strength for adhesives prepared at 1000 rpm. For adhesives prepared at 400 and 1000 rpm the green peel strength appears to increase up to 5 wt%. Furthermore, for TIC concentrations greater than 7 wt% there is an abrupt decrease of peel strength for all adhesives.

Viscosities of polyurethane adhesive containing silica are not affected by stirring speeds lower than 1000 rpm, but higher stirring speeds, for example 1500 rpm, give quite low green peel strengths for TIC percentages greater than 2 wt%. In general, good results are obtained for adhesives prepared at 1000 rpm.

IV CONCLUSIONS

The addition of silica to polyurethane adhesives improves their adhesion properties to non-chlorinated and surface-chlorinated styrene-butadiene rubbers. The following conclusions can be drawn:

1. The viscosity of adhesives increases with increases in the amount of silica and greater time of contact between polyurethane and silica. Silica thickens and gives thixotropy to the adhesive solutions.
2. The greatest green peel strengths are always obtained for adhesives containing 10–20 wt% silica. In the case of the surface-chlorinated rubber, the addition of silica increases the green peel strength values (8 kN/m are obtained). However, silica has no effect on peel strength before or after an ageing process.
3. Chlorination of rubber improves its adhesion with the polyurethane adhesives used in this study and the presence of silica in the adhesive improves the resistance of the polyurethane polymer to degradation by chlorine on the rubber surface. This enhancement in adhesion properties can be explained by considering that silica "consumes" active chlorine of trichloroisocyanuric acid on the rubber surface.
4. The stirring speed is important to disperse the silica in the adhesive solution adequately. A stirring speed of 1000 rpm is found to produce good results. The viscosity increases with the increased stirring speed of the solution, probably because of an improvement in the dispersion of silica in the adhesive.

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