Rheological Properties of Polyurethane Adhesives Containing Silica as Filler: Influence of the Nature and Surface Chemistry of Silica

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Abstract: Four silicas, two fumed silicas (one hydrophilic and one hydrophobic) and two precipitated silicas (one hydrophilic and one hydrophobic), were added as filler to solvent-based polyurethane (PU) adhesive formulations. In general, the addition of silica increased the viscosity, the storage and loss moduli of the PU adhesives but only the hydrophilic fumed silica exhibited pseudoplasticity and thixotropy. The rheological properties imparted by adding fumed silicas to PU adhesive solutions were more noticeable than that of precipitated silicas. Interactions between the hydrophilic fumed silica, the polyurethane and/or the solvent seemed to be responsible for the improved rheological properties of filled PU adhesives.

1. INTRODUCTION

The properties of adhesive formulations may be adequately modified by adding several compounds. Solvent based polyurethane (PU) adhesives are often employed to join styrene-butadiene rubbers (SBR) in the footwear industry [1,2]. Contact adhesives based on thermoplastic polyurethanes are commonly modified by adding fillers to impart viscosity, increase the mechanical properties and modify the rheological properties [3].

Precipitated silicas are manufactured by treatment of silicates with mineral acids to produce fine hydrated silica particles by precipitation. These precipitated silicas are cheap and have a particle size higher than 5 μm. On the other hand, fumed silicas are manufactured by high-temperature hydrolysis of silicon tetrachloride in a flame. Silanol and siloxane

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functional groups are thus created on the silica surface. The hydrophilic fumed silica surface may be modified by reaction with silanes to produce hydrophobic fumed silica.

The addition of hydrophobic and hydrophilic fumed or precipitated silicas to PU adhesives has been previously described [3,4] but a systematic study has not been carried out. In this study, the rheological properties of PU adhesives containing fumed and precipitated silicas (hydrophilic and hydrophobic) have been carried out.

Table 1. Some characteristics of the silicas used in this study.

Trade name	*AEROSIL 200*	*AEROSIL 805*	*FK310*	*SIPERNAT D10*
BET surface area (m^2/g)	200	150	650	90
Average primary particle size	12 nm	12 nm	4 μm	5 μm
PH value[(a)]	3.6-4.3	3.5-5.5	7	10.3
ADHESIVES	*P-A*	*P-R*	*P-FK*	*P-S*

[(a)] pH of 4 wt% silica in water.

2. EXPERIMENTAL

Materials. The PU solvent based adhesives without and with the four different silicas were prepared under similar experimental conditions. Some characteristics of the silicas are given in Table 1. The four silicas were manufactured by DEGUSSA AG (Hanau, Germany). The hydrophobic silicas (AEROSIL 805 and SIPERNAT D10) were prepared from the corresponding hydrophilic silicas (AEROSIL 200 and FK310) by treatment with silanes; this treatment does not modify the particle size but reduces the surface area. Fumed silicas possess much lower primary particle size than the precipitated silicas but tend to agglomerate to produce particles of about 2 μm size. Because the different preparation procedure the fumed silicas are acidic and the precipitated silicas are neutral or basic. The BET surface area of FK310 silica is higher than for the other silicas due to the presence of microporosity.

The PU adhesive solutions contain 170 g polyurethane and 17 g silica in 813 g butan-2-one. Polyester-urethane pellets based on ε-polycaprolactone (*Pearlstick 45-40/15*, Merquinsa S.A.- Barcelona) was used to prepare the PU adhesives solutions. These solutions were prepared in two stages: the silica was mixed with a small amount of butan-2-one at 2500 rpm for 10 minutes. Then, the pellets were added to the solvent-silica mixture, adding simultaneously all the solvent; the mix was stirred at 2000 rpm for 150 minutes to obtain a homogeneous solution. Some measurements were carried out using solvent free PU films prepared by placing about 50 cm^3 of adhesive solution in a mould and allowing the solvent to evaporate slowly. After solvent evaporation, the PU films obtained were about 0.6 mm thick.

Rheology of PU adhesive solutions. The viscosity, pseudoplasticity and thixotropy of filled PU adhesives were analyzed in a *Rheolab MC100 Physica* rheometer. The measurements were carried out at 20°C in the rotational mode using concentric cylinders. 100 cm^3 of PU adhesive solutions were used in the measurements and a solvent trap assured that minimal evaporation of solvent occurred during the experiments.

Rheology of solvent free PU films. The viscoelastic properties of solvent free PU films were determined in a *Bohlin CS50* viscoelastometer by using a plate-plate geometry. Oscillatory experiments were performed by melting the adhesive at 80°C, the target strain was 0.05, and the frequency was varied between 0.01 and 30 Hz. All the experimental results were obtained in the region of linear viscoelasticity.

Dynamic Mechanical Thermal Analysis (DMTA). Dynamic viscoelastic measurements were performed in a *Rheometric Scientific DMTA Mk III* apparatus, using the 3-point bending mode. The samples (0,6 × 10 × 20 mm) were heated from -80 °C to 100 °C using a rate of 5 °C/min., a frequency of 0.3 Hz and an amplitude of 64 μm peak-peak.

3 RESULTS AND DISCUSSION

Rheological characterization of PU adhesive solutions

Figure 1 shows the variation of the viscosity as a function of the shear rate in PU adhesive solutions containing different silicas. The addition of silica in the PU adhesive produces an increase in viscosity. This increase is more marked for the fumed silicas than for the precipitated silicas, and is enhanced in hydrophilic silicas. Moreover, the control (P) and the P-R, P-FK and P-S adhesive solutions exhibit a Newtonian behaviour, whereas the adhesive containing the hydrophilic fumed silica (P-A) is pseudoplastic and thixotropic. The pseudoplastic behaviour of the filled PU adhesive solutions is due to a rupture of the network between the silica (*Aerosil 200)* and the polyurethane and/or the solvent, which becomes gradually broken by increasing the shear rate, giving a decrease in viscosity. This network has been previously [3] ascribed to the creation of hydrogen bonds between the polyurethane and the silanol groups on the hydroplilic fumed silica.

The yield point of these adhesives can be obtained by applying the Casson model:

$$\sqrt{\sigma} = \sqrt{\sigma_0} + \sqrt{(b\,D)}$$

where σ is the shear stress, D is the shear rate and σ_0 is the yield point. The yield point of the adhesive solutions with different silicas obtained applying the Casson model, are the following: 0.001 Pa (P); 5.437 Pa (P-A); 0.023 Pa (P-FK); 0.075 Pa (P-R); and 0.005 Pa (P-S). The P-A adhesive is the unique with a high yield point, indicating the formation of a network between the silica (*Aerosil 200)* and the polyurethane and/or solvent.

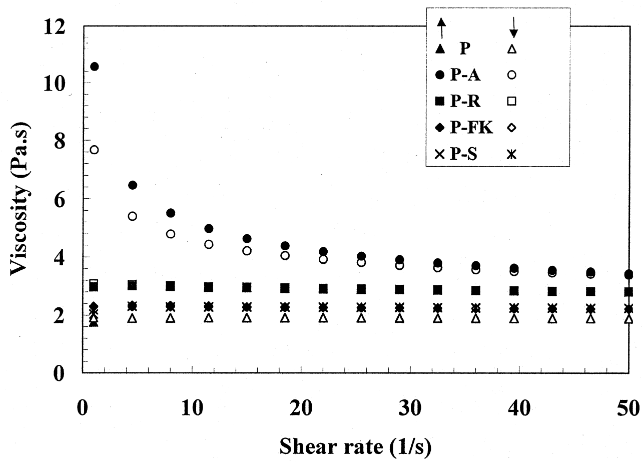
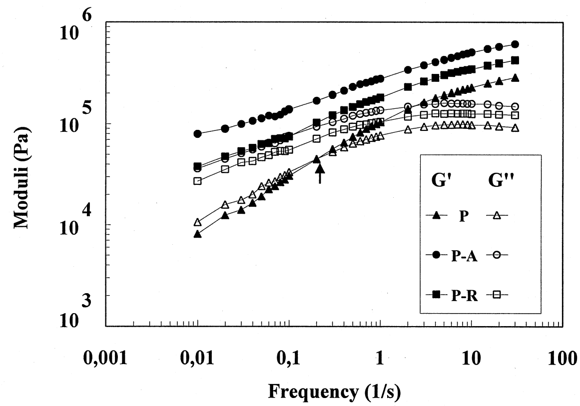


Figure 1. Variation of the viscosity as a function of shear rate in PU adhesive solutions without filler, and containing different silicas. Temperature = 20 °C. Closed symbols : Up (increase in shear rate). Open symbols : Down (decrease in shear rate).

Figures 2.a and 2.b show the variation of the loss and storage moduli as a function of the frequency in the PU films without solvent containing fumed and precipitated silicas, respectively. The addition of silica to polyurethane adhesives produces an increase in the moduli, but the fumed silicas produce an increase more important in the low frequency region. Those fumed silicas impart a greater elasticity to the polyurethane which will probably provide improved mechanical properties. The increase in moduli in the low frequency region indicates the inhibition of the fumed silica-PU blend to flow at those frequencies, because a network between the silica and the polyurethane exists [3]. On the other hand, the control and the PU films containing precipitated silicas (Figure 2.b) show, at a given frequency, a change from viscous to elastic properties due to the entanglement of PU chains. However, in the PU films containing fumed silicas (Figure 2.a) always an elastic behaviour is obtained.

DMTA experiments allow the viscoelastic properties of the adhesives to be determined in the region of low temperature. No important differences in the moduli were found by adding silica to PU adhesives, independently of the silica nature. The T_g of the PU films (taken as the maximum of the loss modulus curves) does not change by adding silica or by changing the surface chemistry of the silica.

a)



b)

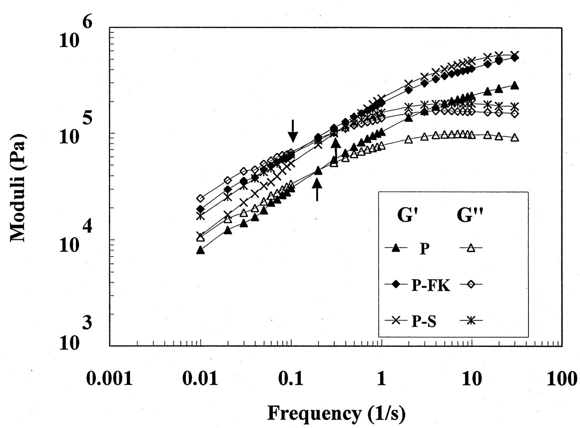


Figure 2. Variation of storage (G') and loss (G'') moduli as a function of the frequency in PU films without filler, and containing silicas. **a)** Fumed silicas; **b)** Precipitated silicas. Temperature = 80 °C. Target strain = 0.05.

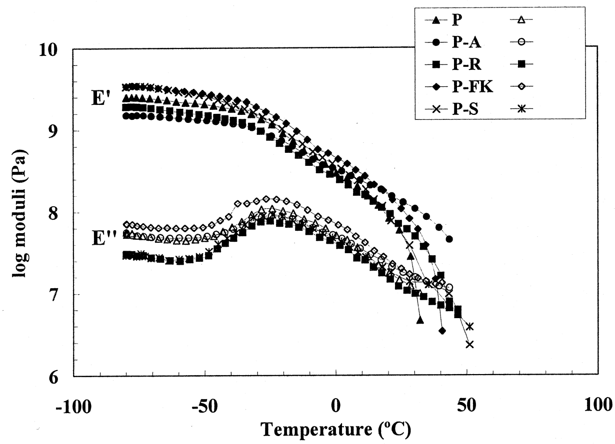


Figure 3. Variation of the storage (E') and loss (E'') moduli as a function of temperature (DMTA curves) in PU films without filler, and containing different silicas. Frequency = 0.3 Hz. Amplitude = 64 μm peak-peak.

4. CONCLUSIONS

The addition of silica produces an increase in viscosity, but only the PU adhesive solution containing the hydrophilic fumed silica exhibits thixotropy and pseudoplasticity. Furthermore, the addition of silica produces an increase in storage and loss moduli in the solvent free PU films, especially for fumed silicas.

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5. REFERENCES

1. M. Nargiello, *Adhesive Age* **32**, 30 (July, 1989).
2. H. P. Raltson, *Adhesive Age* **32**, 32 (July, 1989).
3. T.G. Maciá-Agulló, J.C. Fernández-García, N. Pastor-Sempere, A.C. Orgilés-Barceló and J.M. Martín-Martínez, *J. Adhesion* **38**, 31 (1992).
4. T.G. Maciá-Agulló, J.C. Fernández-García, A. Torró-Palau, A.C. Orgilés-Barceló and J.M. Martín-Martínez, *J. Adhesion* **50**, 265 (1995).