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Use of Calcium Carbonate – Fumed Silica Mixtures as Filler in Polyurethane Adhesives

José Sepulcre-Guilabert, Teresa del Pilar Ferrandiz-Gómez, José Miguel Martín-Martínez*

Adhesion and Adhesives Laboratory, Department of Inorganic Chemistry, University of Alicante, 03080 Alicante, Spain.

SUMMARY: Natural ultramicronized calcium carbonate and mixtures of fumed silica-natural ultramicronized calcium carbonate are proposed as fillers of solvent based polyurethane (PU) adhesives. PU adhesive containing only calcium carbonate shows similar rheological, thermal, mechanical, surface and adhesion properties than the PU adhesive without filler. Addition of 90 wt% fumed silica + 10 wt% calcium carbonate mixture to PU adhesive produced a similar performance than the PU adhesive containing only fumed silica. The increase in the amount of natural calcium carbonate in respect to fumed silica in the filler mixture produced detrimental effect on the rheological and mechanical properties of the PU adhesives (in respect to those provided by the PU adhesive only containing fumed silica), although the surface and adhesion properties were not noticeably modified.

Introduction

Solvent based polyurethane (PU) adhesives are used in the footwear and automotive industries, and are common household adhesives. Their properties are adapted to specific applications by adding different components, the fillers are mostly used to modify the rheological and mechanical properties[1]. Fumed silicas are the most common fillers for PU adhesives[2,3] but they are relatively expensive and have a small particle size, which makes difficult their manipulation during the manufacturing process.

Calcium carbonate is the most common filler in the polymer industry because of its low cost and broad range of particle sizes. Natural calcium carbonate is considered as an inert filler[4] because a poor interaction with the polymer is produced, although the addition of calcium carbonate increases the tensile strength. The use of calcium carbonate in solutions is not common because settling is produced. Recently, the development of ultramicronized calcium carbonate avoids this limitation. In this study, a ultramicronized natural calcium carbonate with small particle size has been added as a filler in PU adhesives formulation. Furthermore, different mixtures of fumed silica

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and calcium carbonate have been used as fillers of PU adhesives, in order to produce a good balance between properties and price.

Experimental

Materials. A natural ultramicronized calcium carbonate (M) - supplied by S.A. REVERTE (Bellvei, Tarragona, Spain) - and a fumed silica - supplied by DEGUSSA AG (Hannau, Germany)- have been used in this study. The particle size of calcium carbonate is lower than 1 μm diameter, its specific surface area is 11 m^2/g, and it has been surface modified with stearic acid derivative. The fumed silica has a specific surface area of 200 m^2/g and a primary particle size of about 10 nm. A thermoplastic polyester-urethane polymer supplied by MERQUINSA S.A., (Barcelona, Spain) was used to prepare the PU adhesive solutions. This polyurethane has short open time and very high crystallization rate. The PU adhesive solutions in acetone containing 18 wt% polymer and 10 wt% fillers (calcium carbonate and/or fumed silica) were prepared in a laboratory mixer. The preparation of PU adhesive solutions was carried out in two consecutive stages: (i) The fillers were mixed for 15 min at 2500 rpm with 1/3 acetone volume required in the adhesive. (ii) The polyurethane and 2/3 acetone required in the adhesive were added to the previous solution, stirring the mixture for 3 hours at 1500 rpm. A PU adhesive solution without fillers (P) was also prepared under the same experimental conditions and used as control. The nomenclature of the PU adhesives consists in the capital letter P + the percentage of fumed silica in the fillers mixture + the capital letter S + the percentage of calcium carbonate in the fillers mixture + the capital letter M. Some experimental results were obtained using PU films, which were prepared by placing the adhesive solution in a mould, allowing a slow evaporation of the solvent for 2 days.

Experimental techniques. Rheology of PU adhesive solutions. The viscosity of PU adhesive solutions containing fillers were analyzed in a Rheolab MC100 Physica rheometer. The measurements were carried out at 20°C in the rotational mode using concentric cylinders (according to DIN 53019). 100 cm^3 of PU adhesive solutions were used in the measurements and a solvent trap assured a minimal evaporation of solvent during the experiments. Controlled shear rate (CSR) experiments were carried out. Viscoelastic properties (mainly the storage, G', and the loss, G'', moduli) of PU solutions were measured at 20°C. The frequency was varied between 0.1 and 50 Hz. All experimentals results were obtained in the region of linear viscoelasticity.

Rheology of PU films. The viscoelastic properties of PU films were determined in a Bohlin CS50 viscoelatometer by using a plate-plate geometry. The diameter of the upper plate used was 20 mm, the gap selected being 0.40 mm. The variation of the storage, G′, and the loss, G′′, moduli as a function of the temperature were carried out at constant frequency (1 Hz). The target strain was 0.005. All the experimental results were obtained in the region of linear viscoelasticity.

T-peel test. Adhesion was measured using T-peel test of plasticized PVC/PU adhesive joints. The surface of plasticized PVC strips (150x30 mm, about 5 mm thick) were wiped using a Kleenex® tissue impregnated with 2-butanone. Subsequently, 100 mg PU adhesive solution was applied to each plasticized PVC strip to be joined and left to dry for 2 hours. After evaporation, a solid PU film was formed, which was suddenly heated to 90°C using infrared radiation. The strips were placed immediately in contact under a pressure of 0.8 MPa for 10 seconds to achieve a suitable joint. The T-peel test was carried out in a Instron 4411 test instrument. The peel rate was 0.1 $m.min^{-1}$ and T-peel force was monitored for different time after joint formation (45 min.to 72 h.). The values obtained were the average of five experimental determinations. Ageing tests of adhesive joints were also carried out at 50°C and 95% relative humidity for 72 h.

Results and Discussion

Figure 1.a) shows the flow curves of PU adhesive solutions. The control and the adhesive containing only $CaCO_3$ show a Newtonian behaviour and exhibit the lowest viscosity. Because the solid content in P10M solution (polymer + $CaCO_3$) is higher than in P (only polymer), the $CaCO_3$ acts as an inert filler. The PU solution containing only fumed silica shows pseudoplasticity and the highest viscosity in the series, due to the formation of a network between the polyurethane, the solvent and the filler[5] which increases the resistance of the adhesive to flow under shear. The addition of $CaCO_3$+SiO_2 mixtures as fillers produces a gradual loss of pseudoplasticity and viscosity as the percentage of $CaCO_3$ increases; however, similar rheological properties are obtained in P10S and P9S1M solutions due to the predominance of the effects produced by the fumed silica. Figure 1 b) shows the variation of the elastic modulus as a function of the frequency in the PU adhesive solutions. The elastic modulus shows a markedly decrease at low frequencies for P and P10M adhesives because the structure is collapsed due to poor interactions between the components in the solutions. The effect is enhanced in P10M adhesive because the $CaCO_3$ interfere the interactions between the PU chains. All adhesive solutions containing fumed silica

show high elastic modulus, and the modulus increases slightly (and only at low frequency) as the percentage of SiO_2 in the filler mixture increases.

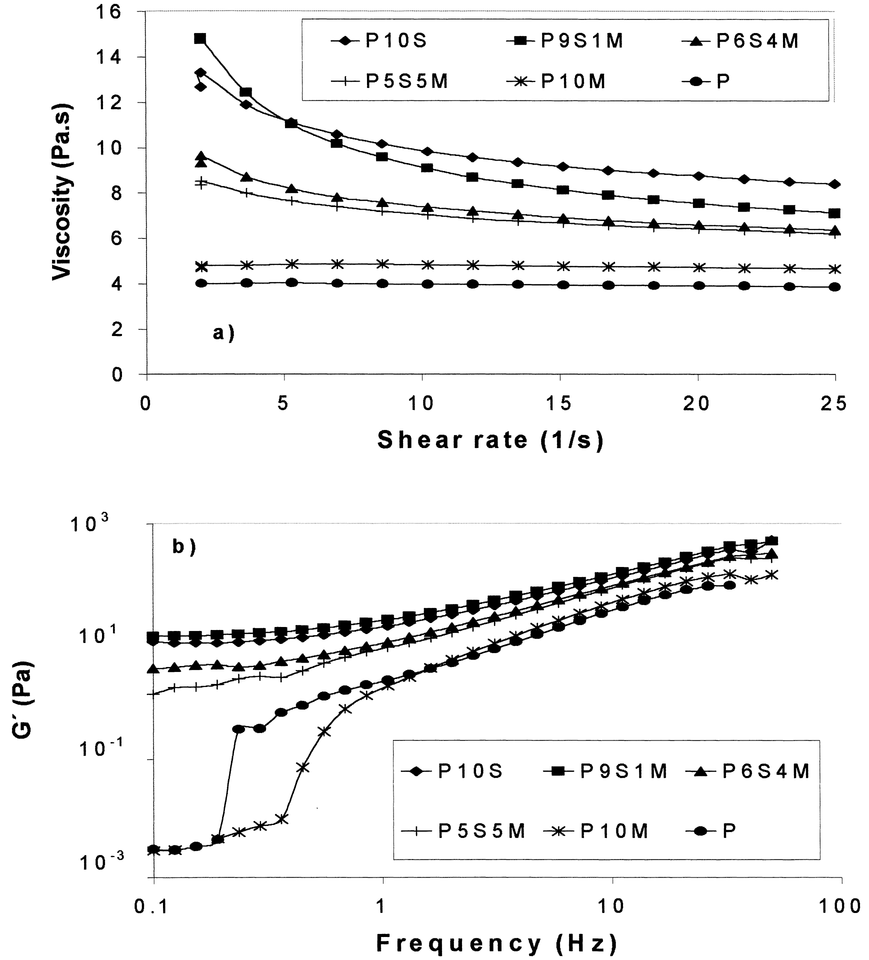

Figure 1. a) Flow curves of PU adhesive solutions, b) Variation of the elastic modulus as function of the frequency in PU adhesive solutions.

The variation of the elastic and viscous moduli as a function of the temperature in PU films are given in Figure 2. The control P shows a cross-over between the elastic and viscous modulus at 63°C. Addition of fumed silica (P10S film) produces an increase in moduli, mainly in elastic modulus which is always higher than the viscous modulus (i.e. no cross-over is produced).

Addition of $CaCO_3$ (P10M film) shows a similar rheological behaviour than the control, although the shift of the cross-over is displaced to lower temperature than in the control (similarly to the P10M solution - Figure 1.b). The addition of $CaCO_3$+ SiO_2 mixtures (P6S4M film) shows an intermediate behaviour between that of the pure fillers, i.e. rheological properties imparted by $CaCO_3$ and fumed silica are obtained.

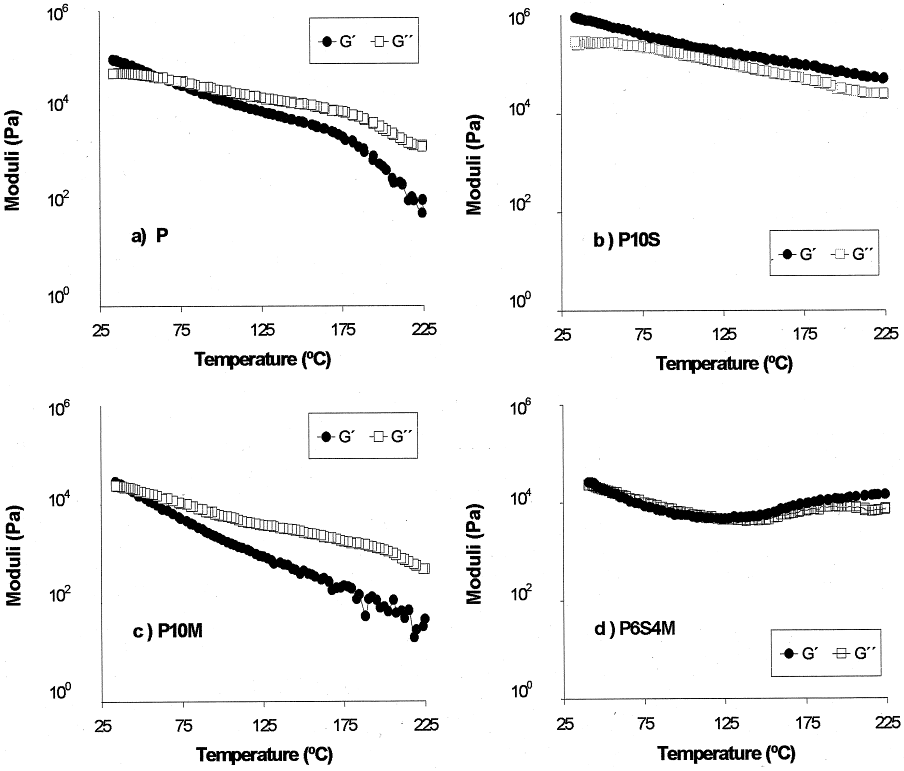

Figure 2. Variation of the G′ and G″ moduli as a function of the temperature in PU films.

Figure 3 shows the T-peel strength of plasticized PVC/PU adhesive joints. The immediate adhesion increased when the P10S and P9S1M adhesives are used, and the cohesive failure in the adhesive was always found. The increase in time after joint formation produces an increase in adhesion and 72 hours after joint formation no differences in peel strength are obtained with any adhesive. An adhesional failure was obtained because the crystallization of the polyurethane was completed. Ageing produces a small decrease in peel strength which is similar for all the joints.

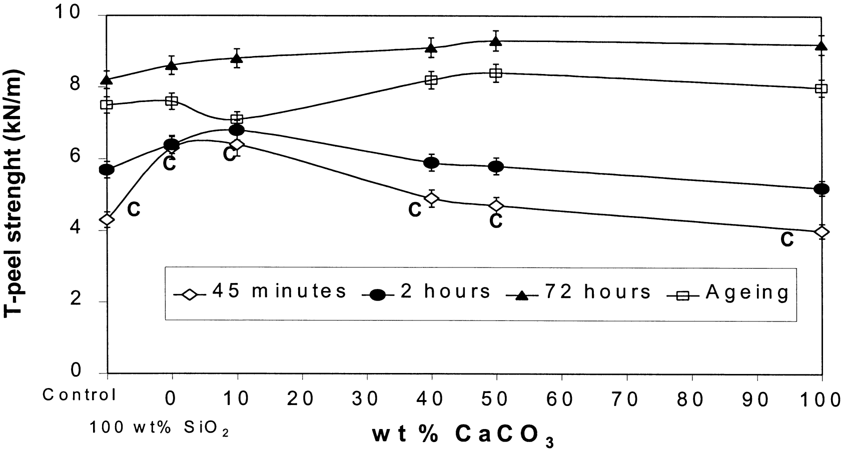

Figure 3. T-peel strength of plasticized PVC/PU adhesive joints. Influence of the time after joint formation. Locus of failure: Always interfacial, except C= cohesive failure in the adhesive.

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References

1. 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).
2. A. Torró-Palau, J.C. Fernández-García, A.C. Orgilés-Barceló, M.M. Pastor-Blas and J.M. Martín-Martínez. *J. Adhesion* **61,** 195 (1997).
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. *Handbook of Fillers for Plastics* 2nd edition. Editors : H.S. Katz and J.V. Milewski. Chapter 6, A. Baker, L. Koller, E. Kummer, "Calcium Carbonate". p.119-142. Van Nostrand Reinhold, New Jersey (1987).
5. T.G. Maciá-Agulló, J.C. Fernández-García, A.C. Orgilés-Barceló, A. Torró-Palau and J.M. Martín-Martínez. *Macromolecular Symp.* **108,** 269 (1996).