Comparative Properties of Thermoplastic Polyurethane Adhesive Filled with Natural or Precipitated Calcium Carbonate

*Jessica Donate-Robles, José Miguel Martín-Martínez**

Summary: The rheological, mechanical and adhesion properties of thermoplastic polyurethane adhesive (TPU) containing natural ultramicronized or precipitated nanometric calcium carbonate filler were compared. Precipitated calcium carbonate addition did not noticeably improve the rheological properties of filled TPU with respect to the effect produced by adding natural calcium carbonate. The precipitated calcium carbonate nanoparticles migrated to the TPU surface due to incompatibility between the filler and the polyurethane. The wettability of the filled TPU was reduced by adding natural calcium carbonate, but it was increased slightly by adding precipitated calcium carbonate. Finally, the immediate adhesive strength in PVC/TPU adhesive/PVC joints increased noticeably when the adhesive contained filler; however, the final adhesive strength was similar irrespective of the filler particle size.

Keywords: adhesive; calcium carbonate; filler; thermoplastic polyurethane

Introduction

Polyurethane adhesives are commonly used in the footwear, textile, construction and automotive industries. Thermoplastic polyurethane adhesives (TPU) are synthesized by reacting an isocyanate, a polyol and a chain extender, and their properties depend on their segmented structure (i.e. degree of phase separation), the amount and nature of the reactants and the reaction conditions, among other.[1] Fillers are added to improve the rheological and mechanical properties of TPUs. The segmented structure determines the structure-properties relationship of TPU,[1,2] and it has been demonstrated[3] that the addition of nanosilica fillers altered the degree of phase separation in the polyurethane structure producing an improvement in the rheological, mechanical and adhesion properties.

Fumed silica is the most common and effective filler for TPU because of its nanometric particle size and the presence of silanol groups on the surface; the effectiveness of the fumed silica filled polyurethane adhesives was ascribed to the creation of hydrogen bonds between the urethane groups in the polymer chains and the silanol groups on the silica surface.[4] However, fumed silica is expensive and difficult to handle because of its extremely low density.

Sepulcre-Guilabert et al. [5] demonstrated that the addition of natural micronized calcium carbonate filler did not improve the rheological, thermal, mechanical, surface and adhesion properties of TPU adhesive. The lack of filler performance was ascribed to the absence of net filler-polyurethane interactions. Jiang et al. [6] studied the influence of the coating on precipitated calcium carbonate (PCC) filler on the rheological and mechanical properties of TPU. It was shown that the storage modulus (G′) increased with PCC loading at low frequencies but decreased at high frequencies; furthermore, the addition of PCC decreased the viscosity of the TPU solutions and the coating nature had an

Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain
E-mail: jm.martin@ua.es

Table 1.
Some properties of the calcium carbonate fillers (taken from the technical data sheets).

Natural calcium carbonate (M)		Precipitated calcium carbonate (S)	
Property	Value	Property	Value
$CaCO_3$ content	98.96 wt.%	$CaCO_3$ content	98.90 wt.%
Free flowing density	500 g/l	Free flowing density	286 g/l
Specific surface area (BET)	13 m^2/g	Specific surface area (BET)	19 m^2/g
Loss on calcination	43.3 wt.%	Loss on drying (105 °C)	0.25 wt.%
Particle size (50% of particles lower than)	0.65 μm	Mean particle diameter (by permeability)	0.07 μm

influence on the TPU properties. Recently, Presser et al. [7] studied the influence of the addition of calcite fillers on the properties of highly filled polyurethanes. Coated precipitated calcite filler imparted thixotropy and increased the viscosity of the polyurethane, and accelerated curing. However, no differences in thermal neither in mechanical properties were found.

To our knowledge, the incidence of the filler particle size and the calcium carbonate origin on the performance of filled TPU adhesives has not been studied yet. Therefore, in this work two calcium carbonate fillers (natural and precipitated) having particle size in the range of micro and nano size were added to a TPU adhesive and their properties were compared.

Experimental Part

Materials

TPU pellets were synthesized by using the prepolymer method. The prepolymer was obtained by reacting a lineal polyester (polyadipate 1,4-butanediol - Mn = 2500, supplied by Synthesia Española, S.A., Barcelona, Spain), a diisocyanate (4,4′-difenilmethandiisocyanate, 98 wt.% purity, supplied by Sigma-Aldrich, Barcelona, Spain), and a chain extender (1,4-butanediol, 99 wt.% purity, supplied by Sigma-Aldrich, Barcelona, Spain). The NCO/OH equivalent ratio used was 1.05.

Natural ultramicronized calcium carbonate Microcarb® 95 (named as M in this study) supplied by Reverté S.A. (Barcelona, Spain) and precipitated nanometric calcium carbonate Socal® 312 (named as S in this study) supplied by Solvay Specialités-France S.A. (Salin de Giraud, France) were used. Some properties of the fillers are given in Table 1. The mean primary particle size of the fillers differs by a factor of ten; M filler has a particle size higher than 0.1 μm and therefore it can be considered to have particles in the micrometric range, whereas S filler has particles in the nanometric range (particle size lower than 100 nm). The particle size and the distribution of the particle sizes of the fillers were analyzed by TEM (Figure 1).

TPU solutions were prepared by adding 20 wt.% polyurethane pellets and 1-2 wt.% of M filler or 1-4 wt.% of S filler in methyl ethyl ketone (MEK). A TPU solution without filler was also prepared as control. The unfilled and filled TPU mixtures were prepared in a Dispermix DL-B laboratory mixer provided with a Cowles type mechanical stirrer (Oliver Batlle, Barcelona, Spain). The preparation of the TPU-filler mixtures was carried out in three consecutive stages: *(i)* the filler was mixed with ½ volume of methyl ethyl ketone at 2335 rpm for 15 min, *(ii)* the polyurethane pellets and the remaining half volume of methyl ethyl ketone were added to the previous solution, stirring the mixture at 2005 rpm for 2 h, *(iii)* the evaporated methyl ethyl ketone solvent was replaced in the solution to adjust the solids content and homogenised at 850 rpm for 5 min. Table 2 shows the nomenclature of the filled TPUs used in this study.

TPU films were prepared by placing 100 ml adhesive solution in a PTFE mould allowing the solvent removal at room temperature for 5 days.

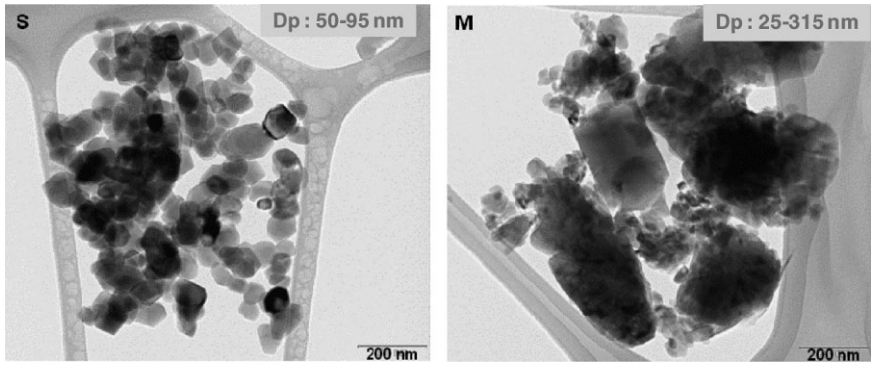

Figure 1.
TEM micrographs of the calcium carbonates.

Table 2.
Nomenclature of the TPUs.

Adhesive	Amount of filler in TPU solution (wt%)	Amount of filler in TPU film (wt%)
TPU	0	0
TPUS-5	1	5
TPUS-10	2	10
TPUS-20	4	20
TPUM-5	1	5
TPUM-10	2	10

Experimental Techniques

Characterization of the TPU Solutions

Rheological Properties and Viscosity. The rheological properties of the adhesive solutions were determined by placing 100 ml of solution in Rheolab MC 100 Physica rheometer (Stuttgart, Germany) by using Z2 DIN concentric cylinders. Rotational test was carried out at $20\,^{\circ}C \pm 1\,^{\circ}C$.

Characterization of the TPU Films

Dynamic Mechanical Thermal Analysis (DMA). The viscoelastic properties (tightly related to the existence of filler-polymer interactions) of the filled polyurethanes were measured in a TA DMA Q800 instrument (New Castle, USA), provided with an air bearing system operating at 410-450 kPa gauge pressure. Samples with dimensions of $10 \times 10 \times 1\,mm^3$ were used. The experiments were carried out in the shear sandwich mode under nitrogen atmosphere. Samples were by heated from $-100\,^{\circ}C$ to $80\,^{\circ}C$ by using a heating rate of $5\,^{\circ}C$/min, a frequency of 1 Hz and a strain of 0.5%.

Transmission Electron Microscopy (TEM). A Jeol TEM-2010 instrument (Tokyo, Japan) was used to analyse the topography and dispersion of the fillers in the polyurethane films; an acceleration voltage of 100 kV was used.

X-Ray Diffraction (XRD). A JSO-Debyeflex 2002 instrument (Ahrensburg, Germany) was used to analyse the crystallinity of polyurethane films; a copper cathode and a nickel filter were used; a scanning of 2θ angles between 5 and 90 degrees was carried out.

Advancing and Receding Contact Angle Measurements. The wettability of the polyurethane films surfaces was evaluated from contact angle measurements using a Ramé-Hart 100 goniometer (Mountain Lakes, NJ, USA). The polyurethane films were placed into the hermetic and isothermal ($25\,^{\circ}C$) chamber of the goniometer previously saturated with ethylene glycol vapour. Drops ($4\,\mu L$) of ethylene glycol (probe liquid) were placed on polyurethane film surface by using a microsyringe provided with a flat end needle, and the advancing and receding contact angle values were measured by using the tilting plate procedure. Measurements were taken was

10 minutes after ethylene glycol drop deposition. The experimental error was ±2°.

Scanning Electron Microscopy (SEM). A JEOL JSM-840 instrument (Tokyo, Japan) was used to analyse the surface of the polyurethane films; an acceleration voltage of 15 kV was used. The samples were gold coated to improve contrast.

Adhesion Properties. The adhesion of the filled polyurethanes was evaluated by T-peel strength test of solvent-wiped plasticized PVC/polyurethane adhesive/PVC joints. The plasticized PVC test samples used had dimensions of 30 mm × 150 mm × 5 mm. Before applying the adhesive, the PVC surface was wiped with methyl ethyl ketone allowing the solvent to evaporate for 30 min under open air. Then, 0.45–0.92 g adhesive solution was applied by brush to each strip to be joined. After solvent evaporation, the adhesive film on the PVC strips was heated to 80 °C for 10 seconds under infrared radiation (reactivation process) and immediately placed in contact and press at 0.8 MPa for 10 seconds to achieve a suitable joint. The T-peel strength was measured in an Instron 4411 universal testing machine (Buckinghamshire, England) at a cross-head speed of 100 mm/min. The values obtained were the average of six replicates. The evolution of the T-peel strength was monitored at different times after joint formation (0.5–72 h). The locus of failure in the joints was determined by ATR-IR spectroscopy analysis of the failed surfaces after T-peel test.

Results and Discussion

TPU Filled with Precipitated Calcium Carbonate (S)

Addition of filler increases the viscosity, the higher the filler loading the higher the increase in viscosity of the TPU solution (Figure 2). On the other hand, the filled TPU solutions containing up to 10 wt.% filler show a Newtonian rheological behaviour because the viscosity does not vary by increasing the shear rate. The TPUS-20 solution shows pseudoplastic behaviour because of the decrease in viscosity by increasing the shear rate.

Figure 3 shows the variation of the storage modulus (G′) as a function of the temperature for the filled polyurethane films. Below the glass transition, the storage modulus does not vary with the temperature, and is higher in the polyurethanes containing filler. In the rubbery plateau, TPUS-20 shows the highest modulus likely due to the creation of van der Waals interactions between the polyurethane chains and the filler particle surface. On the other hand, the glass transition temperature (Tg) of the polyurethane increases slightly by adding PCC filler (from −23 °C in unfilled TPU to −19 °C in TPUS-20).

The dispersion of the precipitated calcium carbonate particles in the polyurethane matrix was studied by TEM (Figure 4). TEM micrographs show the existence of clusters of filler nanoparticles, the higher the amount of precipitated

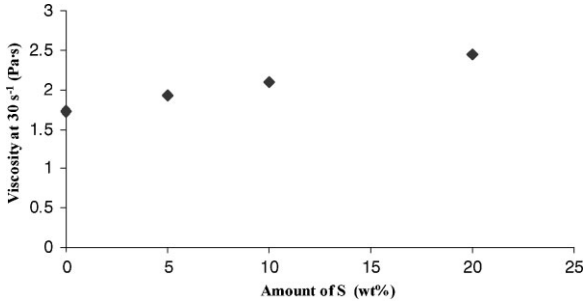

Figure 2.
Variation of the viscosity of the filled TPU solutions as a function of the amount of S filler.

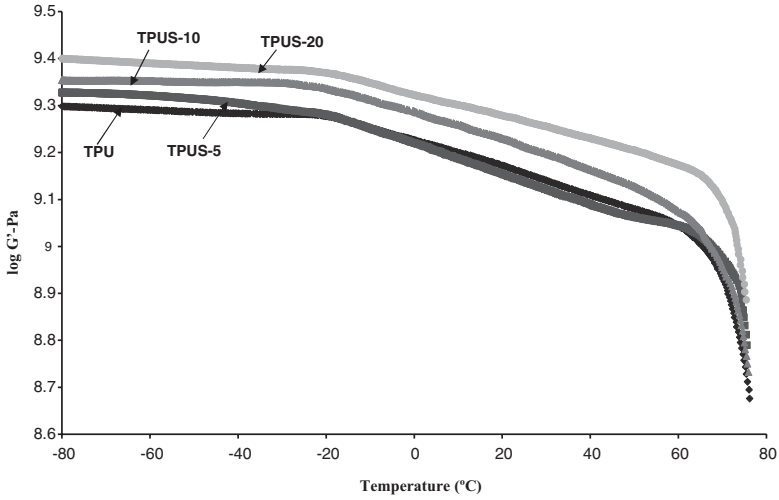

Figure 3.
Variation of the storage modulus (G′) as a function of the temperature of the unfilled and precipitated calcium carbonate filled TPU films. DMA experiments.

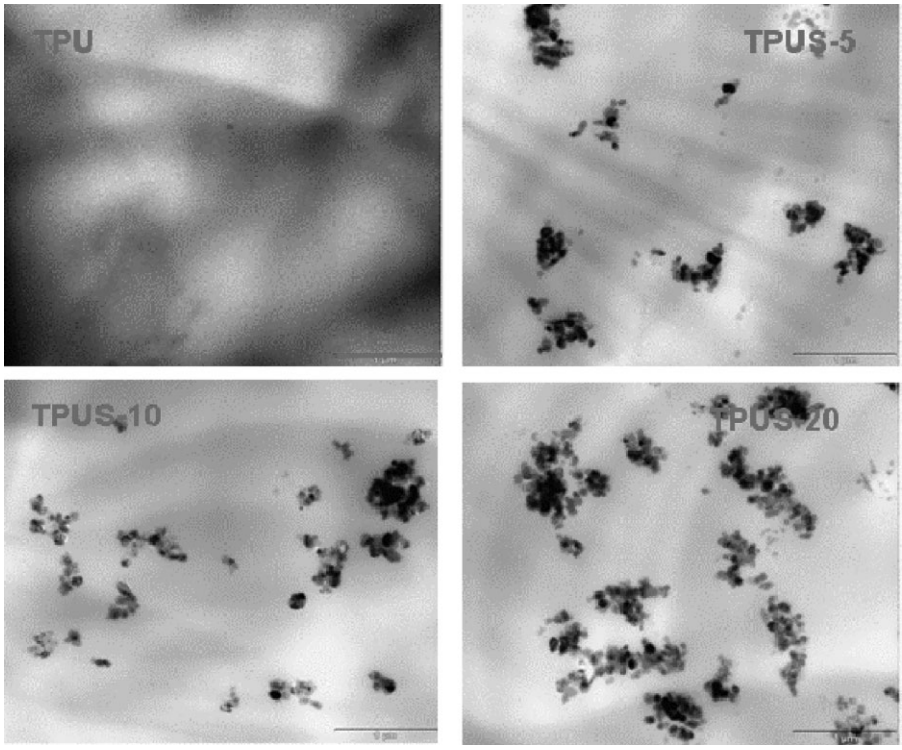

Figure 4.
TEM micrographs of the unfilled and precipitated calcium carbonate filled TPU films.

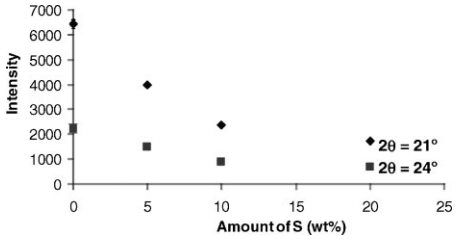

Figure 5.
Variation of the intensity of the main X-ray diffraction peaks of the unfilled and filled polyurethanes as a function of the amount of precipitated calcium carbonate filler.

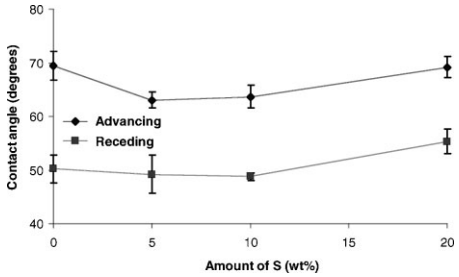

Figure 6.
Advancing and receding contact angle values (ethylene glycol, 25 °C) on unfilled and precipitated calcium carbonate filled TPU films.

calcium carbonate loading the higher the length of the clusters in the polymer matrix.

The unfilled TPU shows two main X-ray diffraction peaks at 2θ values of 21 and 24° both typical of the polyester domains in the polyurethane.[3] Figure 5 shows the variation of the intensity of these peaks as a function of the amount of precipitated calcium carbonate filler in the polyurethane. The higher the intensity of the diffraction peaks, the higher the crystallinity in the polyurethane. Therefore, the crystallinity of the polyurethane decreases by adding filler likely due to van der Waals filler-polyurethane interactions which also favoured the degree of phase separation in the polymer. The extent of these interactions is higher by increasing the filler loading in the polyurethane.

SEM micrographs (not shown here) evidenced the migration and agglomeration of the filler particles on the TPU surface likely due to incompatibility between the filler and the polyurethane. In fact, the ethylene glycol contact angle values on TPUS-5 and TPUS-10 films are lower than for the unfilled polyurethane whereas higher values are obtained on TPUS-20 (Figure 6). The increase in the wettability in the filled polyurethanes is produced up to 10 wt.% filler content.

The T-peel strength values of PVC/polyurethane adhesive/PVC joints as a function of the time after joint formation are given in Figure 7. The immediate T-peel

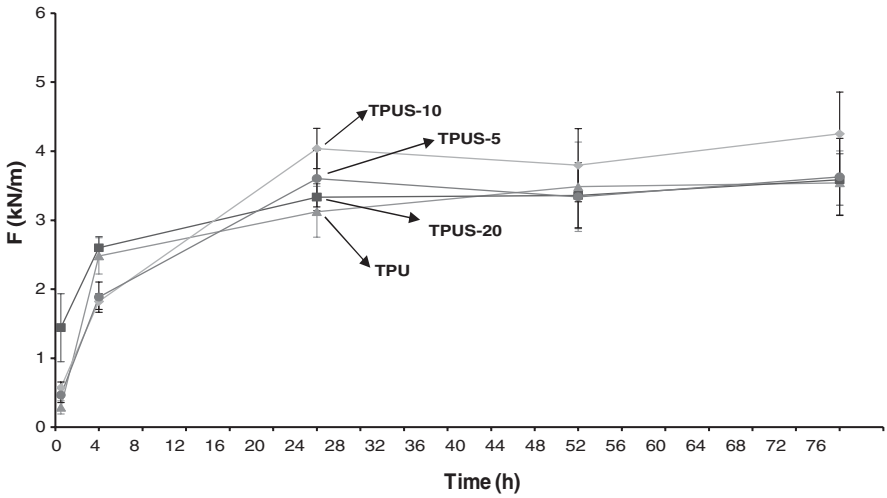

Figure 7.
T-peel strength values of PVC/unfilled or precipitated calcium carbonate filled polyurethane adhesive/PVC joints as a function of the time after joint formation.

strength, which was measured 30 min after joint formation, in the joint made with the unfilled polyurethane is somewhat lower than these of the polyurethanes containing filler. The T-peel strength value increases by increasing the time after joint formation because the crystallization of the polyurethane is produced. The highest peel strength value at 72 h after joint formation corresponds to the joint made with TPUS-10.

The locus of failure of the adhesive joints was assessed from the ATR-IR spectra of the failed surfaces after peel test. A similar locus of failure was obtained in all joints being dominant the cohesive failure in the adhesive for the joints tested 30 min after joint formation and the cohesive failure in the PVC for the joints tested 72 hours after joint formation.

TPU Filled with Natural or Precipitated Calcium Carbonate

The results obtained in the precipitated calcium carbonate filled TPUs shows the best adhesion properties for the adhesive containing 10 wt.% filler. Therefore, a comparison of TPUS-10 and TPUM-10 was made to analyze the influence of adding natural or precipitated calcium carbonate to TPU. In some cases, the results obtained by comparing TPUS-5 and TPUM-5 were shown.

Figure 8 shows the variation of the viscosity as a function of the shear rate in the filled TPU solutions. Both solutions show a Newtonian rheological behaviour and the addition of the nanofiller (S) increases in a greater extent the viscosity of the solution.

Figure 9 shows the variation of the storage (G′) modulus as a function of the temperature of the filled TPU films. Although both filled TPUs have the same value of glass transition temperature, slightly higher G′ value in the rubbery plateau are obtained in the precipitated calcium carbonate-TPU sample, because of more net van der Waals filler-polyurethane interactions.

On the other hand, clusters of natural calcium carbonate microparticles are formed into the TPU matrix. The natural calcium carbonate filler clusters size is bigger than for the precipitated calcium carbonate filler clusters size due to its higher primary particle size (Figure 10).

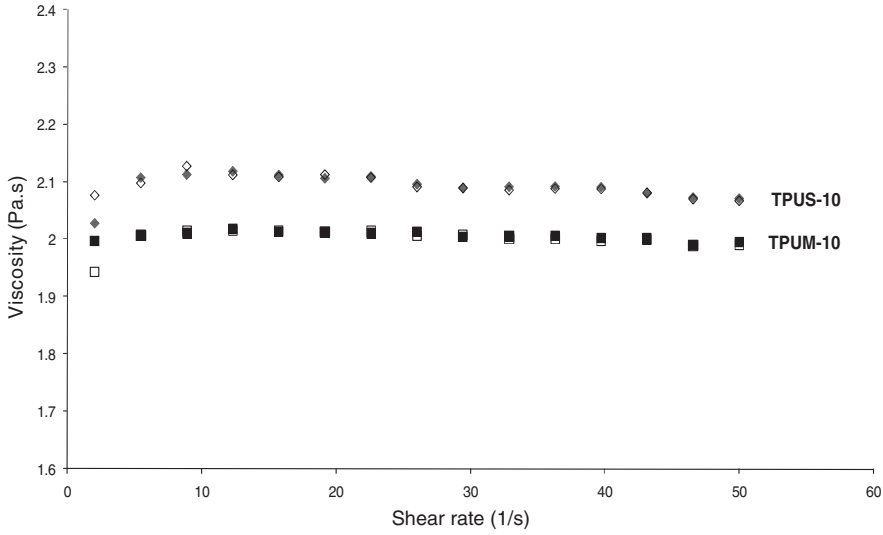

Figure 8.
Variation of the viscosity as a function of the shear rate in the precipitated or natural calcium carbonate filled TPUs. Decreasing (open point) and increasing (solid point) shear rate cycle.

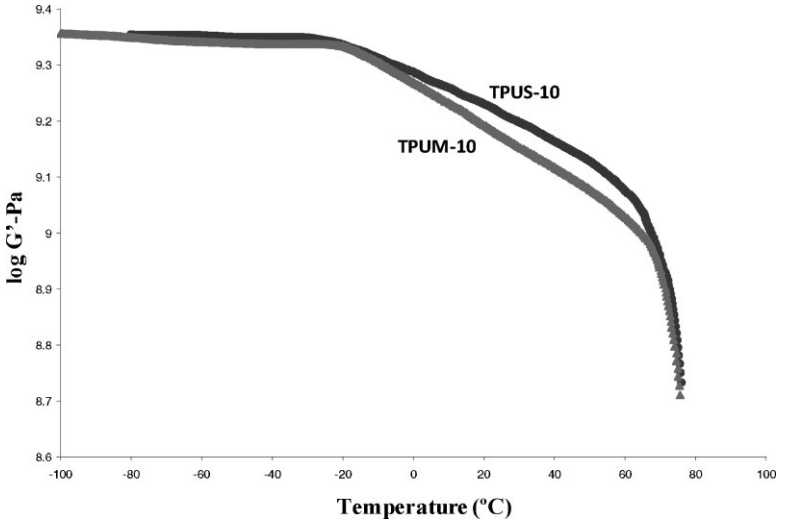

Figure 9.
Variation of the storage modulus as a function of the temperature of the precipitated or natural calcium carbonate filled polyurethanes. DMA experiments.

The surface topography of the filled polyurethanes is modified when micronized natural calcium carbonate is added to the polyurethane (Figure 11). On the other hand, whereas the PCC particles migrate to the TPU surface due to incompatibility with the polyurethane the natural calcium carbonate particles do not.

The ethylene glycol contact angle values on TPUM-5 and TPUM-10 films are lower than for the TPUS-5 and TPUS-10 films (Figure 12), so the addition of nanosized precipitated calcium carbonate reduces somewhat the wettability of the polyurethane.

Adhesion properties were obtained from T-peel test. The immediate adhesion was measured 30 min after joint formation, and this value is higher in the joint produced with natural calcium carbonate filled TPU (Figure 13), the locus of failure is of cohesion in the adhesive. However, the final adhesion values are similar in all joints as similar degree of crystallization in the polyurethane is obtained.

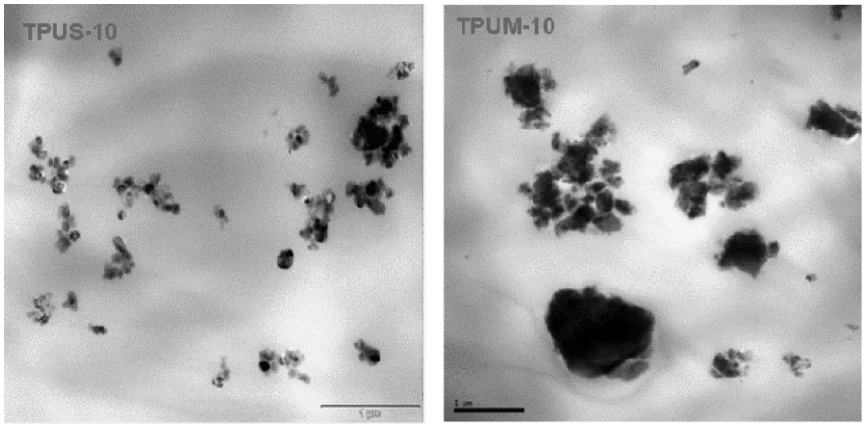

Figure 10.
TEM micrographs of the precipitated or natural calcium carbonate filled polyurethanes.

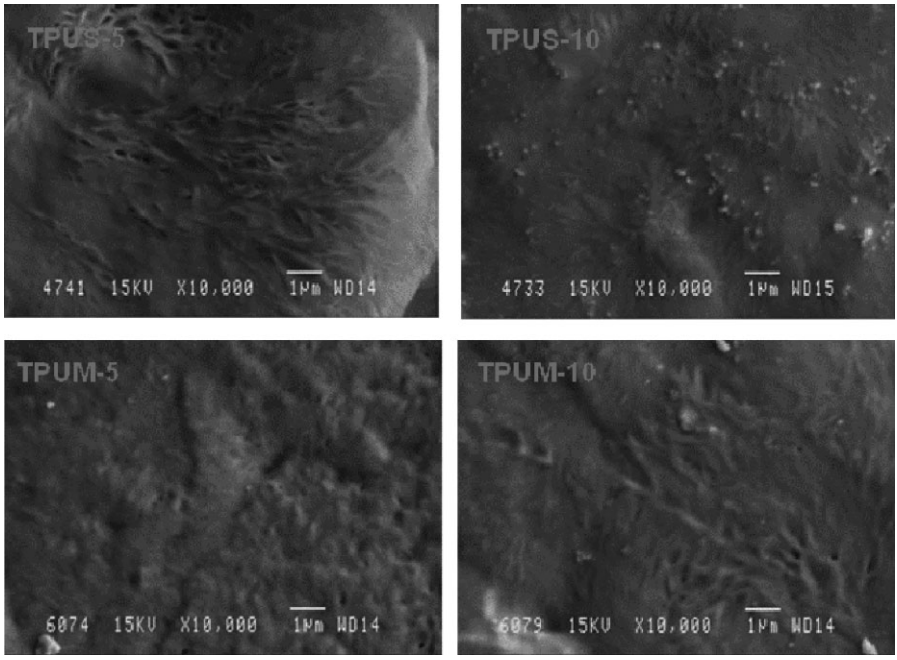

Figure 11.
SEM micrographs of 5–10 wt.% precipitated or natural calcium carbonate filled polyurethanes.

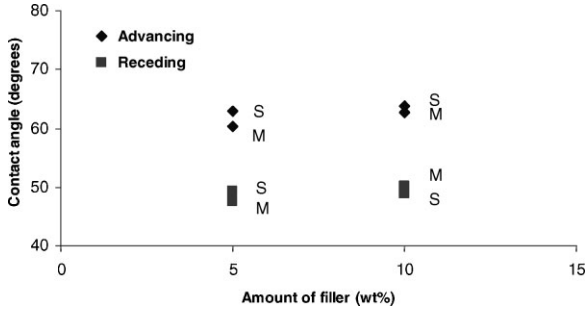

Figure 12.
Advancing and receding contact angle values (ethylene glycol, 25 °C) on the precipitated or natural calcium carbonate filled polyurethane films.

Conclusions

Addition of precipitated calcium carbonate filler increased moderately the rheological and mechanical properties of the TPU with respect to the addition of natural calcium carbonate filler.

The addition of calcium carbonate fillers changed the surface topography of the polyurethane. Precipitated calcium carbonate particles migrated to the polyurethane surface due to incompatibility between the filler and the polyurethane. Thus, the wettability of the polyurethane was reduced by adding nanosized precipitated calcium carbonate filler, but it was increased by adding micronized natural calcium carbonate filler.

The immediate T-peel strength value was improved in joints produced with filled

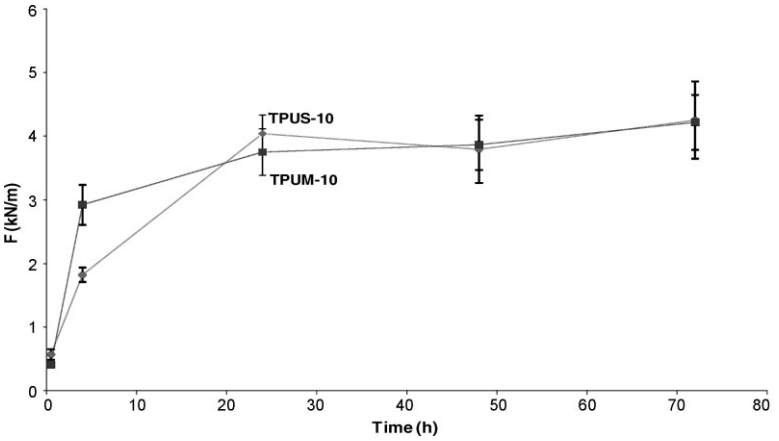

Figure 13.
T-peel strength values of PVC/precipitated or natural calcium carbonate filled polyurethane adhesive/PVC joints as a function of the time after joint formation.

TPU and the locus of failure was cohesive in the adhesive. However, the addition of natural or precipitated calcium carbonate did not caused significant differences in the final adhesion properties.

Acknowledgements: Authors thank Synthesia Española, S.A. (Barcelona, Spain) for providing the polyester polyol, Solvay Spécialités-France S.A. and Reverté S.A. for providing the precipitated and ultramicronized calcium carbonate, respectively, used in this study.

[1] G. Oërtel, *Polyurethane Handbook*, Chapter 2: Chemical and Physical-Chemical Principles of Polyurethane Chemistry, pp 7–39 Chapter 3: Raw Materials, pp 42–89, Chapter 11: Polyurethane Adhesives, pp 548–562 Hanser, Munich **1985**.

[2] K. C. Frisch, Jr., Adhesion Science and Engineering Vol 2: *Surfaces, Chemistry and Applications* Elsevier, Amsterdam **2003**, pp 760.

[3] J. Vega-Baudrit, V. Navarro-Bañón, P. Vázquez, J. M. Martín-Martínez, *Int. J. Adhesion Adhesives*, **2006**, *26*(5), 378.

[4] G. Wypych, *Handbook of Fillers*, ChemTec Publishing & Plastics Desing Library, Toronto, Canada **1999**.

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

[6] L. Jiang, Y. C. Lam, K. C. Tam, D. T. Li, J. Zhang, *Polymer Bulletin* **2006**, *57*, 575.

[7] M. Presser, R. Diedel, H. Doerr, P. L. Geiss, E. Roth, W. Wittwer, *Investigation of the influence of calcite fillers on the properties of highly filled polyurethanes*, 32nd Annual Meeting of the Adhesion Society, Savannah, Georgia. 15–18 February **2009**, pp. 166.

