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Effect of the Amount of Calcium Carbonate as Filler on the Rheological and Adhesion Properties of a Water-Based Polyurethane Dispersion

Ana Belén Muñoz-Milán, Mª Ángeles Pérez-Limiñana, Francisca Arán-Aís, Ana Torró-Palau, A. César Orgilés-Barceló*

INESCOP, Footwear Research Institute. 03600 Elda (Alicante), Spain
E-mail: adhesivos@inescop.es

Summary: In this study, the properties of water-based adhesives based on a polyurethane ionomer (PUD) and a micronised $CaCO_3$ as filler was analysed. Different amounts of a micronised $CaCO_3$ (5-25 wt%) were added to water-based polyurethane (PUD) adhesive formulations in order to reduce its relatively high cost. The addition of a micronised calcium carbonate filler increased the viscosity, the storage and loss moduli of the PUD adhesives, and imparted pseudoplasticity and thixotropy, more noticeably for the adhesive with the highest calcium carbonate content. The creation of acid-base interactions seemed to be responsible for the improvement in the rheological properties of the PUD adhesives containing $CaCO_3$ as filler. On the other hand, the addition of $CaCO_3$ filler might deteriorate the adhesion properties to PUD adhesives.

Keywords: adhesive; calcium carbonate; dispersion; filler; rheology; water-based polyurethane

Introduction

Water-based polyurethane adhesives are an interesting alternative to the current solvent-based polyurethane adhesives used in the footwear industry because of their lack of flammability and toxicity that complies with the restrictive environmental legislation (Directive 99/13/EC) with respect to the emission of organic solvents into the atmosphere. Water-based polyurethane dispersions (PUD) offer an efficient alternative to solvent-based adhesives, the one most commonly used in the upper-to-sole bond in the footwear industry [1]. However, their relatively high cost is one of their drawbacks. Generally, micronised calcium carbonates are mainly used to reduce formulation costs, while to a certain extent controlling the viscosity during the preparation and application of several adhesives [2-3]. For this reason, the effect of incorporating different amounts of a micronised calcium carbonate on the properties of a water-based polyurethane dispersion was studied with the aim of improving some properties and reducing its cost.

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Experimental

Materials. In order to perform a systematic study of the influence of adding $CaCO_3$ on the properties of water-based polyurethane adhesives, PUD adhesives with different percentage of a micronised $CaCO_3$ were prepared. The PUD adhesives contain the polyurethane dispersion and amounts between 0 and 25 wt% micronised $CaCO_3$ with respect to the total adhesive mass. An aliphatic, aqueous thermoplastic polyurethane dispersion based on highly crystalline polycaprolactone polyurethane (Quilastic DEP-170) provided by Merquinsa, Barcelona (Spain) was used to prepare the filled PUD adhesives. It is an anionic ionomer polyurethane dispersion with a mean particle size between 0,1-0,3 μm. The micronised $CaCO_3$ was provided by S.A. Reverté, Tarragona (Spain), and some of its characteristics are included in Table 1 [4].

Table 1. Some characteristics of the micronised calcium carbonate.

PROPERTY	**VALUE**
Size (μm) (95%)	<0,6
BET specific surface area (m^2/g)	14,5
Oil absorption (g/100g)	20
Humidity (%)	<0,1
Apparent density (g/mL)	0,50
Compacted apparent density (g/mL)	0,80
pH	8,8

The filled PUD adhesives were prepared by the following procedure: the micronised $CaCO_3$ was added to the PUD dispersion gradually and the mixture was stirred in a Cowles mixer at 850 rpm for 45 min, after which a homogeneous dispersion was obtained. Some measurements were carried out using water free PUD films prepared by placing about 50 mL of adhesive dispersions in a mould and allowing the water to evaporate slowly under ambient conditions.

Experimental techniques

Determination of solids content. The solids content of the PUD adhesives were determined according to the European Standard EN-827.

pH measurements. pH values were measured using a pH-meter with a silver reference electrode model HI 8418 (Hanna Instruments), at 20°C and according to the European Standard EN ISO 4045.

Rheology of the adhesive solutions. The viscosity, pseudoplasticity and thixotropy as a function of the shear stress of filled PUD adhesives were analysed in a Bohlin CS-50 rheometer. The measurements were carried out at 25°C in the rotational mode using concentric cylinders type C25. 25 mL of PUD adhesive dispersions were used in the measurements.

Rheology of water-free PUD films. The viscoelastic properties of the water-free PUD films were determined in a Bohlin CS-50 rheometer by using a plate-plate geometry. Oscillatory experiments were performed by melting the adhesive film at 70°C which is the reactivation temperature of the PUD adhesives used. The target strain was 0,005, and the frequency was varied between 0,01 and 30 Hz. All the experiments results were obtained in the region of linear viscoelasticity.

T-peel strength tests. Adhesion properties were assessed through T-peel strength on split leather/PUD adhesive/SBR rubber joints. SBR rubber was roughed and subsequently halogenated (2 wt%TCI/MEK), while the split leather was gently roughed and an adhesive primer was applied to it (European Standard EN 1392). After carrying out the surface treatment, the PUD adhesive was applied to each strip surface and left to dry for 30 min. The PUD adhesive film was heated to 70°C using infrared radiation in order to facilitate the interlocking of the polyurethane chains on the split leather and SBR surfaces during the joint formation. The strips were then put into contact and a pressure of 0,8 MPa was immediately applied for 10 s to achieve a suitable joint. T-peel strength was measured using an Instron model 1011 (peel rate = 0,1 m/min). The values obtained were the average of five test replicates (standard deviation was less than 5%). The green (immediate) peel strength was measured 30 s after the joint formation. The evolution in T-peel strength was followed at different times (until 72 h) after joint formation. In order to analyse the durability of the adhesive joints, they were aged at 70°C and 95% relative humidity for 72 h before the T-peel test was carried out.

Results and Discussion

Table 2 shows some properties (pH and solids content) of the aqueous polyurethane dispersions containing different amounts of $CaCO_3$ filler. An increase in the pH value of the dispersion occurs as the $CaCO_3$ content increases, as a consequence of the basic nature of the $CaCO_3$ (pH=8,8).

Waterborne polyurethane adhesives consist in polymer ionomer particles stabilizing in water due to ionic groups located on the particles surface (that act as an internal emulsifier chemically attached to the polyurethane structure) which generate an electrical double layer. Electrostatic forces between particles can be modified by varying the pH because of the double layer size of the particles is modified due to an increase of the electrostatic forces between particles, in agreement with the DLVO (Deryaguin-Landau-Verwey-Overbeek) theory [5-8].

Table 2. pH values and solids content of the water-based polyurethane adhesives containing different amounts of a micronised $CaCO_3$ filler.

$CaCO_3$ content (wt%)	**0**	**5**	**10**	**15**	**20**	**25**
pH	7,9	8,3	8,4	8,4	8,5	8,5
Solids content (wt%)	50,7	53,7	56,0	58,60	61,4	63,6

Unlike solvent-based adhesives, the viscosity of a water-based polyurethane adhesives is not dependent on the molar mass of the polymer but mainly on the solids content and mean particle size of the dispersion and by the presence of other components in the formulation. Therefore, the variation of the viscosity of the dispersions as a function of $CaCO_3$ content was performed. Figure 1 shows the flow curves of the adhesives with different content in $CaCO_3$. The addition of $CaCO_3$ filler produces an increase in viscosity due to the increase in solids content (Table 2), more noticeable for the adhesives containing 15, 20 and 25 wt% $CaCO_3$. Moreover, all the adhesives show a pseudoplastic behaviour, i.e. there is a decrease in viscosity as the shear stress increases, more markedly as the filler content increases [9]. The pseudoplastic behaviour of the filled PUD dispersions is due to a rupture of the network between the filler and the polyurethane particles and/or water, which becomes gradually broken by increasing the shear stress, giving a decrease in viscosity. In this case, this network could be ascribed to the creation of culombic forces or acid-base interactions [10].

When a dispersion is subjected to a shear stress, the polymer particles are orientated into layers, which can flow easily, causing a decrease in viscosity. The increase in viscosity and the pseudoplastic behaviour produced by breaking of the internal network can be ascribed to the formation of aggregates between particles which is more favoured as the $CaCO_3$ content increases. On the other hand, the presence of larger particles (filler) located between the smallest ones (polymer particles) may inhibit the orientation of particles restricting their ability to flow and produces an increase in viscosity.

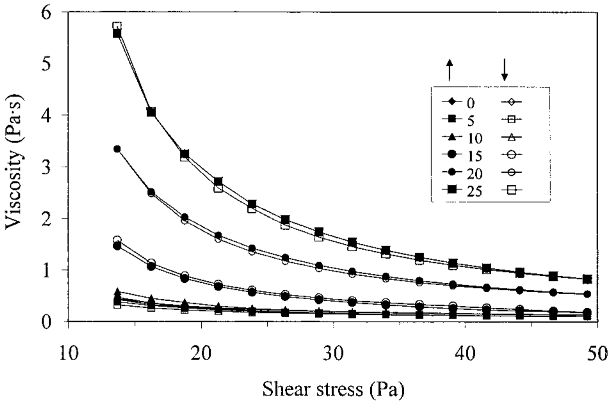

Figure 1. Variation of the viscosity for the filled polyurethane dispersions as a function of the shear stress. (↑ ↓ Increase and decrease in shear rate).

The yield point of the filled solutions (i.e. the minimum shear at which the polyurethane adhesive starts to flow) can be obtained by applying the Casson model to the rheological data:

$$\sigma^{1/2}=\sigma_0^{\ 1/2} + (\eta_\infty \cdot D)^{1/2}$$

where σ is the shear stress, D is the shear rate, σ_0 is the yield point, and η_∞ is the viscosity at infinite rate. The yield point values of the filled PUD adhesives are included in Table 3. The increase in $CaCO_3$ content produces an increase in yield point stress from 15 wt% on. An increase in yield point stress involves a greater interaction between filler, water and polyurethane particles.

Table 3. Yield stress (σ_0) of filled PUD adhesives (obtained from Casson model).

$CaCO_3$ content (wt%)	**0**	**5**	**10**	**15**	**20**	**25**
σ_0 (Pa)	7,58	6,62	6,99	10,32	9,21	9,21

Figure 2 shows the evolution of the storage modulus (G') as a function of the frequency of the filled water-free polyurethane films, obtained at 70°C. The addition of $CaCO_3$ filler to water-based polyurethane adhesives produces an increase in the modulus up to a 20 wt%, more noticeably in the low frequency region of the curves, indicating the resistance of the filler-PUD blend to flow at these frequencies. The improvement in the rheological properties implies the strengthening of the structure up to a $CaCO_3$ content of 20 wt% which can be ascribed to the creation of culombic forces or acid-base interactions. The mechanical properties of a composite depend on the degree of filler dispersion in the polyurethane matrix. In an acid or base polymer matrix, the filler dispersion is favoured due to acid-base interactions [11]. V. Kovacevic *et al.* [12] found that the polar nature of $CaCO_3$ affects the adhesion between the PVAc and the filler. A certain degree of similar interactions can be expected in PUD/$CaCO_3$ composites. The bonding between $CaCO_3$ and PUD phases in a dispersed system can be explained by the establishment of coordinate bonds between the anionic groups of the ionomer polyurethane and the Ca^{2+} ions [12].

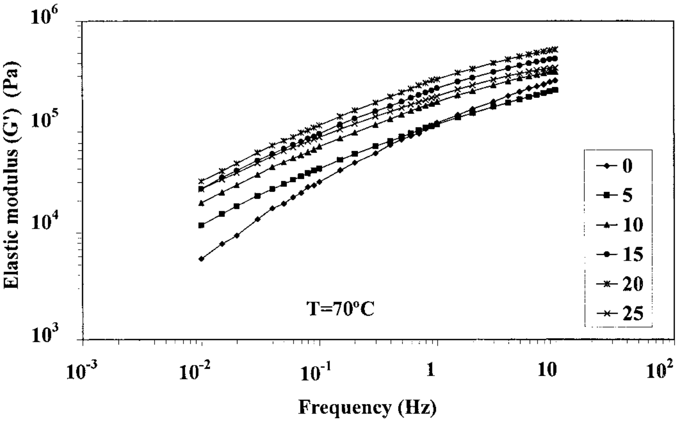

Figure 2. Variation of the storage modulus (G') of the filled PUD films as a function of the frequency.

For filler content higher than 20 wt%, a decrease in the storage modulus is produced. It could be ascribed to the fact that a high content of $CaCO_3$ as filler inhibits the interactions among polyurethane chains, which are the main responsible of the polyurethane structure and therefore of their rheological properties [13].

On the other hand, the PUD films (Figure 3) show, at a given frequency, a change from viscous to elastic properties due to the entanglement of polyurethane chains. It means that there is a cross-over between the storage (G') and loss (G'') moduli. The addition of micronised $CaCO_3$ filler to polyurethane produces a displacement of the cross-over to lower frequencies, regardless of the filler content (Table 4). Therefore, the addition of a micronised $CaCO_3$ to polyurethane improves their rheological properties as it strengthens the structure by avoiding the flow of the polymer chains.

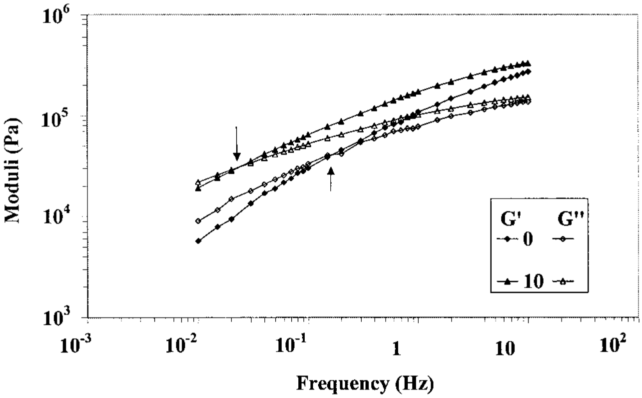

Figure 3. Variation of the elastic (G') and viscous (G'') moduli of the polyurethane films with 0 and 10 wt% of micronised calcium carbonate as a function of the frequency.

Table 4. Frequency ($\omega_{cross-over}$) and modulus ($G_{cross-over}$) values in the cross-over for the different adhesives.

$CaCO_3$ content (wt%)	0	5	10	15	20	25
$G_{cross-over}$ (Pa)	$5{,}5 \cdot 10^4$	$1{,}8 \cdot 10^4$	$2{,}8 \cdot 10^4$	$3{,}8 \cdot 10^4$	$4{,}5 \cdot 10^4$	$3{,}2 \cdot 10^4$
$\omega_{cross-over}$ (Hz)	0,30	0,02	0,02	0,02	0,02	0,02

Finally, the influence of the $CaCO_3$ content on adhesion properties of PUD adhesives was assessed by means of T-peel tests. Figure 4 shows the evolution of the T-peel strength values in leather/PUD adhesive/SBR joints as a function of the $CaCO_3$ content.

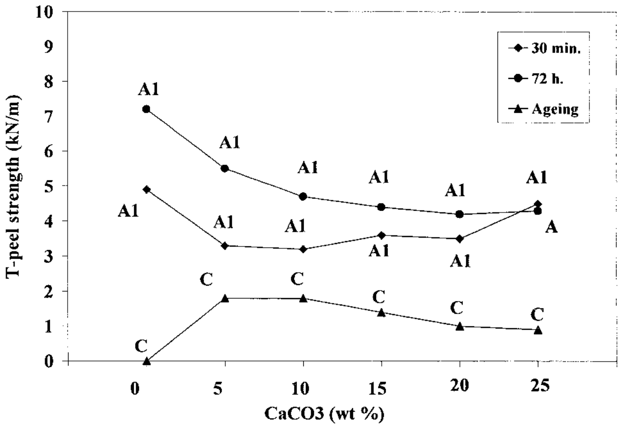

Figure 4. T-peel strength values at different times after formation of leather/polyurethane adhesive/SBR joints as a function of the micronised $CaCO_3$ content. Locus of failure: C= Cohesive failure in the adhesive; A1: Adhesion failure between the PUD adhesive and the leather.

The initial adhesion (30 min) for all joints produced with the adhesives containing filler is, in general, slightly lower than the one produced with the adhesive without filler. Moreover, 72 hours after joint formation the peel strength values decrease as the amount of filler increases, but the peel strength values are always higher than the initial adhesion as a consequence of the crystallisation of the polyurethane chains. An adhesion failure to the leather (A1) was always obtained. It can be ascribed to the higher viscosity of the PUD adhesives containing $CaCO_3$ as filler which may prevent the penetration into the pores of the leather, facilitating the adhesion failure. Moreover, the improvement in the reological properties causes more rigid and fragile films in comparison to the adhesive without filler. On the other hand, ageing produces a decrease in peel strength values in all joints, the decrease is less important if the adhesive contains $CaCO_3$. According to the literature, the calcium carbonate as filler forms a shield that prevent ageing process [14]. During ageing the hydrolysis of polyurethane chains is produced causing a cohesive failure in the adhesive (C).

Conclusions

The addition of a micronised calcium carbonate as filler increased the viscosity, the storage and loss moduli of the PUD adhesives and imparted pseudoplasticity and thixotropy, more noticeably for the adhesive with the highest calcium carbonate content. The creation of acid-base interactions seemed to be responsible for the improvement in the rheological properties of the PUD adhesives containing $CaCO_3$ as filler. However, the addition of $CaCO_3$ produces a decrease in peel strength for leather/polyurethane adhesive/SBR joints more noticeable as the filler content increases.

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[1] J.C. Fernández García, M. Cobo Ulloa, A. Torró Palau, A.C. Orgilés Barceló. *Lederpiel* **1998,** 72 January-February.

[2] J. Sepulcre-Guilabert, T. P. Ferrándiz-Gómez, J.M. Martín-Martínez. *J. Adh. Sci. Technol.*, **2001**, 15, 187.

[3] J. Sepulcre-Guilabert, T.P. Ferrándiz-Gómez , J.M. Martín-Martínez. *Macromolecular Symposia* **2001**, 169, 185.

[4] "*Technical information*". Reverté S.A, Bellvei, Tarragona 1999.

[5] "*Encyclopedia of emulsion technology. Basic theory. Vol. 1*" P. Becher, Ed., Marcel Dekker, Inc., New York 1983.

[6] L. Chan Young, K. Jin Woong, S. Kyung Do. *J. Mater. Sci.,* **1999**, 34, 5343.

[7]. "*Handbook of adhesives*". 3rd ed., I. Skeit, Ed., Van Nostrand Reinhold, New York 1999.

[8] "*Chemistry of Pigments and Fillers*", D. H. Solomon, D.G. Hawthorne, Eds., Krieger Publishing , New York, Chichester 1976.

[9] "*Viscoelastic Properties of Polymers*", Ferry, Ed., Wiley, New York, Chichester 1976.

[10] D. Dietrich in: "*Advances in urethane ionomers*". H.X. Xiao, K.C. Frish, Eds., Technomic, Lancaster, USA 1995. Chapter 1.

[11] M. Ciganez, M. Dressler. *Polym. Composites,* **1989,** 10, 194.

[12] V. Kovacevic, S. Lucic, D. Hace, Z. Cerovecki. *J. Adh. Sci. Techol.*, **1996**, 10, 12, 1273.

[13] "*Szycher's handbook of polyurethanes*". M. Szycher, Ed, CRS Press. Boca Ratón, Florida 1999.

[14] A. Baker, L. Koller, E. Kummer in "*Handbook of filler for plastics*". 2nd ed., H.S. Katzs, J.V. Milewski, Eds. Van Nostrand Reinhold, New Jersey 1987.