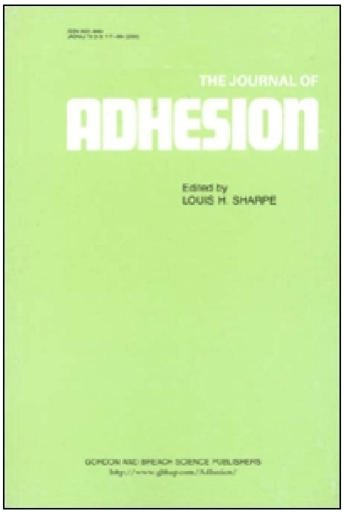

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# Hydrophobic or Hydrophilic Fumed Silica as Filler of Polyurethane Adhesives*

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Two hydrophilic and two hydrophobic fumed silicas of different characteristics were added to solvent-based polyurethane adhesives (PU). IR spectroscopy, contact angle measurements and rheology (viscosity measurements, determination of viscoelastic properties) were used to monitor the variation of properties of PU adhesives produced by addition of silica. Immediate (green) adhesion was determined by T-peel testing of halogenated synthetic rubber/PU adhesive/halogenated synthetic rubber joints. Silica addition produced a noticeable increase in the PU adhesive viscosity which can be related to the variation of viscoelastic properties. Viscosity of PU adhesives containing hydrophilic silica slightly increased with time after preparation; the increase was less significant in PU adhesives with hydrophilic silica. In the rheological studies, silica imparted shear thinning and negative thixotropy to PU adhesives due to a better dispersion of the silica in the polyurethane during shearing. The addition of silica produces an increase in the storage modulus ($G'$) of PU adhesives, the values obtained being independent of the hydrophilic or hydrophobic nature of the fumed silica. The increase of $G'$ and the changes in tan $\delta$ of PU adhesives containing silica corresponded to an improvement in the green adhesion properties of chlorinated rubber/PU adhesive/chlorinated rubber joints. In general, in disagreement with previous results,[1] the presence of silica did affect the properties of solvent-based PU adhesives, but these properties were not dependent on the type of silica (hydrophobic or hydrophilic) used in this study.

KEY WORDS: hydrophobic and hydrophilic nature; fumed silica; solvent-based polyurethane adhesives; rheology; viscoelastic properties; green strength; contact angle; infra-red spectroscopy.

## 1 INTRODUCTION

Inorganic mineral fillers are generally used to modify the rheological properties and adhesion behaviour and to decrease the cost of manufacture of sealants, coatings and adhesives. Specifically, fumed silicas are often used as a component in the formulation of epoxy[2] and PU[3] adhesives, among others, to improve their rheological behaviour, their stability to elevated temperature and their adhesion properties.

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Solvent-based polyurethane adhesives (PU) are often employed to join styrene-butadiene rubber materials (SBR) in the footwear industry. Hydrophilic fumed silica can be added to impart thixotropy and to adjust the rheological behaviour of such PU adhesives. In a previous study,[3] we analyzed the influence of the addition of a hydrophilic fumed silica (*Aerosil-200*) (5–25wt%) to solvent-based PU adhesives on their adhesion properties through un-chlorinated and chlorinated rubbers; the halogen precursor was trichloroisocyanuric acid in 2-butanone solution. In general, the addition of 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%. There appears to be no chemical interaction between silica and polyurethane polymer, although the presence of silica resulted in the improvement of the resistance of the PU adhesive to degradation by chlorinated species on the rubber surface.

Hydrophilic fumed silica may interact with polar solvents (ketones, ethyl acetate) leading to a continuous variation of viscosity with time. To avoid these drawbacks, the use of hydrophobic fumed silica was proposed by Degussa[4]. The proposal was that the use of hydrophobic fumed silica prevents specific interactions with water, produces an increase in adhesion and a "true" enhancement of viscosity, which is usually constant over time. (The creation of hydrogen bonds between OH surface groups on the silica and polar groups of solvent and/or adhesive is avoided).

Fumed silicas are manufactured by high-temperature hydrolysis of silicon tetrachloride in a flame.[5] Silanol functional groups (which are responsible for the hydrophilic character of fumed silica) and siloxane groups (which are responsible for the hydrophobic character of fumed silica) are thus created on the silica surface. Through continuous development of flame technology and chemical after-treatment, it became possible to produce numerous different hydrophilic and hydrophobic silicas. In fact, the silanol groups present on the hydrophilic fumed silica surface may be chemically modified using halosilanes, alkoxysilanes, silazanes or siloxanes,[4] leading to a chemical bond on the silica surface. The resulting product (generally called hydrophobic fumed silica) has a similar particle size but a reduced specific surface area, reduced water vapour adsorption and, of course, a reduced silanol group density, compared with hydrophilic silica.

Hydrophobic fumed silicas have been successfully used as rheological aids to provide effective and stable thickening, and thixotropy of epoxy systems.[1,2] The nature of the epoxy determines the effectiveness of the hydrophobic silica, although, in general, an increase in viscosity (which is maintained over time) and an increase of adhesion to steel films have been reported.[2] A comparison among different hydrophobic and hydrophilic silicas was carried out, showing different effects depending on the nature of the fumed silica.

To our knowledge, no further studies related to the addition of silica to PU adhesives have been carried out. For this reason, the objective of this work is to extend our previous study[3] to a larger number of fumed silicas. We deal specifically with the influence of particle size, specific surface area and the hydrophilic or hydrophobic nature of fumed silica on the rheological properties of PU adhesives and on their adhesion to synthetic rubber.

## EXPERIMENTAL

### II.1 Materials

A polyester-urethane polymer based on ε-polycaprolactone (*Pearlstick 45-40/15*) was used to prepare the solvent-based PU adhesives. This polyurethane, supplied by MERQUINSA S.A. (Barcelona, Spain), has a medium thermoplasticity (reversible tendency to melt under temperature), short open time and very high crystallization rate.

Four fumed silicas (two hydrophobic-*Aerosil* R805 and R812- and two hydrophilic-*Aerosil* 200 and 300), provided by DEGUSSA AG (Hanau, Germany) of specific surface areas between 200 and 300 $m^2/g$ were selected for this study. Some of the properties of the silicas are given in Table I.

PU adhesives (with the nomenclature given in Table II) were prepared by mixing 18 wt% PU and 2 wt% fumed silica in 2-butanone. This mixture was placed in a laboratory mixer (1500 rpm) and stirred for 2 hours at room temperature until a homogeneous dispersion was obtained. The adhesive solutions were kept in an hermetic container until used.

PU adhesives were characterized by using contact angle measurements and infrared spectroscopy. The Brookfield viscosities of the adhesives (at 25°C) using spindle no. 3 and a speed of 20 rpm were measured in an RVT Brookfield Viscometer. The measurements were taken after 1 min. Brookfield viscosities provide incomplete information about the viscous characteristics of adhesives because they do not provide any information related to the rheological behaviour (Newtonian, pseudoplastic) of

TABLE I
Properties of *Aerosil* fumed silicas (taken from Reference 3)

| Property | Hydrophilic | | Hydrophobic | |
|---|---|---|---|---|
| | A200 | A300 | R805 | R812 |
| BET surface area ($m^2/g$) | 200 ± 25 | 300 ± 30 | 150 ± 25 | 260 ± 30 |
| Average primary particle size (nm) | 12 | 7 | 12 | 7 |
| Moisture content (%) | < 1.5 | < 1.5 | < 0.5 | < 0.5 |
| Surface group | -Si-OH | -Si-OH | $-Si-C_8H_{17}$ | $-Si(CH_3)_3$ |
| Bonded carbon (wt%) | – | – | 5 | 2.5 |
| pH | 3.6–4.3 | 3.6–4.3 | 5–7 | 1.0–2.5 |

TABLE II
Nomenclature of solvent-based PU adhesives

| PU adhesive | Fumed silica |
|---|---|
| A0 | None |
| A1 | *Aerosil* 200 |
| A2 | *Aerosil* 300 |
| P1 | *Aerosil* R805 |
| P2 | *Aerosil* R812 |

adhesives. Thus, rheological studies (viscosity measurements and viscoelastic properties) were also conducted on the PU adhesives.

## II.2 Experimental Methods

*II.2.1 Contact angle measurements.* Adhesive films were prepared by placing the PU adhesive solutions in a rectangular mould and allowing the solvent to evaporate slowly to prevent the formation of bubbles. Contact angles were determined with a Ramé-Hart 100 goniometer. Single sessile drops (2 μl) of water (doubly distilled) and ethanediol (99% minimum purity) were placed on the surface of the above-mentioned adhesive film in an hermetic, isothermal (25°C) and solvent-saturated chamber, and the contact angles on both sides of the drops were measured. 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 adhesive film were taken and the standard deviation was always less than 2°.

*II.2.2 FTIR studies.* A Nicolet 510 FTIR spectrophotometer was used with a signal/noise ratio of 0.04% T (at 2000 cm$^{-1}$). A KBr:silica (300:1) mix was pressed to prepare a pellet and then was analyzed by transmission; 80 scans per experiment were carried out.

*II.2.3 Rheological measurements.* Rheological tests were conducted using a Physica MC100 rheometer. Viscosity measurements were carried out in the rotational mode using concentric cylinders type Z2 (according to DIN 53019) with the following technical characteristics: Radius of measuring bob = 2.25 cm; radius of measuring cup = 2.44 cm; radius of shaft = 0.35 cm; measuring cone angle = 120°; length of measuring bob = 6.75 cm; distance of lower edge of measuring bob from bottom to cup = 3.5 cm; immersion of measuring shaft = 2.25 cm. 100 cm$^3$ of PU adhesive solutions were used in the measurements and a solvent trap device assured that minimal evaporation of solvent occurred during the experiments. Controlled shear stress (CSS) experiments were carried out as follows: Shear stress was increased to 200 Pa in one minute, maintained at 200 Pa for three minutes, and finally decreased to 0 Pa in one minute. Previous experiments showed that these experimental conditions produced complete disorder of the PU structure. Some experiments were repeated and an excellent reproducibility was always obtained.

Viscoelastic properties were measured in the oscillatory mode, first by varying the amplitude of a sinusoidal signal between 0.01 and 10 (amplitude sweep)- the frequency selected was 1 Hz- and second by varying the frequency between 1 and 100 Hz- the amplitude selected was 6.

*II.2.4 Peel Strength measurements.* Peel strength of adhesive joints created between strips (150 x 30 mm) of vulcanized styrene-butadiene rubber (SBR)- about 3 mm thick- was measured by a standard T-peel test. The rubber selected in this study is one of the most commonly used in the footwear industry as a reference material to test the peel strength of adhesive joints. Table III includes the SBR formulation.

TABLE III
Formulation of vulcanized styrene-butadiene rubber

| Compound | Percentage |
|---|---|
| SBR 1502 | 100 |
| 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 |

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. After the cleaning process, SBR was halogenated by brushing its surface with 2-butanone solution containing 1 wt% TCI (trichloroisocyanuric acid -1, 3, 5-trichloro-1, 3, 5- triazin-2, 4, 6-trione). After 18 hours, the reaction of TCI with rubber was complete.[6] Subsequently, 100 mg of PU adhesive was applied to the rubber surface and left to dry for 40 min. 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 green (immediate) peel strength was measured 30 seconds after the 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 are given elsewhere.[7]

## III RESULTS AND DISCUSSION

### III.1 Characterization of Fumed Silica

According to Table I, *Aerosil* A200 and R805 silicas have the same average primary particle size (12 nm) and similar BET surface areas (175–225 $m^2/g$), although the hydrophobic silica *Aerosil* R805 has a lower moisture content and is less acidic. BET surface areas were calculated by applying the Brunauer-Emmett-Teller equation[8] to $N_2$/77K adsorption isotherms of the silicas; BET plots were linear in the range of relative pressure between 0.05 and 0.30. *Aerosil* R805 has a smaller number of surface silanol groups than *Aerosil* A200 because a fraction of those were chemically reacted with a silane to form $\text{-Si-C}_8H_{17}$ surface groups. A similar situation applies to *Aerosil* A300 and R812, although the average primary particle size of these silicas is smaller (7 nm) and the BET surface area is higher (260–330 $m^2/g$). *Aerosil* R812 was prepared by reaction of *Aerosil* A300 with a silane to form $\text{-Si(CH}_3)_3$ surface groups; the nature of the silane groups and the experimental treatment conditions results in an acidic silica.

Consequently, the selection of these four fumed silicas enables the influence of several properties (specific surface area, particle size, hydrophilic/hydrophobic nature) to be studied when the silica is added to solvent-based PU adhesives.

IR spectra of the fumed silicas, Figure 1, show typical -Si-O- bands: [9, 10]

- Stretching due to hydrogen bonded OH groups (3245–3658 $cm^{-1}$).
- Bending of OH groups (1632 $cm^{-1}$).
- Bending and stretching bands of Si-O-Si groups (1045–1209 $cm^{-1}$).
- Asymmetric stretching of Si-O-Si groups (979 $cm^{-1}$).
- Symmetric stretching of Si-O-Si groups (808 $cm^{-1}$).

In addition, IR spectra of hydrophobic fumed silicas (Figure 1b) show stretching bands of $CH_2$ and $CH_3$ between 2929 and 2820 $cm^{-1}$. The IR spectrum of *Aerosil* R812 shows a less marked band due to $CH_2$ groups than that of *Aerosil* R805 (in agreement with the different kinds of surface groups in these silicas -Table I).

A relative measurement of the amount of surface silanol groups in the fumed silicas can be obtained from IR spectra by taking the ratio, $R_1$, of the areas under the bands at 3438 $cm^{-1}$ (OH group) and 1100 $cm^{-1}$ (Si-O-Si group). *Aerosil* A200 ($R_1 = 4.1$) is around 25% more hydrophilic (*i.e.* there is a greater amount of silanol groups) than *Aerosil* A300 ($R_1 = 3.1$). The hydrophilic fumed silicas possess 20–30% less silanol groups than the hydrophobic ones, indicating a reduced tendency to form tridimensional aggregates among particles by hydrogen bonding between silanol groups. Following the same argument, the "degree of hydrophobicity" in fumed silica can be obtained from $R_2$, the ratio of the areas under the bands at 2929 $cm^{-1}$ ($CH_2$ group) and 3438 $cm^{-1}$ (OH group); *Aerosil* R805 ($R_2 = 0.20$) is around 60% more hydrophobic (*i.e.*

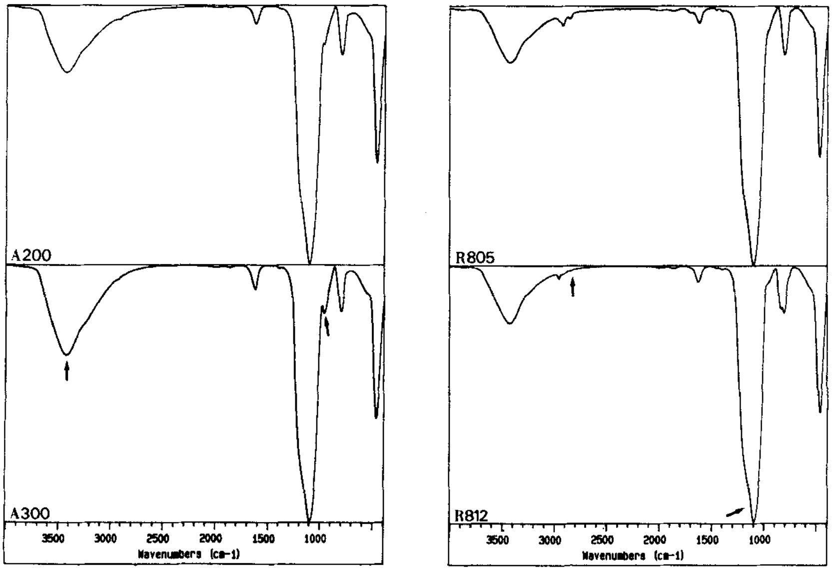

FIGURE 1 IR spectra of fumed silica. a) Hydrophilic silica. b) Hydrophobic silica.

there is a smaller amount of silanol groups) than *Aerosil* R812 ($R_2 = 0.12$). The larger value of $R_2$ for *Aerosil* R805 is in good agreement with the ratio of bonded carbon atoms to silanol groups in those silicas (Table I). Therefore, *Aerosil* A200 is the most hydrophilic and *Aerosil* R805 is the most hydrophobic fumed silica used in this work.

### III.2. Characterization of Solvent-Based PU Adhesives Modified with Silica

Brookfield viscosity (25°C) of the PU adhesives was monitored with time after their preparation (Fig. 2). Addition of silica to the adhesives produced an increase of at least 50% in Brookfield viscosity. The Brookfield viscosities are similar and do not vary with time in adhesives A1 and P1 (containing *Aerosil* 200 and R805, respectively), except that there is a slight increase of viscosity during the first week after preparation of adhesive A1. However, adhesives A2 and P2 show an increase of around 10% in viscosity with time, which is more gradual in the adhesive containing hydrophobic silica, P2. The increase of viscosity with time shown by these PU adhesives can be ascribed to the larger BET surface areas and the smaller particle size compared with adhesives A1 and P1. A more comprehensive study of the influence of such properties of silica on the flow properties of the PU adhesives has been assessed with rheological studies.

Previous results[1,11] related to the addition of different fumed silicas to liquid systems and epoxy adhesives showed a different trend. Hydrophilic fumed silica interacted by hydrogen bonding with solvent and/or polymer leading to higher viscosity than was found with hydrophobic silica. The fact that, under the experimental conditions used in this study, the hydrophobic or hydrophilic silicas gave similar results indicated a lack of chemical interaction with the PU adhesives.

Flow curves were obtained in the rheometer under controlled shear stress (CSS). Figure 3 shows the variation of viscosity as a function of shear rate obtained for all PU adhesives. Adhesive A0 (without silica) gives Newtonian behaviour, and the addition of silica partially modifies this behaviour towards pseudoplastic. The addition of silica to the PU adhesives produces an increase of viscosity for a given shear rate, this increase being more marked for the adhesives containing silica with high BET surface area and

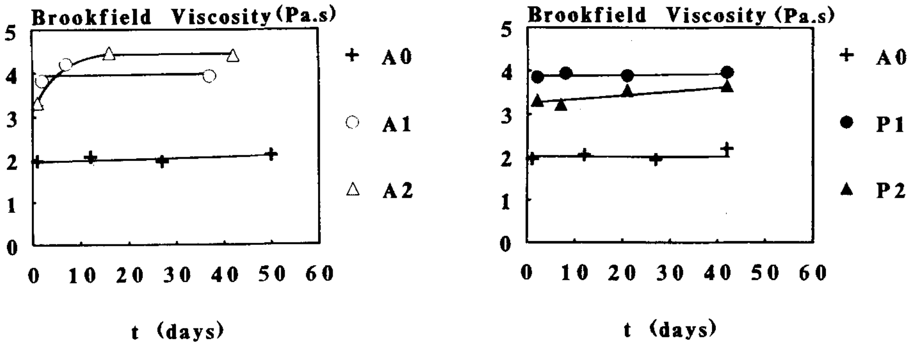

FIGURE 2 Variation of Brookfield viscosity (25°C) of silica-modified, solvent-based PU adhesives with time after preparation. a) PU adhesives containing hydrophilic silica. b) PU adhesives containing hydrophobic silica.

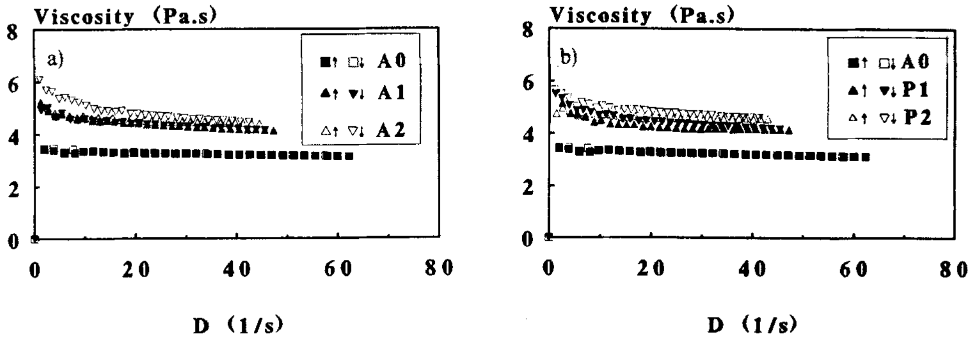

FIGURE 3 Flow curves of silica-modified PU adhesives. a) PU adhesives containing hydrophilic silica. b) PU adhesives containing hydrophobic silica.

small particle size; the hydrophilic or hydrophobic nature of fumed silica does not seem to modify the flow curves of the adhesives, probably because no chemical interaction (*i.e.* hydrogen bond formation between silanol groups of silica and OH groups of polyurethane) between silica and polyurethane polymer occurs.

The flow curves of Figure 3 were recorded with increasing as well as with decreasing load. Between both sections there was a short holding time (three minutes) under constant load. Whereas for the PU adhesive without silica both curves were coincident, in the case of PU adhesives containing silica the viscosity for any given shear rate was higher when the decreasing load experiment was carried out (negative thixotropy). The area between the up and down curve as a measure of thixotropy has proven useful.[12] Flow curves in Figure 3 show a slightly higher degree of negative thixotropy in PU adhesives containing hydrophilic silica with high surface area (*Aerosil* 300). Negative thixotropy can be attributed to a disordering of the physical structure of polyurethane in the solvent by increasing the load (shear stress) during the rheological experiment, in such a way that a higher resistance to deformation is obtained upon reduction of the load. In fact, this kind of modification is quite stable because a second rising-decreasing load experiment carried out immediately after the first run provides a flow curve without any thixotropy and which is coincident with the decreasing curve obtained in the first rheological run. Therefore, the modification of PU adhesive structure during the rheological experiment probably consists of a better dispersion of the silica particles in the adhesive matrix, in such a way that a more effective contact between polyurethane and/or solvent and silica is produced. Although the nature of such interaction needs further study, perhaps negative thixotropy can be explained by a competition between solvent and polyurethane to interact with silica.

Viscoelastic properties of the solvent-based PU adhesives have been assessed using the rheometer operating in an oscillatory mode. Amplitude sweep studies were carried out at a frequency of 1 Hz and the variations of storage modulus ($G'$), loss modulus ($G''$) and loss factor (tan $\delta$) were monitored. Figures 4 and 5 show the variation of $G'$ and tan $\delta$, respectively, as a function of the strain for a frequency of 1 Hz. Addition of silica increases the storage modulus and decreases the loss factor of the PU adhesives due to an improvement of their viscous properties. The loss modulus ($G''$) is much larger than

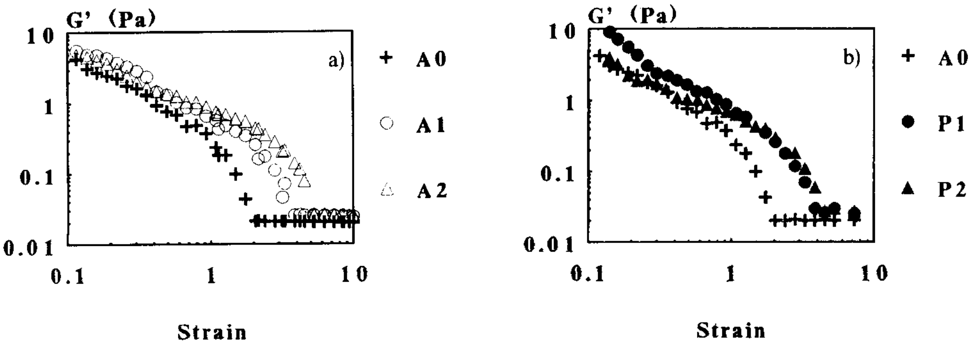

FIGURE 4 Variation of storage modulus ($G'$) as a function of amplitude. Frequency = 1 Hz. a) PU adhesives containing hydrophilic silica. b) PU adhesives containing hydrophobic silica.

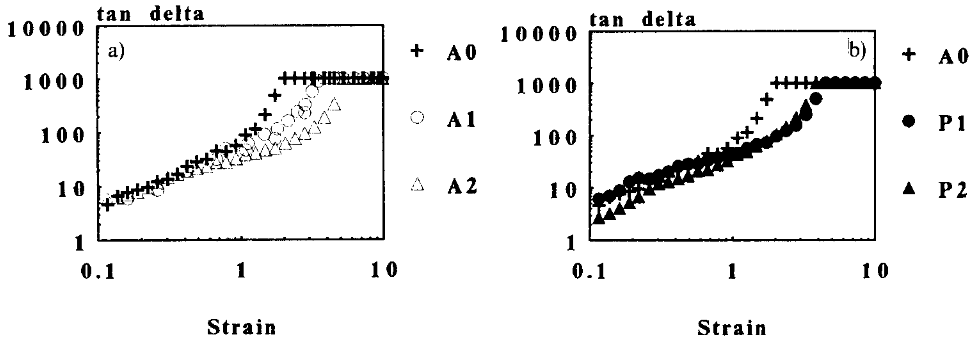

FIGURE 5 Variation of loss factor (tan $\delta$) as a function of amplitude. Frequency = 1 Hz. a) PU adhesives containing hydrophilic silica. b) PU adhesives containing hydrophobic silica.

the storage modulus ($G'$) because of the essentially viscous nature of the PU adhesive solutions. There is a continuous decrease of $G'$ with strain (Fig. 4) which becomes more marked for strain values between 1 and 3 in the PU adhesive without silica. The addition of silica retards the strain value at which the sudden decrease of $G'$ occurs (between 2 and 4), and at the same time that decrease of $G'$ is more abrupt. Therefore, the addition of silica improves the viscous properties of the adhesives and facilitates the maintenance of such viscous properties in a broader range of strain. The most noticeable modification of viscoelastic properties of the adhesives is produced by addition of hydrophilic fumed silica *Aerosil* A300 (adhesive A2), the fumed silica with the largest specific surface area and smaller particle size among those selected in this study. However, variations in $G'$ (and in tan $\delta$) for adhesives P1 and P2 (prepared with hydrophobic silica) and A1, are very similar, such variations being independent of the specific surface area and particle size of silica.

Figure 6 shows the variation of $G'$ for PU adhesives as a function of frequency; a strain of 6 (where $G'$ was found to be independent of the strain, according to Figure 4)

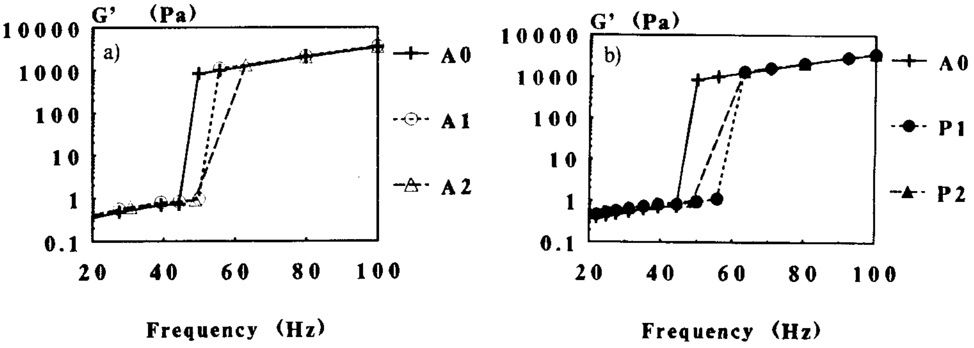

FIGURE 6 Variation of storage modulus ($G'$) as a function of the frequency. Amplitude = 6. a) PU adhesives containing hydrophilic silica. b) PU adhesives containing hydrophobic silica.

was chosen to carry out the experiments. $G'$ (and tan $\delta$) values are similar for all the adhesives, the presence of silica in the PU adhesives being irrelevant. For frequencies lower than 40–50 Hz, tan $\delta$ ($= G''/G'$) is very high (tan $\delta \rightarrow \infty$) because the viscous properties predominate over the elastic properties of adhesives; for higher frequencies, however, tan $\delta$ is very small (tan $\delta \rightarrow 0$) and the elastic properties predominate over the viscous ones. The addition of silica to the PU adhesives increases the frequency at which the change from viscous to elastic properties is produced. Thus, whereas this change is produced at 47 Hz for adhesive A0, the frequency is displaced to 53 Hz (adhesive A1) and 58 Hz (adhesive A2) for PU adhesives containing hydrophilic silica (Fig. 6a). In the case of the adhesives containing hydrophobic silica, the change from viscous to elastic properties is produced at 54 and 57 Hz for adhesives P1 and P2, respectively. Thus, the addition of the fumed silica with high specific surface area and small particle size modifies more effectively the viscous properties of the PU adhesives.

In summary, the addition of silica to PU adhesives enhanced their viscoelastic properties (increase of $G'$ and decrease of tan $\delta$). No differences between the PU adhesives containing hydrophobic or hydrophilic silica were found, but those silicas with high specific surface area and small particle size produced a more noticeable effect. Furthermore, although *Aerosil* A200 possesses the largest amount of silanol groups among all the fumed silicas selected in this study, *Aerosil* A300 has a more marked effect upon the rheological properties. This may indicate that no hydrogen bond between silica and polyurethane is produced. This can also be confirmed with IR spectroscopy.

Figure 7 shows the IR spectra of all PU adhesives. All the IR spectra are very similar and present bands typical of urethane and O-Si-O groups. There are no new bands or noticeable modification in the intensity of those bands, indicating that no chemical interaction between silica and polyurethane is produced. Furthermore, the nature of the fumed silica added to the PU adhesive does not affect the IR spectra of the adhesives.

Table IV shows the contact angles of ethanediol and water on PU adhesive films. Contact angles measured with water are higher than those obtained with ethanediol, although the trend followed by the different adhesives is similar. Addition of silica to

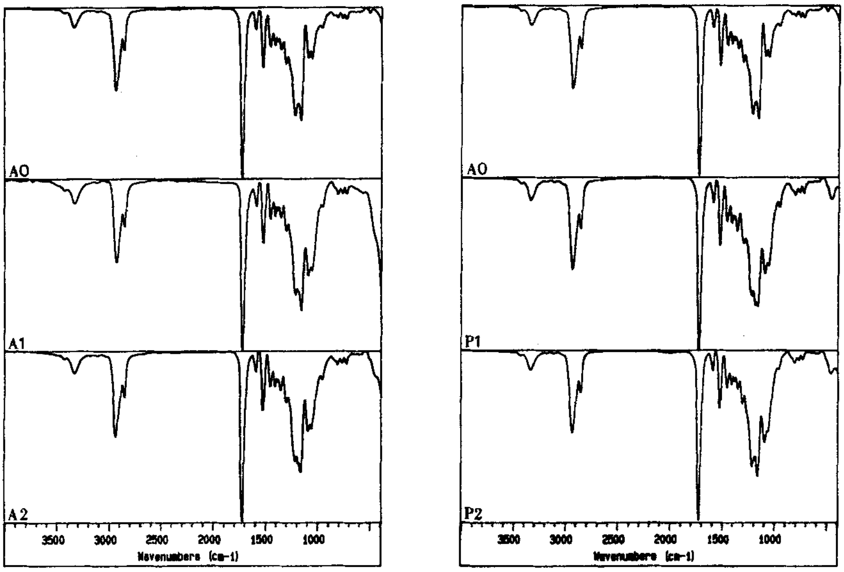

FIGURE 7 IR spectra of PU adhesives. a) PU adhesives containing hydrophilic silica. b) PU adhesives containing hydrophobic silica.

PU adhesives produces a decrease in contact angle (more marked with water) but there are no great differences between the contact angles of PU adhesives containing silica. Dispersion ($\gamma_s^d$), polar ($\gamma_s^p$), and total ($\gamma_s$) surface energies of PU adhesive films were calculated by applying the Owens and Wendt method:[13, 14]

$$\gamma_L(1+\cos\theta)=2(\gamma_s^d\gamma_L^d)^{1/2}+2(\gamma_s^p\gamma_L^p)^{1/2}$$

Surface tension values of test liquids were:

- Water: $\gamma_L^p = 51.0$ mN/m; $\gamma_L^d = 21.8$ mN/m; $\gamma_L = 72.8$ mN/m.
- Ethanediol: $\gamma_L^p = 19.0$ mN/m; $\gamma_L^d = 29.3$ mN/m; $\gamma_L = 48.3$ mN/m.

According to Table IV, adhesive A0 has a relatively important polar component of the surface energy, due to the polar nature of polyurethane polymer. Addition of silica

TABLE IV

Total ($\gamma_s$), polar ($\gamma_s^p$) and dispersive ($\gamma_s^d$) components of the surface free energy of PU adhesive films

| ADHESIVE | $\theta_{\text{Water}}$ (degrees) | $\theta_{\text{Ethanediol}}$ (degrees) | $\gamma_s^p$ (mJ/m$^2$) | $\gamma_s^d$ (mJ/m$^2$) | $\gamma_s$ (mJ/m$^2$) |
|---|---|---|---|---|---|
| A0 | 78 | 50 | 12.4 | 16.3 | 28.7 |
| A1 | 69 | 48 | 27.9 | 6.3 | 34.2 |
| A2 | 70 | 47 | 24.6 | 8.2 | 32.8 |
| P1 | 68 | 47 | 29.1 | 6.1 | 35.2 |
| P2 | 65 | 47 | 36.3 | 3.5 | 39.8 |

increases the surface free energy of PU adhesive films, and a decrease of dispersive component and an increase of the polar components of the surface free energy oι adhesive are produced. Thus, the addition of silica might affect the orientation of the polyurethane and, thus, an increase of polarity of the surface is produced. On the other hand, in general, the specific surface area, the particle size and the hydrophilic/hydrophobic nature of silica do not seem to modify greatly the surface free energy of PU adhesives.

Consequently, the addition of silica to PU adhesives modifies their viscosity, enhances their viscous properties and increases their surface free energy. The nature of different silicas influences the viscoelastic properties of PU adhesives, but does not affect their surface free energy.

### III.3 Adhesion Properties of PU Adhesives to Surface Chlorinated Rubber

Immediate (green) T-peel strength of synthetic SBR rubber/PU adhesives containing silica/synthetic SBR rubber joints are given in Figure 8. Silica definetly has an effect on adhesion. The adhesion to rubber of PU adhesives containing silica is nearly twice that of the PU adhesive without silica. However, the specific surface area, particle size and hydrophilicity/hydrophobicity of fumed silica do not affect green T-peel.

The improved adhesion of PU adhesives containing silica can be related to the enhancement in viscosity and the modification of viscous properties, and with the increased surface free energy produced when silica is added to PU adhesives.

## IV CONCLUSIONS

1. Addition of silica to solvent-based PU adhesives increases their viscosity and modifies their viscous properties and their wettability. Furthermore, the addition of silica to PU adhesives increases the immediate adhesion to chlorinated rubber. The presence of silica imparts "negative thixotropy" to the polyurethane/2-butanone system.

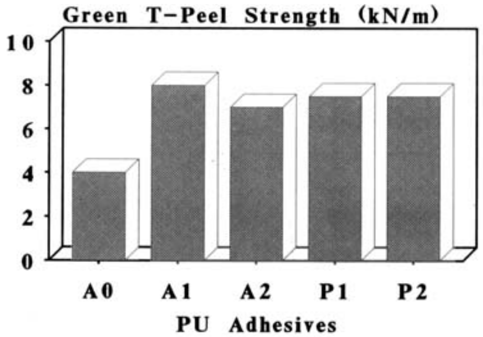

FIGURE 8 Immediate T-peel strength for chlorinated SBR/PU adhesive/chlorinated SBR joints.

2. Four fumed silicas were selected in this study with different specific surface area, particle size and hydrophobic/hydrophilic nature. Differences in properties, in general, do not greatly affect the viscosity, viscoelastic properties, surface free energy and adhesion properties of PU adhesives.

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