NANOSILICA-POLYURETHANE INTERACTIONS EVIDENCED BY PLATE-PLATE RHEOLOGY AND DMTA

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Summary: Fumed nanosilicas with various silanol groups percent were added in thermoplastics polyurethanes (TPU's) to increase the rheological and mechanical properties. The higher the silanol content of the nanosilica showed the higher the storage modulus and the stability against the temperature of the nanosilica-TPU composite. DMTA experiments also confirm the degree of interactions between the TPU and the nanosilicas with different silanol content. Addition of nanosilica decrease the area under the tan δ curve, as a consequence of a greater degree of crosslinking in the TPU produced by the nanosilica. Therefore, the silanol content in the silica determinates the rheological behavior of nanosilica-TPU composites.

Key words: Polyurethane; nanosilica; adhesive; thermoplastic polymer; adhesion.

Introduction

Thermoplastic polyurethanes (TPU) are a versatile group of multi-phase segmented polymers that have good mechanical and elastic properties, and hardness. TPU usually exhibit a two-phase microstructure, which arises from the chemical incompatibility between the soft and the hard segments. The hard rigid segment segregates into a glassy or semicrystalline domain, and the polyol soft segments form amorphous or rubbery matrices in which the hard segments are dispersed [1].

Fumed silica nanoparticles (nanosilicas) are commonly added to increase the rheological and mechanical properties of TPUs [2-5]. This improvement has been ascribed to the creation of hydrogen bonds between the silanol groups on the nanosilica surface and the urethane and/or hydroxyl groups in the soft segments. To confirm this hypothesis, in this study a nanosilica was treated with silanes by Wacker-Chemie to gradually decrease its silanol content. Then, different TPUs containing 10 wt% fumed silicas with different degree of silanization were characterized using plate-plate rheometry and DMTA. Both are structure-sensitive techniques able to establish the silica-TPU degree of interaction.

Experimental

Fumed silicas (nanosilicas) were specially manufactured by Wacker-Chemie (Burghausen, Germany) for this study. The degree of silanization was varied between 15.5 and 100 % by treatment of a raw fully silanized nanosilica with a silane. Primary particle size was 7 nm in all nanosilicas. Table 1 shows some properties of the nanosilicas provided by Wacker-Chemie. Additionally, the specific surface area of the nanosilicas were measured in a Quantachrome system (BET model) at 77K in liquid nitrogen. The silicas were degasified at 100ºC during 8 h (10^{-6} torr).

Table 1.- Properties of the nanosilicas$^{(a)}$.

Sample	**SiOH (%)**	**Carbon (%)**	**mmol SiOH/g HDK**
HDK N20	100	0	0.60
HDK H20	57.5	1.2	0.34
HDK H20TD	15.0	4.7	0.09

$^{(a)}$ Data provided by Wacker-Chemie.

The wettability test in silicas was carried out. The samples were wet with destiled water (w), ethanol (e) or ethanol/water (e/w). The results were expressed in ml of used solvent /g silica. The IR spectra of the nanosilicas were also obtained. It was used a Bruker Tensor 27 model. To obtain transmission electronic microscopy -TEM, It was used a JEOL model JEM-2010 with an acceleration tension of 100kV.

TPU were synthesized using 4,4-diphenyl methane diisocyanate –MDI-, polyadipate of 1,4-butanediol (Hoopol F-530, Hoocker) as macroglicol and 1,4-butanediol as chain extender. A hard/soft segment (NCO/OH) ratio of 1.05 was used. 10 wt% nanosilica was added to the TPU. The nomenclature of samples was PU0 (for the TPU without silica), and PU15.5, PU57.5 and PU100 (for the TPUs containing 15.5, 57.5 and 100 % silanol, respectively).

TPU 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 200ºC to 30ºC, using a cooling rate of 5 ºC/min. Furthermore, dynamic mechanical analysis was performed in a Rheometric Scientific DMTA Mk III instrument using the two-point bending mode. The experiments were carried out was from –80ºC to 80ºC with a heating rate of 5ºC/min.

Results and Discussion

a. Characterization of the nanosilicas.

Figure 1 shows the N_2/77K adsorption isotherms of nanosilicas with different degree of silanization. Isotherms belong to the type II in the BDDT classification which corresponds to non-porous materials.

Figure 1. N_2/77K adsorption isotherms of fumed silicas

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 HDK H20RD fumed silica shows less adsorption capacity than the HDK N20 (fully silanized). Further, the nitrogen-nanosilica interactions are smaller in the HDK H20RD nanosilica according with the low relative pressure region showed in the figure 2.

In fact, the application of the BET equation to the 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 15.5 % silanol containing nanosilica) and the C value (related to the adsorptive-nanosilica interaction) is also reduced from 114 for HDK N20 to 14 for HDK H20RD (table 2). Therefore, because porosity cannot be developed, the treatment with silanes reduces the silanol content and facilitates the particle agglomeration of the nanosilica.

Figure 2. The low relative pressure region in the N_2/77K adsorption isotherms of fumed silicas

Table 2.- Results obtained from N_2/77K adsorption isotherms of fumed silicas.

Sample	**SiOH (%)**	**Specific surface area (m^2/g)**		**C parameter**
		Nominal (a)	**Experimental**	
HDK N20	100	200 ± 30	161	14
HDK H20	57.5	170 ± 30	175	55
HDK H20RD	15.5	200	97	14

(a) Data provided by Wacker-Chemie.

The particle agglomeration of the nanosilica is illustrated by Transmission Electronic Microscopy –TEM in the figure 3. When the silanol content is decreased, a bigger agglomeration starts to be more evident.

(a)

(b)

(c)

Figure 3. Transmission Electronic Microscopy –TEM at 100 nm of (a) HDK N20 (100 % silanol contents), (b) HDK H20 (57,5 % silanol contents) and (c) HDK H20RD (15% silanol contents).

The wettability test for hydrophilic (HDK N20) silica sample showed a behaviour in according with their Sa. The wettability test presented an unique value for ethanol for HDK H20RD, with 4.7% of carbon content, but for HDK H20 with 1.2 %, the silica surface was wet by w/e, too. This different behaviour between two hydrophofic silica could be due to the superficial grafting, contacting with silanol groups, which can occupy positions inaccessible to water or ethanol/water, respectively.

Table 3. Wettability test for silicas.

Silica	Carbon (%)[a]	Silanol (%) [a]	w (ml/g)	w/e (ml/g)	e (ml/g)
HDK N20	0	100	9.3	11.2	15.8
HDK H20	1.2	57.5	0	15.5	13.7
HDK H20 RD	4.7	15	0	0	9.1

[a] Data provided by Wacker-Chemie.

The surface chemistry of the nanosilicas was characterized with IR spectroscopy (Figure 4). The most important bands are assigned in Table 4.

Figure 4.- IR spectra of fumed silicas.

Table 4.- IR absorption bands of the nanosilicas.

$\bar{\nu}$ (cm^{-1})	Species	Vibration
~3440	SiO-H	Stretching (st)
~2960	C-H	Stretching (st)
~1630	SiO-H	Bending (δ)
~1260	Si-O, Si-H	Stretching (st), bending (δ)
1110-1000	Si-O-C, Si-O-Si	Stretching (st)
~810	Si-OH, Si-OC, Si-O-Si	Stretching (st)

The removal of silanol groups by treatment of the nanosilica with silanes can be noticed in the gradual reduction of the relative intensity of the bands at 1630 and 3440 cm^{-1}; furthermore, the bands due to C-H (2960 cm^{-1}) and Si-O-C (810 and 1260 cm^{-1}) becomes more marked.

The broad adsorption band positioned in the range 3000–3800 cm^{-1} is due to H-bonded silanols. The amount of bonding is much greater on silica that is precipitated from solution than on prepared by flame oxidation as is HDK N20. In addition, this band is attributed to the presence of hydroxyl groups for water present on the surface.

Additionally, bands corresponding to Si-O-Si symmetric and asymmetric vibrations are located at 812 and 1104 cm^{-1}, respectively. The small shoulder at 959 cm^{-1} can be assigned to the Si-OH group. During the heat treatment procedures employed, the silica surface is progressively dehydroxylated, the numerous investigations[6] have correlationed surface dehydroxylation with two bands at 490 cm^{-1} (called D_1) and 604 cm^{-1} (D_2) that are superimposed on the broad band at about 440 cm^{-1}, which is the most intense signal in the spectrum of ν-SiO$_2$. The FT-IR spectra shows up a band at 469 cm^{-1} that could be assigned to D_2. Different structural models have been proposed for D_2, mainly defects such as a broken Si-O bond or with the formation of cyclotrisiloxanes (three-membered rings) named surface siloxane brigde belonging to an (SiO-)$_3$.

Finally, in HDK H20 RD and HDK H20 the peaks around 2900 cm^{-1} are due to organic group as -CH2- and -CH3 vibrations attributed to compund presents in the synthesis of silica[7].

b. Rheological characterization of the TPU-nanosilica composites.

Figure 5 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 those containing nanosilicas. Furthermore, there is a noticeable decrease in storage modulus by increasing the temperature if the TPU without nanosilica. The higher the silanol content of the nanosilica, the higher the storage modulus and the stability against the temperature of the nanosilica-TPU composite. This is due to the creation of interactions between the nanosilica and the TPU chains whose become greater by increasing the silanol content of the nanosilica.

Figure 5. Variation of the storage modulus as a function of the temperature for the different nanosilica-TPU composites.

On the other hand, Figure 6 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 moduli at 65 ºC due to the change in rheological regime of the polyurethane. This cross over disappears in all nanosilica-TPU 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 degree of interaction between the nanosilica and the polyurethane chains. Therefore, the nanosilica interacts with the TPU chains in the composite, in a greater extent by increasing the silanol content in the nanosilica.

Figure 6. Variation of the storage and loss moduli as a function of the temperature for the different nanosilica-TPU composites.

DMTA experiments also confirm the degree of interactions between the TPU and the nanosilicas with different silanol content. Figure 7 shows the variation of the storage modulus and tan δ vs temperature of the composites.

Figure 7. Variation of the storage modulus and tan δ as a function of the temperature for the different nanosilica-TPU composites (DMTA experiments).

The curves show the existence of the T_g of the soft segments of the polyurethane at about –22ºC, which does not vary by adding nanosilicas. 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 in the TPU produced by the nanosilica. The higher the silanol content in the nanosilica, the lower the area under the tan δ curve, i.e. the greater the degree of crosslinking. Furthermore, the melting of the TPU is produced at higher temperature as the silanol content in the nanosilica increases. All those evidences support the relevance of the silanol groups in the interactions with the polyurethane chains.

Conclusions

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

The silanol content in the silica greatly determine the rheological performance of nanosilica-TPU composites.

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