Interactions in Nanosilica-Polyurethane Composites Evidenced by Plate-Plate Rheology and DMTA

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Summary: Fumed nanosilicas with different degree of silanization were used to obtain nanosilica-polyurethane (TPU) composites to modify their rheological and mechanical properties. The higher the silanol content of the nanosilica, the higher the storage modulus and the thermal stability of the silica-TPU composite. DMTA experiments confirmed that the TPU-silica interactions increased by increasing the silanol content of the nanosilica.

Keywords: adhesion; adhesive; nanosilica; polyurethane; rheology

Introduction

Thermoplastic polyurethanes (TPU) are fully reacted segmented block polymers having good mechanical and elastic properties. TPUs are produced by reaction of an isocyanate, a polyol and a chain extender, and they contain urethane moieties. The two-phase microstructure of the TPU is due to incompatibility between the soft and the hard segments. [1] The hard rigid segments (produced by reaction of the isocyanate and the chain extender) segregate into a glassy or semicrystalline domain, and the polyol soft segments form amorphous rubbery matrices in which the hard segments are dispersed.

Fumed silica nanoparticles (nanosilicas) are commonly added to improve the rheological and mechanical properties of TPU adhesives. [2-5] This improvement has been ascribed to the creation of hydrogen bonds between the silanol groups on the nanosilica surface and the urethane groups in the soft segments. To confirm this hypothesis, in this study a full silanated nanosilica was treated with a silane by Wacker-Chemie (Burghausen, Germany) to produce different nanosilicas with decreased silanol content. Then, different TPU composites containing 10 wt% nanosilicas with different degree of silanization were prepared and characterized using plate-plate rheometry and DMTA.

Experimental

Fumed silicas (nanosilicas) were manufactured by Wacker-Chemie (Burghausen, Germany) for this study. The degree of silanization was varied between 15.5 and 100 % by treatment with a silane (Di-Me-Di). Primary particle size was 7 nm in all nanosilicas. Table 1 shows some properties of the nanosilicas provided by Wacker-Chemie.

Table 1. Some properties of the nanosilicas.[1]

Nanosilica	SiOH (%)	Carbon content (%)	mmol SiOH/g silica
N20	100	0	0.60
H20	57.5	1.2	0.34
H20RD	15.5	4.7	0.09

[1] Data provided by Wacker-Chemie.

The specific surface area of the nanosilicas was obtained from N_2/77K adsorption isotherms measured in a Quantachrome adsorption system. The nanosilicas were outgassed at 100°C for 8 h at 10^{-6} torr before adsorption isotherms were obtained. On the other hand, the wettability of the nanosilicas was obtained as a measure of their hydrophilicity by placing them in deionized bidistilled water, ethanol, and ethanol/deionized bidistilled water mixture. The IR spectra of the nanosilicas were obtained in a FTIR Bruker IFS 66 system equipped with a MTEC 300 photoacoustic cell (Institut Fertgungstechnik Materialforschung – IFAM, Germany) and transmission electron microscopy – TEM - was used to analyze the degree of aggregation of the nanosilicas in a JEOL JEM-2010 instrument by using an acceleration voltage of 100kV.

TPU was synthesized by reacting 4,4-diphenyl methane diisocyanate –MDI-, polyadipate of 1,4-butanediol (Hoopol F-530, Hoocker) and 1,4-butanediol. A hard/soft segment (NCO/OH) ratio of 1.05 was used. 10 wt% (based on the polymer) nanosilica was added to 18 wt% TPU in MEK solution and stirred at 2500 rpm for 3 hours to produce a good dispersion of the nanosilica in the polymer. About 100 ml adhesive solution was placed in a teflon mould which was placed into a desiccator fully saturated of MEK vapour, to allows a slow evaporation of MEK and avoid bubbles formation in the TPU-nanosilicas composites. One week after, the mould was placed under open air for 3 days to allow complete evaporation of MEK, and thus the TPU-nanosilica composites were obtained. The nomenclature of the composites used in this study was PU0 (TPU without silica), and PU15.5, PU57.5 and PU100 (TPUs containing 15.5, 57.5 and 100 % silanol groups, respectively).

The rheological properties of the TPUs were characterized in a Bohlin CS50 stress controlled rheometer using a plate-plate (20 mm diameter) geometry. The experiments were carried out in oscillatory mode at a frequency of 1 Hz to determine the storage and loss modulus as a function of the temperature. The experiments were carried out from 200°C to 30°C, using a cooling rate of 5 °C/min. Furthermore, dynamic mechanical thermal analysis (DMTA) was performed in a Rheometric Scientific DMTA Mk III instrument using the two-point bending mode. The experiments were carried out from −80°C to 80°C using a heating rate of 5 °C/min and a frequency of 1 Hz.

Results and Discussion

a. Characterization of the nanosilicas

Figure 1a shows the N_2/77K adsorption isotherms of the nanosilicas with different degree of silanization. The adsorption isotherms belong to the type II of the BDDT classification which corresponds to non-porous materials. The monolayer region is well-defined and the capillary condensation starts at a relative pressure of 0.85. Although it has been claimed that the treatment with silanes does not modify the adsorption capacity of the nanosilicas [3], the H20RD fumed silica (15.5 % silanol) shows less adsorption capacity than the N20 (fully silanated), mainly in the region of low relative pressure (Figure 1b).

The application of the BET equation to the N_2/77K adsorption isotherms shows a reduction in the specific surface area (from 161 m^2/g in the fully silanized nanosilica to 97 m^2/g in the nanosilica containing 15.5 % silanol) and the C_{BET} value (related to the adsorptive-nanosilica interactions) is also reduced from 114 for N20 to 14 for H20RD (Table 2). Therefore, because porosity is not developed in the nanosilicas by treatment with silanes, agglomeration of primary particles in the nanosilica might be produced. The degree of particle agglomeration in the nanosilicas was studied by TEM. Figure 2 shows that when the silanol content decreases, a bigger degree of particles agglomeration is produced.
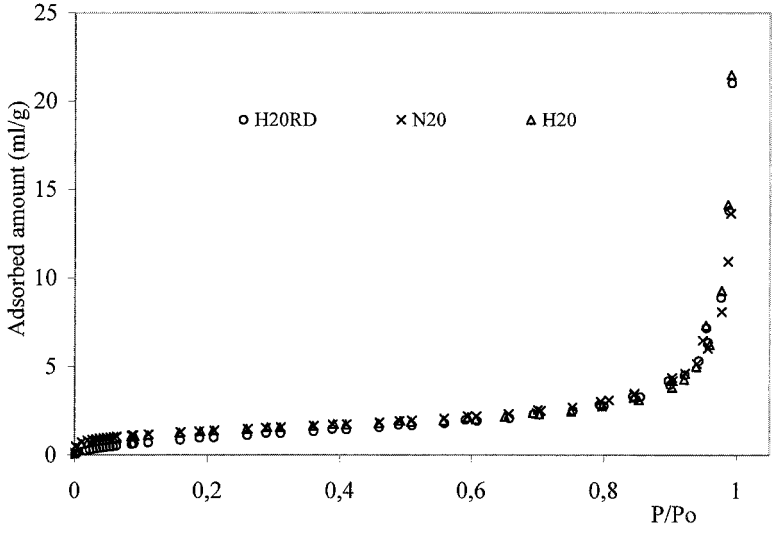
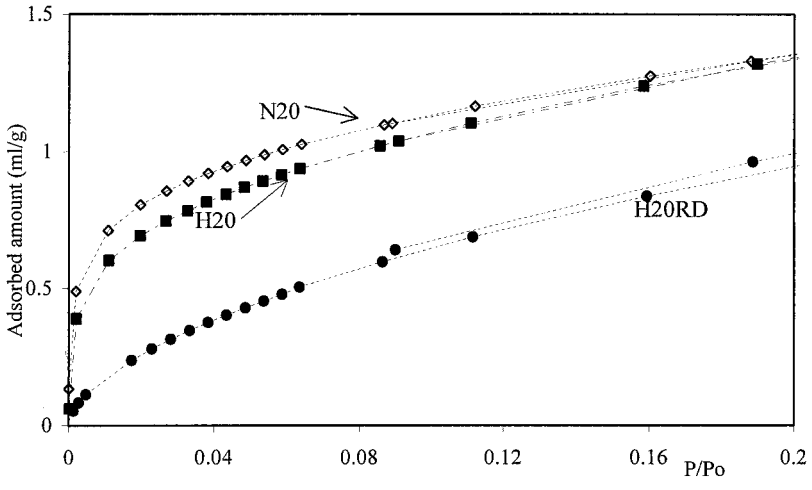Figure 1a. N$_2$/77K adsorption isotherms of nanosilicas.

Figure 1b. Low relative pressure region (N$_2$/77K adsorption isotherms of nanosilicas.

Table 2. Results obtained from the application of the BET equation to $N_2/77K$ adsorption isotherms of nanosilicas.

Nanosilica	SiOH (%)	Specific surface area (m^2/g)		C_{BET} parameter
		Nominal [a]	Experimental	
N20	100	200 ± 30	161	114
H20	57.5	170 ± 30	175	55
H20RD	15	200	97	14

a) Data provided by Wacker-Chemie.

100% silanol   57.5% silanol   15% silanol
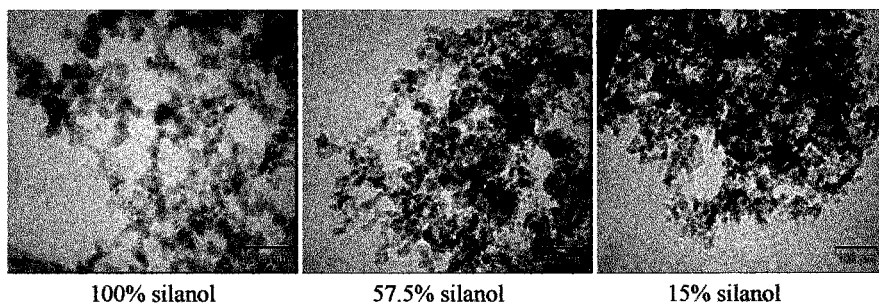
Figure 2. Transmission Electron Microscopy – TEM – micrographs of the nanosilicas.

The wettability of the nanosilicas is given in Table 3. The most hydrophilic nanosilica (N20) is well wetted by all polar solvents, whereas the partially silanated nanosilicas are not wetted by water. The higher the carbon content in the nanosilica, the lower the wettability in ethanol.

Table 3. Wettability of nanosilicas.

Nanosilica	Carbon (%)[a]	Silanol (%) [a]	Water (ml/g)	Water/ethanol (ml/g)	Ethanol (ml/g)
N20	0	100	9.3	11.2	15.8
H20	1.2	57.5	0	15.5	13.7
H20 RD	4.7	15	0	0	9.1

a) Data provided by Wacker-Chemie.

The differences in the wettability in ethanol and water/ethanol mixture of the nanosilicas containing 1.2 and 4.7 % carbon is due to the presence of different amounts of reacted and unreacted silanol surface groups.

The surface chemistry of the nanosilicas was obtained by photoacustic IR spectroscopy (Figure 3). The sharp peak at 3740 cm^{-1} is due to SiOH groups. A very broad peak due to water bonded to the silanol groups on the nanosilica is observed between 3000 and 3600 cm^{-1}. Additionally, bands corresponding to symmetric and asymmetric Si-O-Si absorption are located at 806 and 1110 cm^{-1}, respectively.
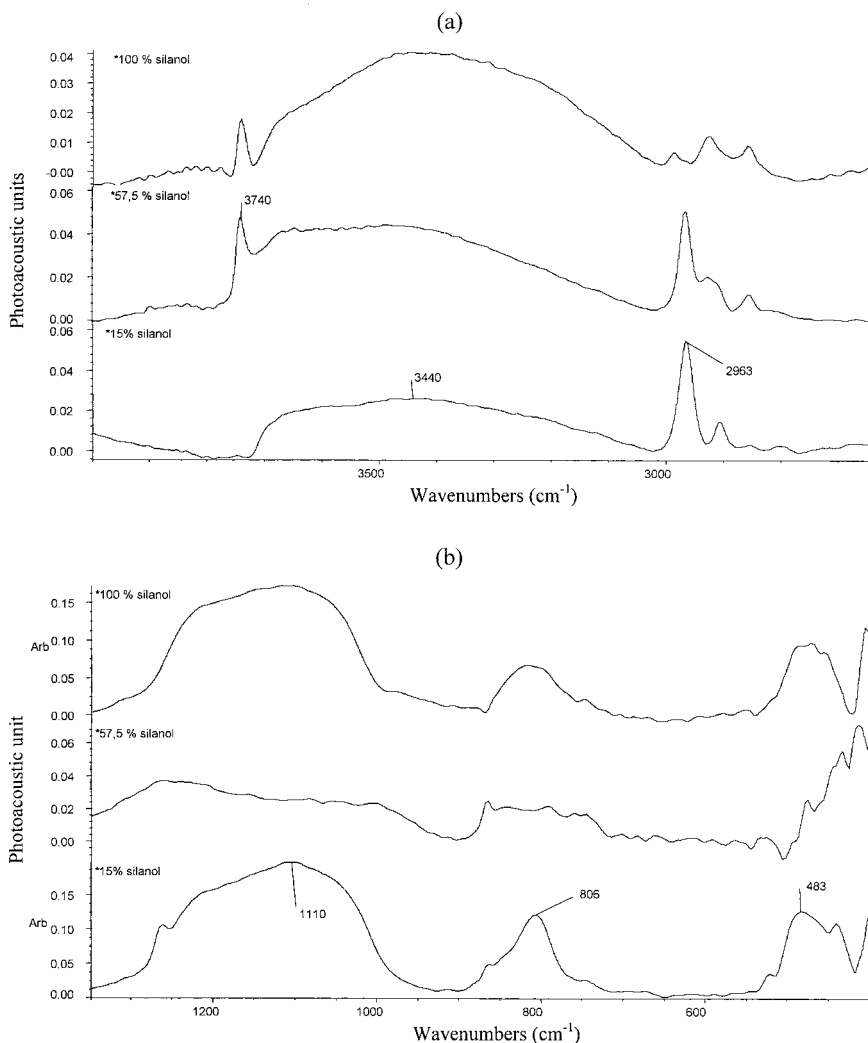

Figure 3. IR spectra of the nanosilicas. (a). 2500-4000 cm^{-1} region. (b) 400-1300 cm^{-1} region.

b. Characterization of the TPU-nanosilica composites

Figure 4a shows the variation of the storage modulus as a function of the temperature for the different nanosilica-TPU composites. The TPU without nanosilica shows lower storage modulus than for the composites containing nanosilicas, and there is a noticeable decrease in the storage modulus by increasing the temperature due to the softening of the polyurethane chains. The higher the silanol content in the nanosilica, the higher the storage modulus and the thermal stability of the nanosilica-TPU composite. This is due to the creation of interactions between the nanosilica and the polyurethane but also the formation of a network of silica particles interacting by hydrogen bonds could contribute.
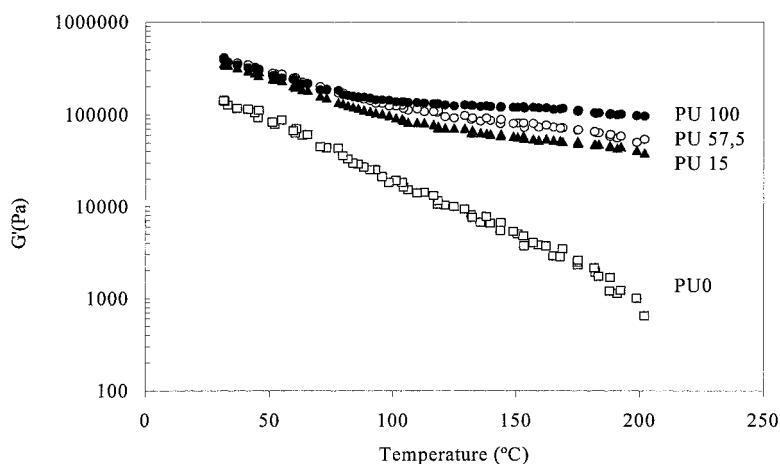

Figure 4a. Variation of the storage modulus as a function of the temperature for the TPU-nanosilica composites.

On the other hand, Figure 4b shows the variation of the storage and loss moduli as a function of the temperature for the nanosilica-TPU composites. The TPU without nanosilica shows a cross over of the loss and storage moduli at 65 °C due to the change in rheological regime of the polyurethane. This cross-over disappears in all TPU-nanosilica composites, and the storage modulus becomes dominant in all of them. The higher the silanol content of the nanosilica, the higher the separation between the storage and loss moduli, i.e. the greater the degree of interaction between the nanosilica and the

polyurethane chains. This means that the nanosilica interacts with the TPU chains in the composite, in a greater extent by increasing the silanol content in the nanosilica.
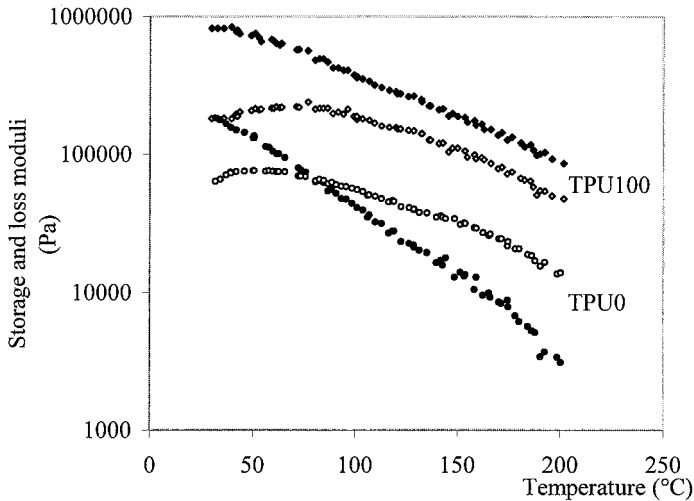

Figure 4b. Variation of the storage (G') and loss (G'') moduli as a function of the temperature for the PU0 and PU100 composites. G', open symbol; G'', closed symbol.

DMTA experiments also confirm the different degree of interactions between the TPU and the nanosilicas with different silanol content. Figure 5 shows the variation of the storage modulus and tan δ vs temperature for the composites. The DMTA curves show the T_g of the soft segments of the polyurethane at about –22°C, and this value does not vary by adding nanosilica. Addition of nanosilica increases the storage modulus and decrease the area under the tan δ curve, as a consequence of a greater degree of crosslinking (physical interactions) and therefore the chain mobility in the polyurethane is reduced by adding nanosilica. The higher the silanol content in the nanosilica, the lower the area under the tan δ curve, which confirms the results discussed earlier. Furthermore, the TPU melts at higher temperature as the silanol content in the nanosilica increases. All those evidences support the relevance of the silanol groups in the interactions of nanosilicas with the polyurethane chains.
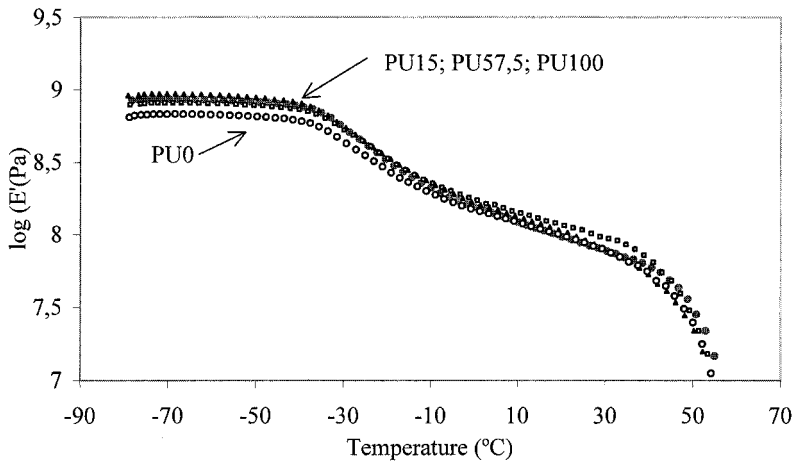
Figure 5a. Variation of the storage modulus as a function of the temperature for the TPU-nanosilica composites (DMTA experiments).
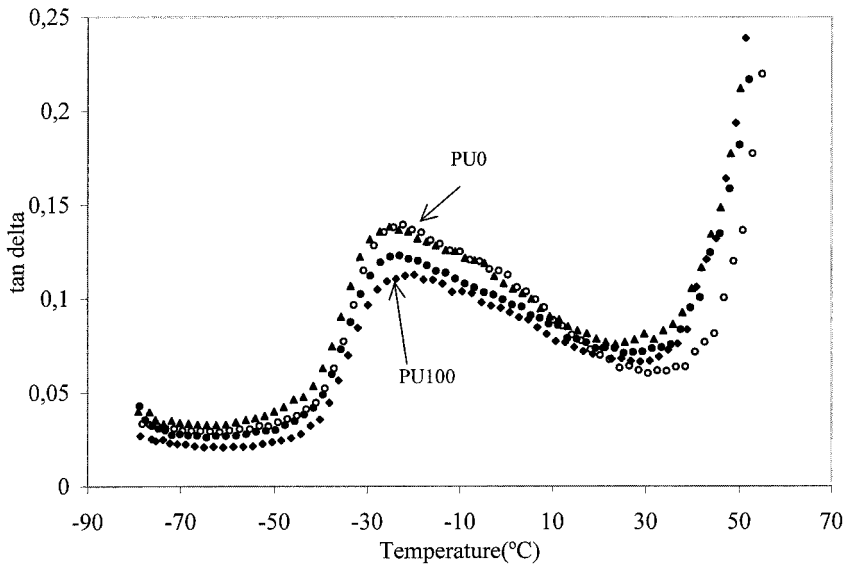

Figure 5b. Variation of the tan δ as a function of the temperature for the TPU-nanosilica composites (DMTA experiments).

Conclusions

Treatment of nanosilicas with silanes increases the degree of agglomeration of the primary particles, giving a reduced specific surface area.

The silanol content in the silica greatly determine the rheological performance of TPU-nanosilica composites, due to the different degree of interactions between the nanosilica and the polyurethane chains. On the other hand, hydrogen bonds between the silanol groups on the nanosilica and the urethane group in the polyurethane are responsible of the improved rheological performance of the nanosilica-polyurethane composites.

Acknowledgments

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