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Modification of the Rheological Properties of Polyurethanes by Adding Fumed Silica: Influence of the Preparation Procedure

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Summary: The way of addition of fumed silica determined the rheological properties of polyurethane (PU) adhesives. The higher the shear rate during preparation of fumed silica containingPU adhesives, the higher viscosity and improved plasticity and thixotropy in the solutions. The improved properties of these adhesive solutions were ascribed to the creation of interactions between the silanol groups on the fumed silica, the polar groups in the soft segments of the polyurethane and/or the solvent. However, the way of incorporate the fumed silica in the polyurethane did not affect the rheological properties of fumed silica-PU composites (obtained by solvent removal from the solutions), indicating the key role of the solvent in the rheology of PU adhesive solutions.

Introduction

Fumed silicas are common rheological fillers in coatings and adhesives[1]. Addition of fumed silica increases the viscosity of PU solutions and also imparts pseudoplasticity and thixotropy[2]. Furthermore, the mechanical properties of PU-fumed silica composites are enhanced.

Several properties of the fumed silicas affect the performance of PU-fumed silica systems. It has been stated that the specific surface area and particle size[3], the surface chemistry[4] and the amount of fumed silica[2] greatly determine the performance of both the fumed silica-PU solutions and composites. However, due to the small particle size of fumed silicas and their easy tendency to aggregate, the way of addition of the fumed silica to the PU may also affect their properties. In this study, the way of incorporation of a fumed silica in a PU in butanone solution was varied, and the rheological properties of solutions and composites were determined.

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Experimental

Materials. A hydrophilic fumed silica (Aerosil 200) provided by Degussa AG (Hanau, Germany) was used as filler in PU adhesive solutions. Some characteristics of this fumed silica are : Primary particle size =12 nm; specific surface area (BET – N_2/77K) = 200 m^2/g ; pH = 4.3. Solid pellets of ε-polycaprolactone based polyurethane (*Pearlstick 45-40/15*, Merquinsa S.A., Barcelona, Spain) were used to prepare the PU adhesive solutions. This polyurethane has a medium thermoplasticity (reversible tendency to melt under heating), short open time and very high crystallization rate.

The PU solutions contain 16.5 wt% polyurethane, 1.65 wt% fumed silica and 81.85 wt% butanone. These solutions were prepared in a Cowles type mixer (stirrer diameter=50 mm) using two different procedures : *i).* PU/SiO_2 : High shear stirring (2.500 rpm, 15 min) of the fumed silica in 1/3 total volume of butanone in the adhesive solution, followed by addition of the polyurethane and the 2/3 volume of butanone (this mixture was stirred at 2.000 rpm for 120 min); *ii).* PU+SiO_2 : Addition of the polyurethane in the butanone (stirring at 2.000 rpm for 105 min) followed by addition of the fumed silica under stirring at 2.000 rpm for 15 min. As control, a PU adhesive only containing the polyurethane and the solvent (PU) was also prepared.

Experimental conditions. Rheology of the PU solutions. The viscosity of PU/SiO_2 and PU+SiO_2 solutions were analyzed in a Rheolab MC100 Physica rheometer. The measurements were carried out at 20°C in the rotational mode using concentric cylinders type Z2 (according to DIN 53019). 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. Controlled shear rate (CSR) experiments were carried out. In addition, the viscoelastic properties of the PU adhesive solutions were measured at 10 °C in the oscillatory mode by varying the frequency between 0.1 and 50 Hz. The amplitude used was 40.6 mrad and all the measurements were obtained in the region of linear viscoelasticity.

Rheology of the PU films. The solvent from the adhesive solutions was removed and solid PU/SiO_2 and PU+SiO_2 composite films were obtained. These composites were characterized using stress controlled plate-plate rheology in a *Bohlin CS50* viscoelastometer. Oscillatory experiments were performed by melting the adhesive at different temperatures (50, 80, 120°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 and master curves were obtained using 50°C as reference temperature.

Results and discussion

Rheological behaviour of PU adhesive solutions.

Figure 1 shows the variation of the viscosity as a function of the shear rate for the PU, PU/SiO_2 and PU+SiO_2 adhesive solutions. The PU solution shows a Newtonian behaviour because the viscosity does not vary by increasing the shear rate. However, the solutions containing fumed silica show pseudoplasticity (i.e. the viscosity decreases by increasing the shear rate) and thixotropy (i.e. the viscosity increase by increasing the shear rate and an increase in viscosity is obtained by decreasing the shear rate). These improved rheological properties can be ascribed to the interactions between the silanol groups on the fumed silica and the polar groups in the polyurethane chains and/or the solvent[3-5]. In fact, the increase in the yield stress (σ_o – Table 1) of PU solution by adding fumed silica indicates that higher stresses are necessary to allow flowing of these solutions, i.e. stronger interactions between the components in the solutions are produced.

Table 1. Shear Thinning Index (STI), thixotropy and yield stress (σ_o – obtained from Casson model applied to the rheological curves of solutions).

Adhesive solution	STI	Thixotropy (Pa/s.cm^3)	σ_o (Pa)
PU	1.01	0.01	0
PU+SiO_2	1.54	1.66	2.89
PU/SiO_2	2.17	3.06	8.76

The way to incorporate the fumed silica influences the rheological properties of the solutions. The viscosity, the thixotropy and the pseudoplasticity of PU/SiO_2 are higher than those of the PU+SiO_2 solution (Table 1), indicating the improved rheological properties obtained when a high shear stress is produced during the mixing of the fumed silica and the polyurethane in butanone. Because the solids content in both solutions is similar, the improved rheological properties of PU/SiO_2 should be ascribed to a higher degree of interactions as indicated by its higher yield stress value (Table 1).

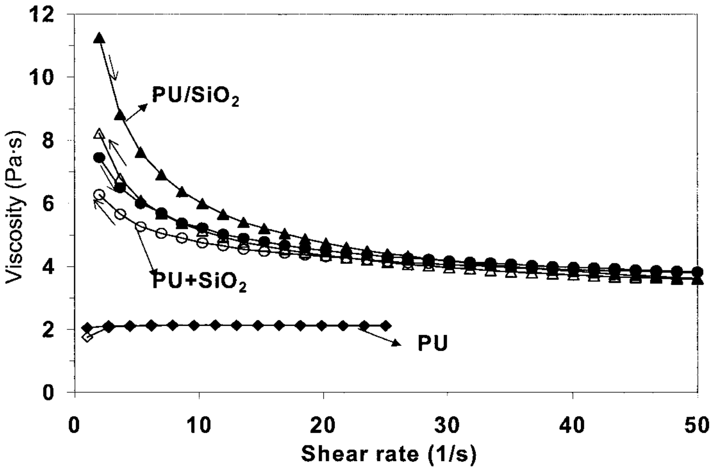

Figure 1. Viscosity vs. shear rate in the adhesive solutions.

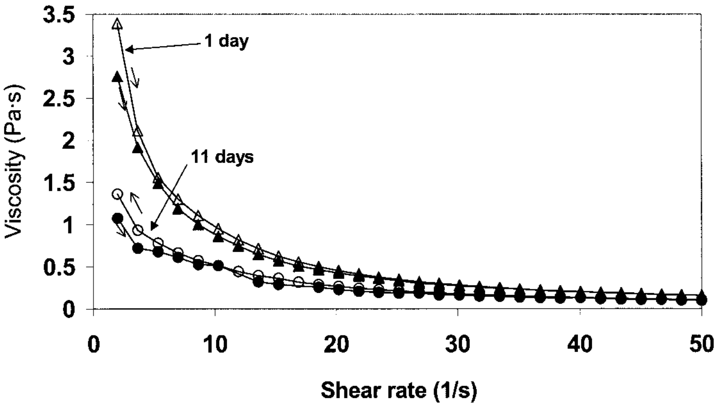

Figure 2. Viscosity vs. shear rate for a solution of 10 wt% fumed silica in butanone.

The solvent (butanone) strongly interacts with the fumed silica. Figure 2 shows the variation of the viscosity vs. shear rate for a butanone solution containing 10 wt% fumed silica. The fumed silica imparts pseudoplasticity and some thixotropy to the butanone, and these improved rheological properties decline by increasing the time after preparation of the solution, i.e. when the effects due to shearing become lost.

Figure 3 shows the variation of the storage modulus (G′) and loss modulus (G”) of the adhesive solutions as a function of the frequency at an amplitude of 24.3 mrad. The storage modulus in PU/SiO_2 is higher than is in PU+SiO_2, being this increase more noticeable in the low frequency region (flow region), indicating the creation of a network in the adhesive solution PU/SiO_2 which inhibits the flow of the solution. For PU/SiO_2 a change in the behaviour of the solution is produced and it is observed a cross-over between the storage and loss moduli at a frequency of 0.24 Hz. The better dispersion of the fumed silica (i.e. the higher shearing during mixing) favours the interactions of fumed silica with the components of the adhesive.

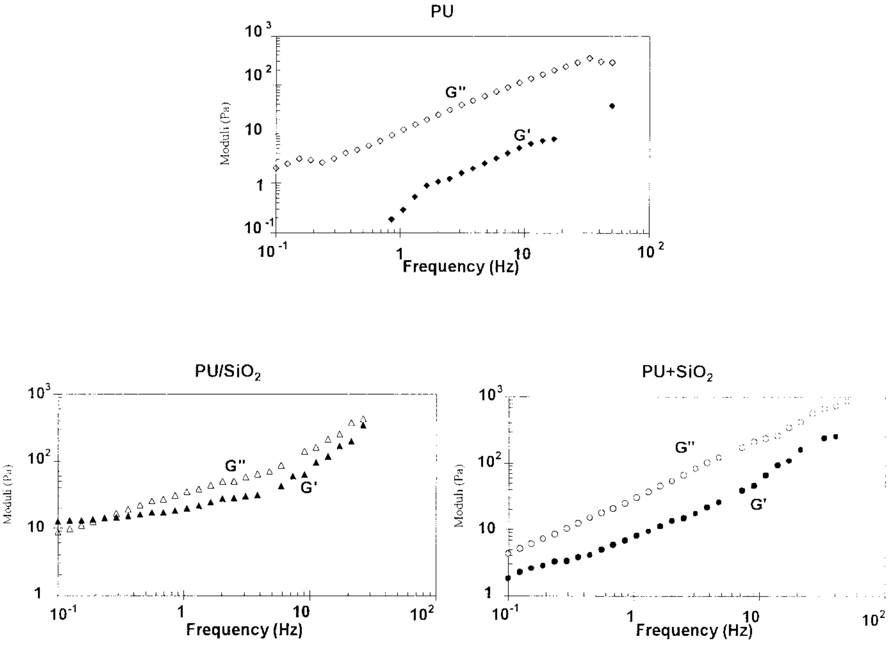

Figure 3. Variation of the storage and loss moduli of adhesive solutions vs. frequency.

The presence of silanol groups on the fumed silica surface allows the easy formation of hydrogen bonds with the polyurethane, facilitating the creation of network in solution as polymer matrix. Such a structure influences strongly the rheological properties of PU-fumed silica systems, allowing higher storage moduli and improved viscoelastic properties.

Rheology of fumed silica+PU composites

Figure 4 shows the master curves of PU, PU+SiO_2 and PU/SiO_2 films (obtained after solvent removal). The PU film shows a cross-over between the storage and the loss modulus at about 5.10^{-2} Hz. Addition of fumed silica increases the moduli, mainly the storage modulus and the cross-over is not produced. This is due to the creation of a network between the fumed silica and the polyurethane which produces an increase in the mechanical properties of fumed silica+PU composites. However, similar rheological curves are obtained for PU+SiO_2 and PU/SiO_2 indicating that the shearing during mixing mainly affects the interactions between the butanone and the fumed silica.

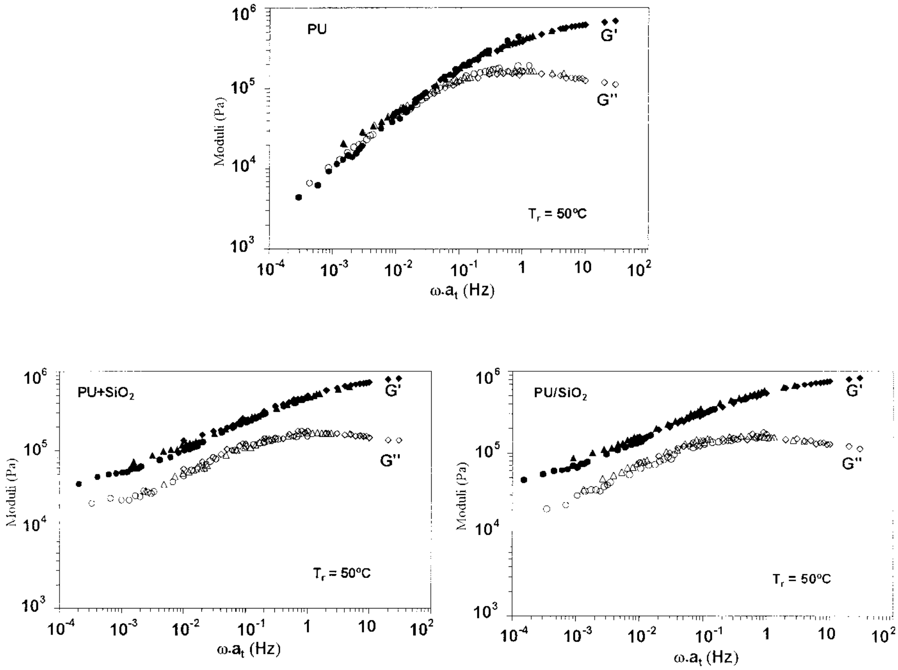

Figure 4. Variation of the storage and elastic modulus in fumed silica-PU composites.

Conclusion

1. The shearing during polyurethane–fumed silica mixing determines the rheological properties of the solutions. The higher shear speed during the preparation of polyurethane-fumed silica solutions favoured thixotropy and pseudoplasticity.

2. After solvent removal, the properties of polyurethane–fumed silica films were similar, independently of the shear speed used during the preparation of the solutions.

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