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# Comparison of the Properties of Polyurethane Adhesives Containing Fumed Silica or Sepiolite as Filler

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Fumed silica is a well-known mineral filler of epoxy and polyurethane adhesives. Although effective, the small particle size and the relative high cost of fumed silicas suggest the need for an alternative filler. In this study, the usefulness of adding a natural hydrated magnesium silicate (sepiolite) as a new filler in solvent-based polyurethane (PU) adhesive formulations has been demonstrated. The rheological and adhesion performance of the sepiolite-filled PU adhesive was compared with that in PU adhesives containing fumed silicas. The addition of a filler to PU adhesives provided an increase in viscosity, imparted thixotropy and pseudoplasticity to the adhesive solution, produced an increase in storage and loss moduli, and improved the rheology of the PU. The mechanical properties of adhesive films were increased by adding filler, mainly with fumed silica. On the other hand, the immediate T-peel strength of roughened or (roughened + chlorinated) styrene-butadiene rubber/PU adhesive joints was greatly improved in filled PU adhesives. The effects produced by adding sepiolite or fumed silica to the adhesives were very similar, although in general more noticeable in fumed silica filled PU due to the formation of hydrogen bonds between the filler and the solvent and/or the polyurethane (in sepiolite-filled adhesives, van der Waals forces seemed to be responsible for the interactions between the filler and the solvent and/or polyurethane).

**Keywords:** Sepiolite; solvent-based polyurethane adhesive; fumed silica; rheology; T-peel strength

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## 1. INTRODUCTION

Most adhesives need fillers as rheological modifiers. The role of fillers is critical to obtain an adequate performance of adhesive joints in several applications. Fumed silica is a well-known mineral filler for epoxy and polyurethane adhesives [1]. Although effective, the small particle size and the relatively high cost of fumed silicas suggest the need for alternative fillers. In this study, a natural hydrated magnesium silicate (sepiolite) is proposed as a new filler in solvent-based polyurethane (PU) adhesive formulations, and the rheological and adhesion performance are compared with PU adhesives containing fumed silicas.

Previous studies [2–7] have shown the usefulness of adding fumed silica to suspensions, and the addition to polyurethane adhesives [8–12] showed improved rheological properties for PU adhesives containing hydrophilic or hydrophobic fumed silicas. Fumed silicas produced an increase in viscosity, and imparted thixotropy and pseudoplasticity to PU adhesive solutions. Furthermore, the storage ( $G'$ ) and the loss ( $G''$ ) moduli were increased in PU adhesive films due to the creation of a network between the filler and the solvent and/or the thermoplastic PU chains. On the other hand, the addition of fumed silica to PU adhesives increased the immediate (green) T-peel strength of roughened or chlorinated styrene-butadiene rubber/PU adhesive joints and, furthermore, enhanced the performance of the joints under ageing with temperature and humidity.

Sepiolite is a natural magnesium hydrated silicate with the ideal formula:



The fibrous structure of sepiolite is composed of talc-like ribbons with two sheets of tetrahedral silica units, linked by means of oxygen atoms to a central octahedral sheet of magnesium in such a way that the tetrahedral sheet of silicon is continuous, but with the directions of the apical extreme of the tetrahedral sheet of silica inverted after every six tetrahedral units (Fig. 1). This determines the presence of channels ( $3.6 \times 10.6\text{Å}$ ) oriented in the longitudinal direction of the fibers [13].

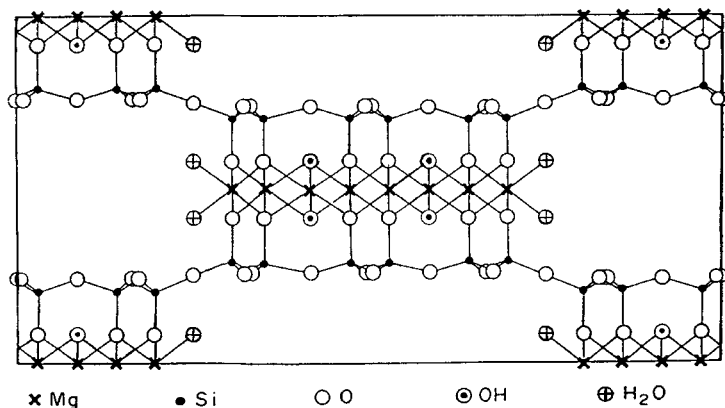


FIGURE 1 Schematic structure of sepiolite [20].

Sepiolite has found use as an adsorbent of vapours and liquids, as well as a filler in rubber compounding [14]. The use of sepiolite as a filler in adhesives has not already been described because after preparing the adhesives, the sepiolite precipitates from the solution and the adhesive solutions present a cream colour. However, the addition of a small amount of sepiolite prevents the colouring of the adhesives and the addition of a small amount of tensioactive may avoid the precipitation of sepiolite from the suspensions. In a suspension the fine particles of a solid are dispersed in a liquid. The area of contacting surface with the liquid increases sharply when the filler exists as small particles. Stabilization of solid suspensions in nonaqueous liquids is difficult to connect with any electrical effect. The stabilizing solute in these systems is adsorbed on the solid, but the mechanism whereby the sorbed film tends to prevent the particle agglomerating is not fully explained. Suspending agents differ widely in their effectiveness [15], and there is evidence that suspending agents which are very strongly or irreversibly sorbed are more effective than those which are weakly and reversibly sorbed [16].

The aim of this study is to analyze the performance of solvent-based PU adhesives containing sepiolite, and a comparison with the results obtained for PU adhesives containing a fumed silica will be carried out. The study will be mainly focused on the rheological and adhesion properties of the adhesives.

## 2. EXPERIMENTAL

### Materials

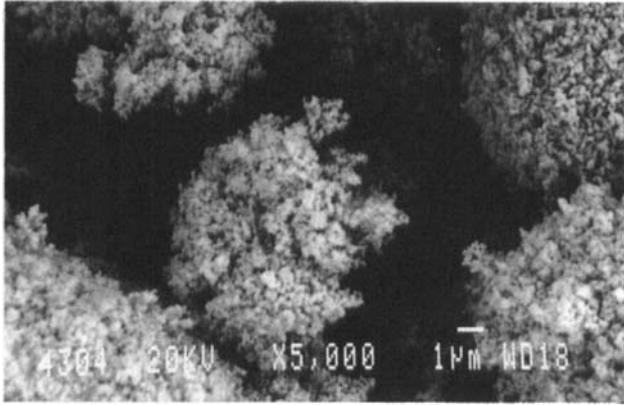
The fillers used in this study were a fumed silica (*Aerosil 200*) provided by Degussa AG, Hanau (Germany), and a partially sized sepiolite (*Pangel S9*) provided by Tolsa S. A., Madrid (Spain). Some characteristics of the fillers are given in Table I. The particles of the two fillers present a different shape. Figure 2 shows the globular shape of the *Aerosil 200* aggregated particles (with a diameter about 10  $\mu\text{m}$ ), whereas needle-shaped aggregated particles (about 10  $\mu\text{m}$  length) can be seen in the sepiolite. The aspect ratio in the sepiolite particles is high (between 20 and 200). The shape of the particles may determine the rheological properties of the adhesives. The specific surface area ( $\text{N}_2$ -BET surface area) is somewhat higher in the sepiolite due to the presence of pores in its structure which will produce an enhancement in BET surface area, whereas the fumed silica is a non-porous solid and the adsorption is only produced on the surface of the particle.

A thermoplastic polyester urethane polymer (*Desmocoll 510*) provided by Bayer, Leverkusen (Germany) was used to prepare the adhesive solutions. The solvent used was 2-butanone. The PU adhesive solutions contain 17 wt% polyurethane and 2 wt% filler, and were prepared in two stages. i) The filler was mixed with a small amount of solvent (2-butanone) at 2500 rpm for 10 minutes in a laboratory mixer, *Dispermix DL-M* (Oliver-Battle, Barcelona, Spain), to facilitate the adequate dispersion of the filler in the solvent; in the case of the sepiolite, a small amount of a quaternary ammonium salt tensioactive

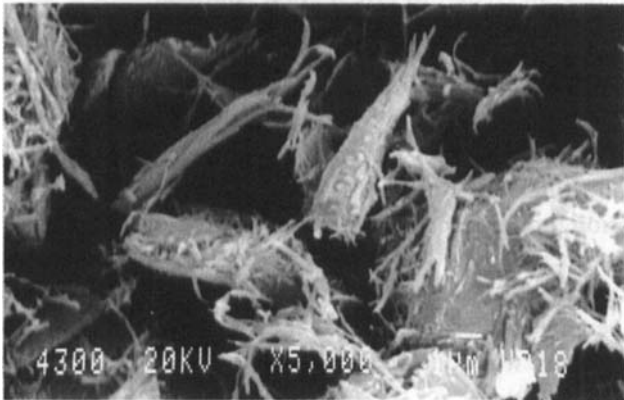
TABLE I Characteristics of the fillers

Property	<i>Aerosil 200</i>	<i>Pangel S9</i>
Particle size	12 nm	5 $\mu\text{m}$
BET surface ( $\text{m}^2/\text{g}$ )	200	310
Bulk density ( $\text{g}/\text{cm}^3$ )	–	2.0–2.3
Apparent density ( $\text{g}/\text{l}$ )	50	60
Colour	White	Light cream
pH <sup>a</sup>	3.6–4.3	7.5–8.5
Loss at 100°C (wt%)	< 1.5	–

<sup>a</sup>pH in water solution containing 4 wt% of filler.



### SILICA



### SEPIOLITE

FIGURE 2 SEM micrographs of *Aerosil 200* (fumed silica) and *Pangel S9* (sepiolite). ( $\times 5000$ ).

was added to the solvent. ii) The polyester urethane was added to the solvent-filler mixture, adding simultaneously all the solvent; the mix was stirred in the laboratory mixer at 2000 rpm for 150 minutes, and a homogeneous solution was obtained. That preparation procedure avoids the precipitation of filler from the solution with storage (monitored for three months after preparing the adhesive).

The nomenclature of PU adhesives used in this study was as follows: A = Blank (PU adhesive without filler); AB = PU adhesive containing *Pangel S9* sepiolite; AC = PU adhesive containing *Aerosil 200* fumed silica. Both the PU adhesive solutions and the dried films obtained from them were characterized. In order to prepare the PU films, about 50 cm<sup>3</sup> of adhesive solution was placed in a mould and the solvent allowed to evaporate slowly (to avoid the formation of air bubbles). The PU films obtained were about 0.6 mm thick.

## Experimental Techniques

*Scanning Electron Microscopy (SEM)*. The physical aspect and the shape of the filler particles (*Aerosil 200*, *Pangel S9*) were analyzed in microphotographs obtained in a *Jeol SEM JMS 840* microscope. Fillers were gold coated to give a good contrast.

*Thermal Mechanical Analysis (TMA) Measurements*. The deformation experienced by PU films was measured in a *Setaram TMA 92-16,18* apparatus. Film test pieces of 10 mm length, 10 mm width and 0.5–1.0 mm thickness were used. All experiments were carried out in compression mode under helium atmosphere using a constant force of 0.1 N produced by a semi-spherical test probe. Temperature was maintained at 25°C for 1 minute and subsequently increased to 200°C using a heating rate of 5°C/min; at the last stage of the measurement, the temperature was constantly maintained at 200°C for 10 minutes.

*Rheology of PU adhesive Solutions*. The viscosity, pseudoplasticity, thixotropy and viscoelastic properties of filled polyurethane adhesives were analyzed in a *Rheolab MC 100 Physica* rheometer. Viscosity measurements were carried out at 20°C 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<sup>3</sup> of PU adhesive solutions were used in the measurements and a solvent trap assured that minimal

evaporation of solvent occurred during the experiments. Controlled shear rate (CSR) experiments were carried out as follows: Shear rate was increased to  $1 \text{ s}^{-1}$  and maintained for one minute to provide a uniform and standardized state in all the solutions. The experiments were carried out by increasing, in 120 seconds, the shear rate to  $10 \text{ s}^{-1}$ ; this shear rate was maintained for 60 seconds and then, it was decreased to  $0 \text{ s}^{-1}$  in 120 seconds. Some experiments were repeated and an excellent reproducibility was always obtained. Viscoelastic properties were measured in the oscillatory mode by varying the frequency between 0.1 and 50 Hz, the amplitude selected was 0.5 (40.6 mrad).

*Rheology of PU Films.* The viscoelastic properties of PU film containing filler were determined in a shear stress controlled rotational *Bohlin CS50* viscoelastometer by using a plate-plate geometry. The diameter of the upper plate (*long shaft PP20* model) used was 20 mm, the gap selected being 0.45 mm. Oscillatory experiments were carried out to determine the viscoelastic properties (mainly the elastic,  $G'$ , and storage,  $G''$ , modulus) of the PU films. Experiments were performed by melting the adhesive at  $120^\circ\text{C}$  (the same temperature used to produce the adhesive joints), the target strain (which is related to the amplitude of sinusoidal signal) was 0.05, and the frequency was varied between 0.01 and 50 Hz. All the experimental results were obtained in the region of linear viscoelasticity.

*T-Peel Strength Measurements.* T-peel strength was measured in adhesive joints created between strips ( $150 \times 30 \text{ mm}$ ) of two vulcanized styrene-butadiene rubbers (R1, R2) – about 3 and 5 mm thick, respectively. The two rubbers selected in this study have been previously described [17] and the formulations are given in Table II. Depending on the nature of the rubber, two distinct surface treatments were used:

- i) R1 rubber was roughened (in a scouring machine at 2800 rpm using a no. 60 sandpaper of 200 mm diameter) to remove the most external rubber layer (about 0.5 mm was removed). Thus, the



TABLE II Composition of R1 and R2 vulcanized synthetic rubbers

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

influence of the addition of filler to the PU adhesive solutions on the practical adhesion was tested.

- ii) R2 rubber was roughened (similarly to R1 rubber) until 0.5 mm was removed, and immediately the surface was halogenated by brushing with 2-butanone solutions 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 [18, 19]. This treatment showed the influence on T-peel strength of the filled adhesives when a chemical treatment is applied to the rubber surface.

After carrying out the surface treatment, 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 120°C using infrared radiation in order to facilitate the interlocking of the chains of polyurethane applied to the two identically surface treated rubber strips. The strips were then placed in contact and a pressure of 0.8 MPa was immediately applied for 10 seconds to achieve a suitable joint.

T-peel strength was measured on an Instron 1011 (peel rate: 0.1 m/min). The values obtained were the average of five tests (standard deviation was less than 5%). The green (immediate) peel strength was measured 30 seconds after the two strips were joined. The evolution in T-peel strength was followed for a different time (until 72 hours) after joint formation.

### 3. RESULTS AND DISCUSSION

#### Rheological Characterization of Filled PU Adhesive Solutions

Figure 3 shows the variation of shear stress (Fig. 3a) and viscosity (Fig. 3b) as a function of shear rate for the adhesive solutions. The blank (PU adhesive without filler) shows a slightly pseudoplastic (almost Newtonian) behaviour and it does not show thixotropy. The filled PU adhesive solutions exhibit a pseudoplastic behaviour, and an increase in viscosity in respect to the blank, and the solutions show thixotropy. In the filled PU adhesive solutions, the pseudoplastic

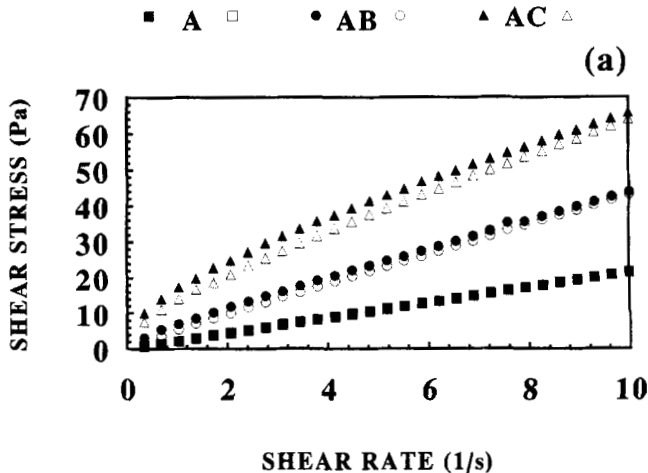


FIGURE 3 Variation of a). Shear stress, and b). Viscosity, as a function of shear rate in PU adhesive solutions without filler, and containing fumed silica or sepiolite. Open symbols: Increase in shear rate run; Closed symbols: Decrease in shear rate run.

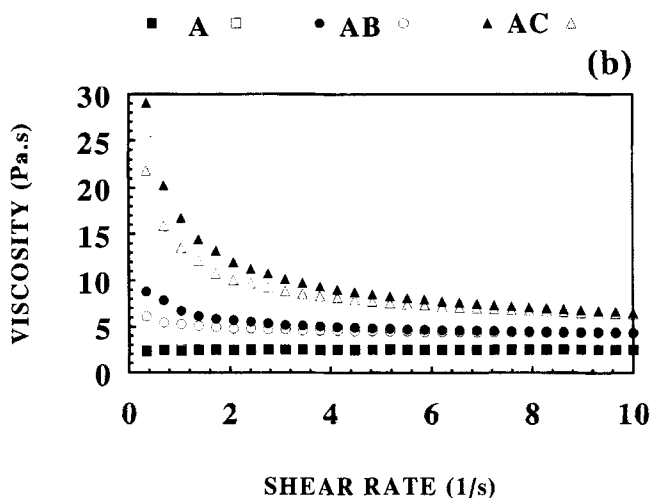


FIGURE 3 (Continued).

behaviour is responsible for the decrease in viscosity (Fig. 3a) upon increasing the shear rate, followed by an increase in viscosity when the shear rate is decreased. Furthermore, the curves of Figure 3b show an hysteresis loop due to the existence of thixotropy in the filled adhesives. The addition of silica produces a more marked increase in viscosity, and more thixotropy and pseudoplastic behaviour and an increase in viscosity in respect to the blank, and the solutions show thixotropy. In the filled-PU adhesive solutions, the pseudoplastic behaviour is provided to the adhesive. The pseudoplastic behaviour of silica-filled PU adhesive solutions has been previously ascribed [8,9] to the formation of hydrogen bonds between the silanol groups on the silica surface and some OH groups in the polyurethane and/or the solvent which facilitates the creation of a three-dimensional network. The higher particle size and the different shape of sepiolite in respect to the silica may facilitate a different and more reduced degree of interaction with the polyurethane and/or the solvent (probably van der Waals forces) and, therefore the increase in viscosity and the pseudoplasticity are less marked. The degree of pseudoplasticity can be quantified using the Shear Thinning Index (STI) – defined as the ratio of the shear stress values obtained for two different shear rates (10 and  $1 \text{ s}^{-1}$  were used in this study) – and it is given in Table III, where the

TABLE III Viscosity and STI ("Shear Thinning Index") of PU adhesive solutions

PU adhesive	Viscosity (Pa.s)	STI
A (blank)	2.2	0.97
AB (sepiolite)	4.4	1.53
AC (silica)	6.4	2.55

adhesive viscosity (measured at a shear rate =  $10 \text{ s}^{-1}$ ) is also included. The addition of silica or sepiolite produces a noticeable increase in viscosity, as well as creates pseudoplasticity, in the adhesive solutions, the variations being more significant in the silica filled-PU adhesive.

The variation in the viscoelastic properties of PU adhesive solutions is given in Figure 4. The behaviour of the solutions is mainly viscous, and the storage ( $G'$ ) and loss ( $G''$ ) moduli increase as the frequency increases. On the other hand, the storage and loss moduli increase after adding a filler, mainly silica. The increase is more noticeable in the low frequency region and in the storage modulus, indicating the creation of a network which inhibits the flow of the adhesive (more marked when the adhesive contains silica). Therefore, the fumed silica imparts more noticeable rheological modifications to the PU adhesive

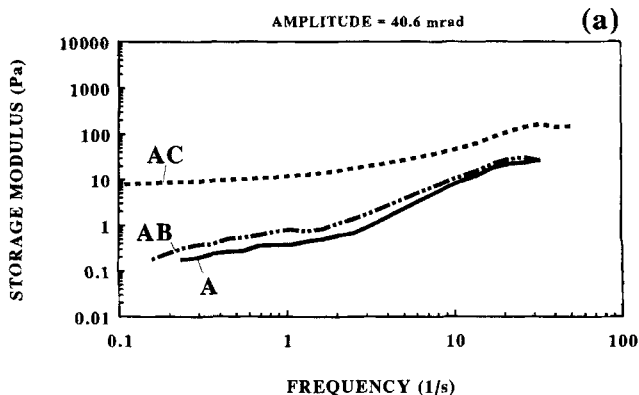


FIGURE 4 Variation of a). Storage modulus ( $G'$ ), and b). Loss modulus ( $G''$ ), as a function of frequency in PU adhesive solutions without filler, and containing fumed silica or sepiolite. Temperature =  $10^\circ\text{C}$ . Amplitude =  $40.6 \text{ mrad}$ .

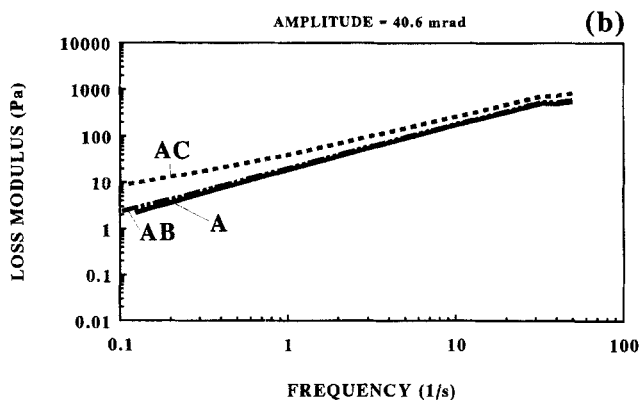


FIGURE 4 (Continued).

solutions than the sepiolite, although for both fillers an improvement in viscosity, thixotropy and pseudoplasticity is always obtained.

### Characterization of Filled PU Films

The properties of the adhesive films (*i.e.* in absence of solvent) determine the adhesion strength of PU, because the mechanical and viscoelastic properties, among others, of the adhesive films affect the measured practical adhesion. The mechanical properties of the adhesive films were determined using TMA, and the viscoelastic properties were measured in a plate-plate rheometer.

Figure 5 shows the TMA curves obtained with the different adhesives. Whereas the mechanical properties of PU without filler are strongly reduced by temperature, in the PU containing fillers the mechanical properties are maintained with the temperature (mainly in silica-filled PU). Therefore, the degree of deformation during the green T-peel test (in which the adhesive films are still hot) experienced by the filled PU adhesive films will be reduced, allowing an improvement in cohesive properties of the adhesive.

Figure 6 shows the variation of  $G'$  and  $G''$  in the PU films at a temperature of 120°C. This temperature was selected because the adhesive is melted at 120°C before the adhesive joint formation. The trends obtained agree with those found in the adhesive solutions

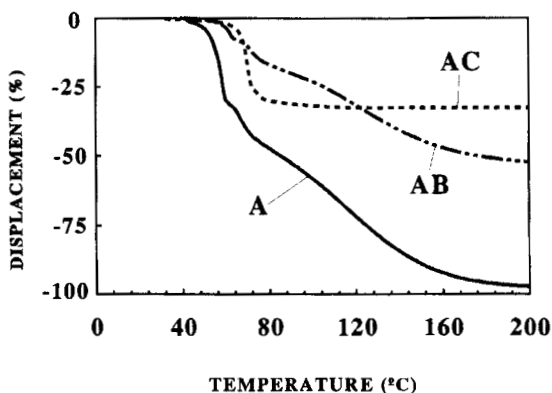


FIGURE 5 TMA curves of PU adhesive films without filler, and containing fumed silica or sepiolite.

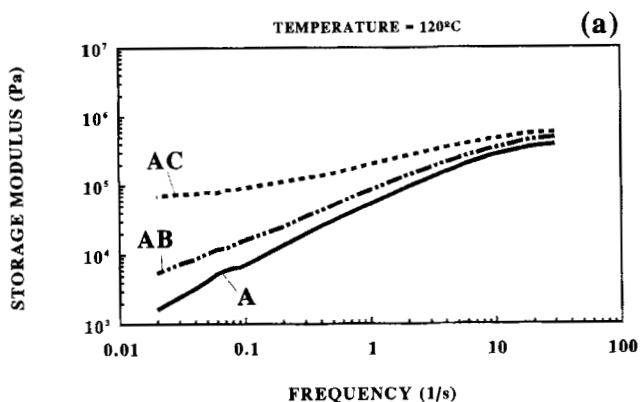


FIGURE 6 Variation of a), Storage modulus ( $G'$ ), and b), Loss modulus ( $G''$ ), as a function of frequency in PU adhesive films without filler and containing fumed silica or sepiolite. Temperature = 120°C. Target strain = 0.05.

(Fig. 4), although higher moduli are obtained and the differences among the adhesives are more marked. The addition of a filler increases the moduli, especially in the low frequency region and in the PU adhesive containing silica. The higher storage modulus in filled PU films means improved elastic properties in the melt and probably improved mechanical properties at room temperature, which will allow an increase in its adhesion properties. This also agrees with the

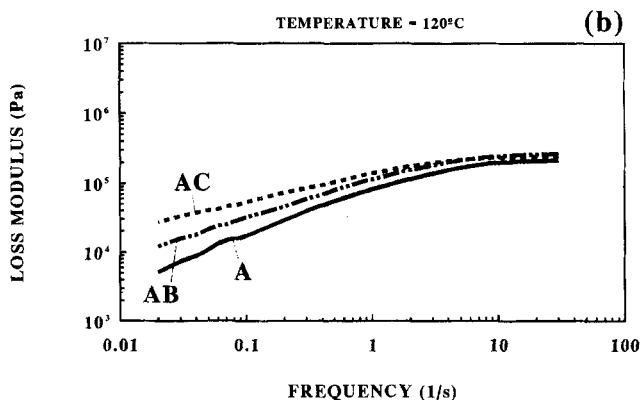


FIGURE 6 (Continued).

improved mechanical properties measured with TMA. On the other hand, the improvement in  $G'$  and  $G''$  can be ascribed to polyurethane/filler interactions because the solvent is removed in the PU films. Therefore, some "specific" interactions in the PU films between the silica or the sepiolite and the polyurethane chains can be produced.

### Adhesion Properties of Rubber/Filled PU Adhesive Joints

Figure 7 shows the immediate T-peel strength obtained in surface-treated rubber/PU adhesive joints. A noticeable increase in practical adhesion is obtained in the joints carried out with filled PU adhesives (independently of the filler nature). The increase is more pronounced in the roughened R1/PU adhesive joints where an adhesion (interphasic) failure is observed, whereas in the roughened + chlorinated R2/PU adhesive joints a cohesive failure in the adhesive is produced. The improvement in practical adhesion in chemically-treated R2 rubber joints may be related to the improved mechanical and viscoelastic properties in the filled PU adhesives.

The variation of T-peel strength with the time after bond formation is given in Figure 8. Independently of the surface treatment, the improved T-peel strength of joints produced with filled adhesives can be noticed for times after bonding smaller than 30 minutes (in respect to the blank), no important variations being produced by increasing the

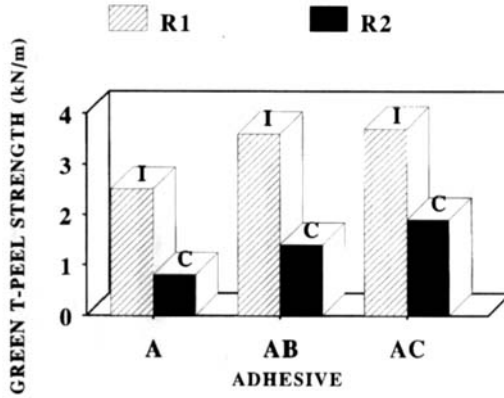


FIGURE 7 Immediate T-peel strength (30 seconds after bond formation) of surface-treated rubber/PU adhesive joints. PU adhesives without filler, and containing fumed silica or sepiolite. Surface treatments: R1 rubber = Roughened; R2 rubber = Roughened + Chlorinated with 1 wt% TCl. Locus of failure of the joints: I = Interphasial (adhesion) failure; C = Cohesive failure in the adhesive.

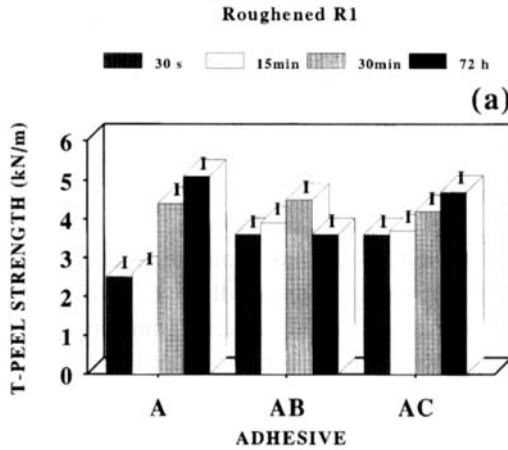


FIGURE 8 Variation of T-peel strength as a function of time after bond formation. PU adhesives without filler, and containing fumed silica or sepiolite a). Roughened R1 rubber/PU adhesive joints. b). Roughened + Chlorinated (1 wt% TCl) R2 rubber/PU adhesive joints. Locus of failure of the joints: I = Interphasial (adhesion) failure; C = Cohesive failure in the adhesive.

time. An adhesion failure of the joints was always found. The increase of the time after bond formation in chemically-treated R2 rubber produces a large increase in practical adhesion, but the unfilled and



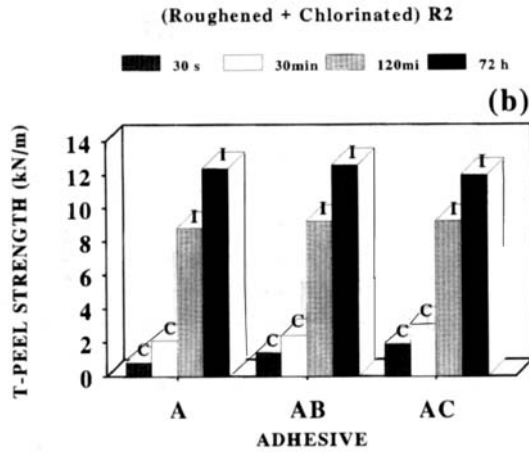


FIGURE 8 (Continued).

filled PU adhesives provide similar results 30 minutes after bond formation.

#### 4. CONCLUSIONS

The results obtained show that sepiolite is competitive with fumed silicas as a filler in solvent-based adhesives, providing improved viscosity, thixotropy and pseudoplasticity, and high values of storage and loss moduli. Immediate T-peel strength is greatly improved in filled PU adhesives. The effects produced by adding sepiolite or fumed silica to the adhesives were very similar, although in general more noticeable in fumed silica filled PU due to the formation of hydrogen bonds between the filler and the solvent and/or the polyurethane. In sepiolite filled adhesives, van der Waals forces seemed to be responsible for the interactions between the filler and the solvent and/or polyurethane. The use of sepiolite as a filler for solvent-based polyurethane adhesives is interesting due to the acceptable adhesion and rheological properties that it produces and because of its low price (eight-fold lower, at least, than fumed silicas).

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