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Addition of nanosilicas with different silanol content to thermoplastic polyurethane adhesives

José Vega-Baudrit[a], Virtudes Navarro-Bañón[b], Patricia Vázquez[c], José Miguel Martín-Martínez[b,*]

[a]*Polymer Laboratory—POLIUNA, Universidad Nacional, 86-3000 Heredia, Costa Rica*
[b]*Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain*
[c]*Research and Development Centre for Applied Sciences (CINDECA), CONICET-UNLP, 47 n 257, B1900AJK La Plata, Buenos Aires, Argentina*

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Abstract

Three nanosilicas with different silanol contents were prepared by treatment of hydrophilic fumed silica with dimethyldichlorosilane. This treatment reduced the silanol content and produced the particle agglomeration of the nanosilicas. Thermoplastic polyurethane (TPU) adhesives containing nanosilicas were prepared and characterized by FTIR spectroscopy, differential scanning calorimetry (DSC), plate–plate rheology, dynamic mechanical thermal analysis (DMTA), transmission electron microscopy (TEM) and stress–strain testing. Adhesive strength was obtained from T-peel tests of PVC/polyurethane adhesive joints.

The addition of hydrophilic nanosilicas favoured the degree of phase separation between the hard (i.e. isocyanate + chain extender) and soft (i.e. polyol) segments in the TPUs; the higher the silanol content on the surface of silica, the higher the degree of phase separation, and the crystallinity of the polyurethane (due to the soft segments) was also increased. Hydrogen bonds between the ester carbonyl groups in the TPU and the silanol groups on the silica surface were created and more favoured by increasing the silanol content. The tensile strength increased and the elongation at break of the polyurethane decreased by increasing the silanol content of the nanosilica. Addition of nanosilica increased the immediate adhesion of the polyurethane adhesives to PVC, irrespective of the silanol content on the nanosilica. The higher the mechanical and the rheological properties of the polyurethanes containing nanosilicas with different silanol content, the higher the final adhesive strength.

Keywords: A. Polyurethane; C. Infrared spectra; C. Rheology; D. Mechanical properties of adhesives

1. Introduction

Thermoplastic polyurethanes (TPUs) are multi-phase, segmented polymers that 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]. TPUs are commonly used as adhesives to join different materials in the footwear, automotive and general use adhesives.

Fumed silica nanoparticles (nanosilicas) are fillers commonly added to improve the thermal, rheological and mechanical properties of TPU adhesives [2–7]. This improvement in properties has been previously ascribed to the creation of hydrogen bonds between the silanol groups on the nanosilica surface and the ester carbonyl groups of the polyester groups (i.e. the soft segments) in the polyurethane, favouring the degree of phase separation [8–10]. In this study, a nanosilica was treated with a chlorosilane to reduce its silanol content, and fillers with different degree of hydrophilicity were obtained. It can

*Corresponding author. Tel.: +34 96 5903977; fax: +34 96 5903454.
E-mail address: jm.martin@ua.es (J.M. Martín-Martínez).

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be anticipated that the number of hydrogen bonds between the polyurethane and the silica will be reduced by decreasing the hydrophilicity of the nanosilica. To a TPU, 10 wt% treated nanosilicas were added and the mixtures obtained were characterized by FTIR spectroscopy, differential scanning calorimetry (DSC), plate–plate rheometry, dynamic mechanical thermal analysis (DMTA), transmission electron microscopy (TEM), stress–strain testing and peel test.

2. Experimental

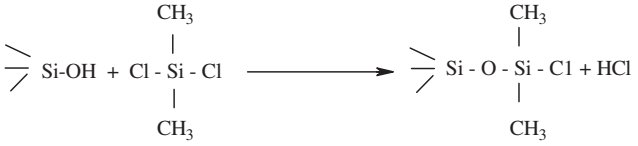
2.1. Materials

Different fumed silicas (nanosilicas) were manufactured by Wacker-Chemie (Burghausen, Germany). A fully silanized nanosilica (HDK N20, Wacker-Chemie) was progressively modified by chemical reaction with dimethyldichlorosilane (DMCS)—Scheme 1

The original level of silanization was decreased to 15.0 and 57.5%. The nominal primary particle size in all nanosilicas was 7 nm. To assure the absence of residual moisture in the nanosilicas, they were heated in an oven at 120 °C overnight. Table 1 shows the nomenclature of the nanosilicas and some of their characteristics provided by Wacker-Chemie. According to Wacker-Chemie, the nominal specific surface area of all nanosilicas was 200 m^2/g.

The TPU was prepared using the prepolymer method. The prepolymer was obtained by reacting the polyadipate of 1,4-butanediol ($M_w = 2440$ Da) with 4,4-diphenyl methane diisocyanate—MDI; an isocyanate/macroglycol equivalent ratio of 1.05 was used. 1,4-butanediol was used as chain extender. High-purity solid MDI was supplied by Aldrich (Cat. 25.643-9), a mixture of 98 wt% of the 4,4′-isomer and 2 wt% of the 2,4′-isomer. The NCO content of the prepolymer was determined by titration with dibutylamine (UNE-EN 1242 standard). The polyadipate of 1,4-butanediol (Hoopol F-530) was supplied by Hooker S.A. (Barcelona, Spain) and was heated for 4 h at 70 °C under reduced pressure (5 Torr) to remove the residual water. The 1,4-butanediol was supplied by Aldrich (Cat. B8.480-7) and was dried using 4 Å molecular sieves.

To avoid cross-linking reactions during polyurethane synthesis, the reaction temperature was kept below 65 °C under a stirring speed of 80 rpm. The synthesis of the polyurethane was carried out in dry nitrogen atmosphere to avoid the presence of water in the reactor. The prepolymers containing unreacted isocyanate ends were completely reacted at 65 °C for 2 h at 80 rpm with the necessary stoichiometric amount of 1,4-butanediol. After cooling down, the resulting solid polyurethanes were annealed in an oven at 80 °C for 12 h.



Scheme 1.

Table 1
Some characteristics of the nanosilicas[a]

Nanosilica	SiOH (%)	mmol $SiOH/g_{nanosilica}$
HDK N20	100	0.60
HDK H20	57.5	0.34
HDK H20RD	15.0	0.09

[a]Data provided by Wacker-Chemie.

With the polyurethane in 2-butanone solution, 10 wt% nanosilica was mixed by using a Dispermix DL-A laboratory mixer provided with a Cowles mechanical stirrer (diameter = 50 mm) and a water jacket to maintain the temperature at 25 °C during the preparation of the nanosilica–polyurethane mixtures. The preparation of the mixtures was carried out in two consecutive stages: (i) the nanosilica was mixed for 15 min at 2500 rpm with 1/3 butanone volume required in the solution, (ii) the polyurethane and 2/3 butanone volume were added to the previous solution, stirring the mixture for 2 h at 2000 rpm. The resulting solutions containing 20 wt% polyurethane and 2 wt% nanosilica were kept in a hermetic container until use. A solution containing 20 wt% polyurethane (without filler) was also prepared as control. Most of the properties of the nanosilica–polyurethane mixtures were measured using solid films which were prepared by placing about 100 cm^3 of adhesive solution in a mould and allowing a slow evaporation of the solvent at room temperature. The polyurethane films obtained were 0.7–0.9 mm thick.

The nomenclature of the polyurethane–nanosilica mixtures were PU0 (i.e. TPU without silica), and PU15, PU57.5 and PU100 (TPUs containing nanosilicas with 15, 57.5 and 100% of the original silanol groups content in the HDK N20 silica, respectively).

2.2. Experimental techniques

TPU films were characterized by FTIR spectroscopy, DSC, plate–plate rheometry, DMTA, TEM and stress–strain test.

2.2.1. FTIR spectroscopy

KBr/nanosilica pellets were prepared to obtain the IR spectra of the nanosilicas. KBr was extensively dehydrated by heating at 105 °C overnight. In a HandiPress 0.1 mg of nanosilica and 80 mg KBr were mixed and pressed until an homogeneous pellet was obtained. The

IR spectra of the nanosilicas were obtained in the transmission mode in a Bruker Tensor 27 spectrophotometer, and 100 scans were collected at a resolution of $4\,cm^{-1}$.

The IR spectra of the polyurethane films were obtained in the transmission mode using a Bruker Tensor 27 spectrophotometer, and 80 scans were collected at a resolution of $4\,cm^{-1}$.

2.2.2. $N_2/77\,K$ adsorption isotherms

The specific surface area of the nanosilicas were obtained from $N_2/77\,K$ adsorption–desorption isotherms measured in a Quantachrome adsorption system. Prior to adsorption measurements, the nanosilicas were outgassed at 100 °C for 8 h at a residual pressure of 10^{-6} Torr.

2.2.3. DSC experiments

DSC experiments were carried out in a TA instrument DSC Q100 V6.2. Aluminium pans each containing 12–15 mg of sample were heated from –80 °C to 80 °C under nitrogen atmosphere. The heating rate was 10 °C. The first heating run was carried out to remove the thermal history of the samples. From the second run, the glass transition temperature (T_g), the melting temperature (T_m), the crystallization temperature (T_c), the melting enthalpy (ΔH_m), and the crystallization enthalpy (ΔH_c) of the TPUs were obtained. The crystallization rate was estimated by melting the polyurethane film at 100 °C, followed by a sudden decrease to 25 °C and the evolution of heat with time under isothermal conditions was monitored for 30 min at 25 °C until a crystallization peak appeared.

2.2.4. Plate–plate rheometry

The rheological properties of the polyurethane films were determined in a shear stress-controlled Bohlin CS50 rheometer, using parallel plates (upper plate diameter = 20 mm); the gap selected was 0.4 mm. Oscillatory experiments were performed to determine the rheological properties (mainly the storage, G', and loss, G'', moduli) of the polyurethane films. Experiments were performed by melting the polyurethane film at 200 °C and cooling down to 30 °C at a cooling rate of 5 °C/min; the target strain was 0.005 and the frequency was set to 1 Hz. All the experimental results were obtained in the region of linear viscoelasticity.

2.2.5. DMTA experiments

The viscoelastic properties of the polyurethanes were measured in a Rheometric Scientific DMTA Mk III instrument using the two-point bending mode (single cantilever). The experiments were carried out by heating the sample from −80 °C to 100 °C, using a heating rate of 5 °C/min, a frequency of 1 Hz and a strain of 64 μm peak–peak.

2.2.6. Transmission Electron Microscopy

A JEOL JEM-2010 microscope was used to analyse the morphology of the nanosilicas and the polyurethane–nanosilica mixtures; an acceleration voltage of 100 kV was used. The nanosilicas were placed directly into the rounded support used for TEM analysis. The polyurethane films were obtained by casting highly diluted polyurethane adhesive solutions containing about 1 wt% solids on the rounded support. The solvent was allowed to evaporate at room temperature for 2 h, and the resulting polyurethane films were analysed.

2.2.7. Stress–strain measurements

The mechanical properties of the polyurethane films were obtained in an Instron 1011 using dog-bone test pieces of 0.8 mm thick and 4 mm width (in the centre of the test sample), and following the test procedure given in the ISO 37–77 standard, a cross-head rate of 100 mm/min was used.

2.2.8. T-peel strength measurements

Adhesive strength was obtained from T-peel tests of solvent-wiped plasticized PVC/polyurethane adhesive joints. Table 2 shows the composition of the plasticized PVC used to prepare the adhesive joints. The PVC test samples used had dimensions of 30 mm × 150 mm × 5 mm. Before applying the adhesive, the smooth PVC surface was wiped with a cotton cloth soaked in 2-butanone allowing the solvent to evaporate for 30 min under open air. After solvent wiping of the PVC, 1.5 ml of adhesive solution was applied by brush to each strip to be joined, and left to dry for 1 h. After evaporation, an uniform solid polyurethane film about 50 μm thick was formed which was rapidly heated to 80 °C by infrared radiation (reactivation process). The strips were immediately placed in contact and a pressure of 0.8 MPa was applied for 10 s to achieve a suitable joint. The resulting adhesive thickness in the joints was about 100 μm.

The T-peel strength was measured in an Instron 1011 at a cross-head speed of 100 mm/min. The values obtained were the average of five replicates (standard deviation was less than 5%). The evolution of the T-peel

Table 2
Composition of the plasticized PVC used to produce the adhesive joints

Component	Percentage (wt%)
Poly(vinyl chloride)	57.1
Dioctyl phthalate	36.5
Epoxydized soy oil	1.9
Calcium carbonate	2.3
Heat stabilizer	1.7
Titanium dioxide	0.5

strength was monitored at different times after joint formation (0.5–120 h).

3. Results and discussion

3.1. Characterization of the nanosilicas

The ATR–IR spectrum of the fully silanated—100% silanol—nanosilica (Fig. 1) shows the typical stretching broad band of Si–O–Si centred at 1107 cm^{-1}, and several bands due to the silanol groups : 3442 (SiO–H stretching), 1629 (SiO–H bending) and 1260 cm^{-1} (Si–O stretching). The treatment of the fully silanated nanosilica with DMCS creates new C–H (2960 cm^{-1}) and Si–O–C (810 cm^{-1}) bands—Fig. 1, and a reduction in the intensity of the bands at 1260, 1629 and 3442 cm^{-1} due to silanol groups is produced. The higher the degree of reaction of the nanosilica with DMCS (or the lower the silanol content), the higher the intensity of the C–H and Si–O–C bands.

The N_2/77 K adsorption isotherms of the nanosilicas are given in Fig. 2a. All isotherms belong to the type II of the Brunauer–Deming–Deming–Teller classification, typical of non-porous solids [11]. The capillary condensation starts at a relative pressure of 0.85. The lower the amount of silanol groups, the lower the adsorption capacity of the nanosilica, mainly in the region of relative pressure lower than 0.2 (Fig. 2b). The application of the BET equation [12] in the region of relative pressure between 0.05 and 0.30 allows the calculation of the monolayer adsorption capacity in ml/g (V_m) of the nanosilicas:

$$\frac{(P/P_o)}{[V(1-P/P_o)]} = \frac{1}{(V_m C)} + \frac{(C-1)(P/P_o)}{(V_m C)}, \quad (1)$$

where V is the amount adsorbed of N_2 in ml/g, P/P_o is the relative pressure, and C is a parameter related to the adsorptive-nanosilica interactions.

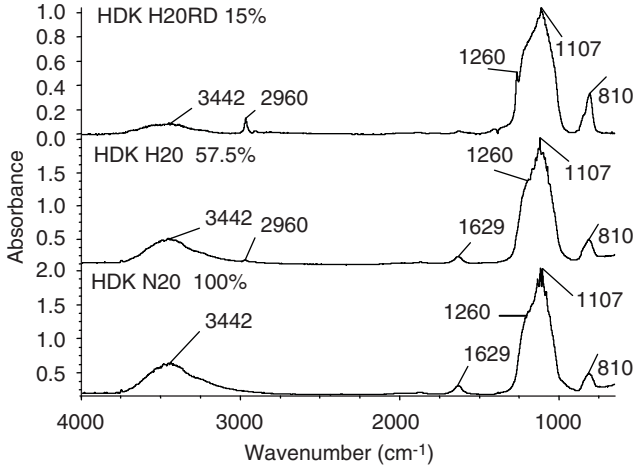


Fig. 1. IR spectra of the nanosilicas.

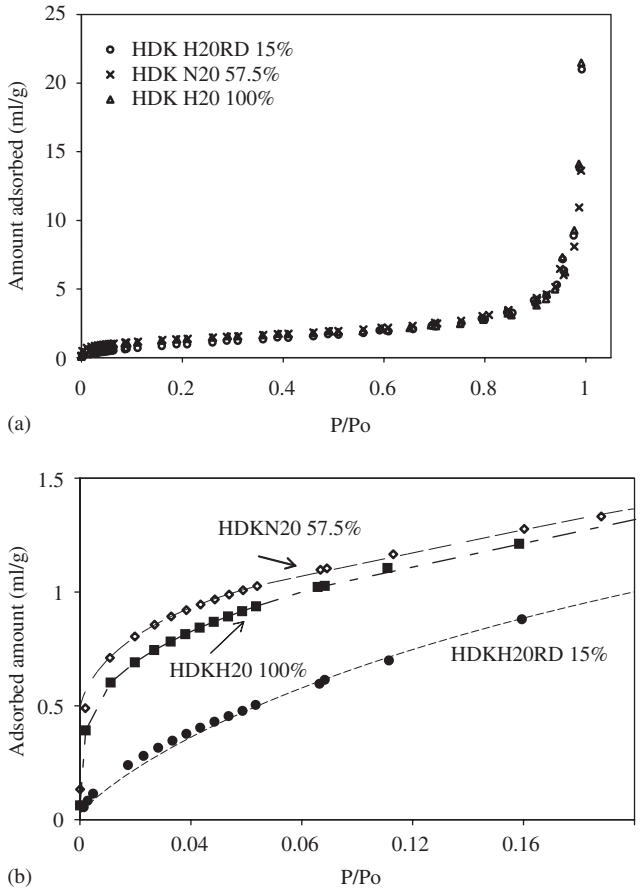


Fig. 2. (a). N2/77K adsorption isotherms of the nanosilicas. (b). Region of low relative pressure between 0 and 0.16.

Table 3
Some parameters obtained from the N_2/77 K adsorption isotherms of the nanosilicas

Nanosilica	Specific surface area (m^2/g)	C_{BET}
HDK N20	161	114
HDK H20	175	55
HDK H20RD	97	14

The specific surface area (S_{BET}) was obtained from the V_m values by applying

$$S_{BET} = \frac{a_m V_m N_A}{v_M}, \quad (2)$$

where a_m is the cross-section of the N_2 molecule (16.2×10^{-20} m^2), N_A is the Avogadro number, and v_M is the N_2 molar volume (22414 cm^3/mol).

Table 3 shows a decrease in the specific surface area of the nanosilica by decreasing the amount of silanol groups. Furthermore, the C parameter decreases by decreasing the amount of silanol groups on the surface of nanosilica. Therefore, the treatment of the fully

silanated nanosilica with DMCS produces some degree of agglomeration of the primary particles. In fact, the TEM micrographs (Fig. 3) show that the higher the silanol content, the lower the degree of agglomeration and the lower the particle size of the nanosilica. This conclusion is in contradiction with some previous works [13–15] that reported that a higher silanol content causes more moisture adsorption on the silica surface and therefore the filler–filler interactions increase. This in turn leads to agglomeration of the filler particles. However, in this study the reduction in the silanol groups content was due to reaction with the chlorosilane, so the nanosilica surface becomes more hydrophobic and the water adsorption is less favoured.

3.2. Characterization of the polyurethane–nanosilica mixtures

Fig. 4 shows the IR spectra of the polyurethane films without and with nanosilicas. All IR spectra show the bands due to the polyurethane at 3440 (free N–H stretching), 3348 (hydrogen-bonded N–H), 1735 (C = O of urethane), 1550 (N–H bending) and 1535 cm^{-1} (C–N). The bands due to the C–O–C of the polyester at 1174, 1224 and 1457 cm^{-1} also appear. Because the band due to the isocyanate at 2250 cm^{-1} is not present, the polyurethane is fully reacted. The polyurethane–nanosilica mixtures also show the bands due to silica at 1073 (Si–O–C and Si–O–Si) and 811 cm^{-1} (Si–OH, Si–OC and Si–O–Si). There are no differences between the IR spectra of the mixtures containing nanosilica with different silanol contents because of the small amount added to the polyurethane.

Because the IR bands at 3445 and 3348 cm^{-1} correspond to the free and hydrogen-bonded N–H stretching, respectively, it is possible to calculate the degree of phase separation (DPS) and the degree of phase mixing (DPM) in the polyurethanes. DPS and DPM can be readily obtained, respectively, from [8]:

$$\mathrm{DPS} = \frac{\mathrm{NH}_{\mathrm{bonded}}}{\mathrm{NH}_{\mathrm{bonded}} + \mathrm{NH}_{\mathrm{free}}}, \tag{3}$$

and

$$\mathrm{DPM} = 1 - \mathrm{DPS}, \tag{4}$$

where $\mathrm{NH}_{\mathrm{bonded}}$ is the intensity of the characteristic absorbance at 3348 cm^{-1} and $\mathrm{NH}_{\mathrm{free}}$ is that at 3445 cm^{-1}.

The DPS and DPM values of the polyurethane–nanosilica mixtures are given in Fig. 5 as a function of the silanol content in the nanosilica. DPS increases and DPM decreases as the silanol content on the surface of nanosilica increases.

The TPUs consist of alternating flexible soft and rigid segments displaying a two-phase morphology due to segmental incompatibility. Several factors influence the

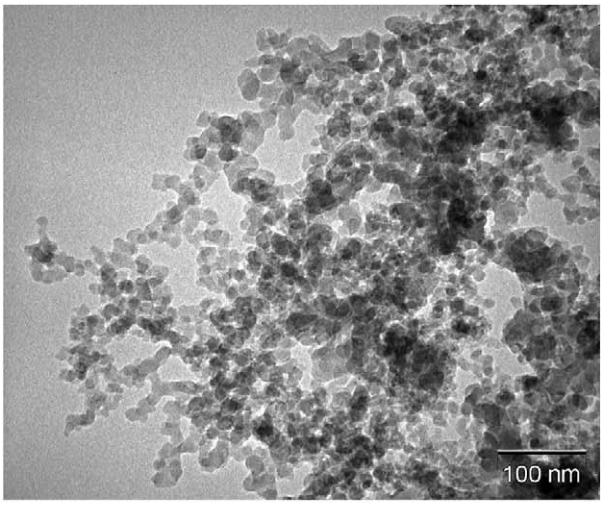


Fig. 3. TEM micrographs of the nanosilicas.

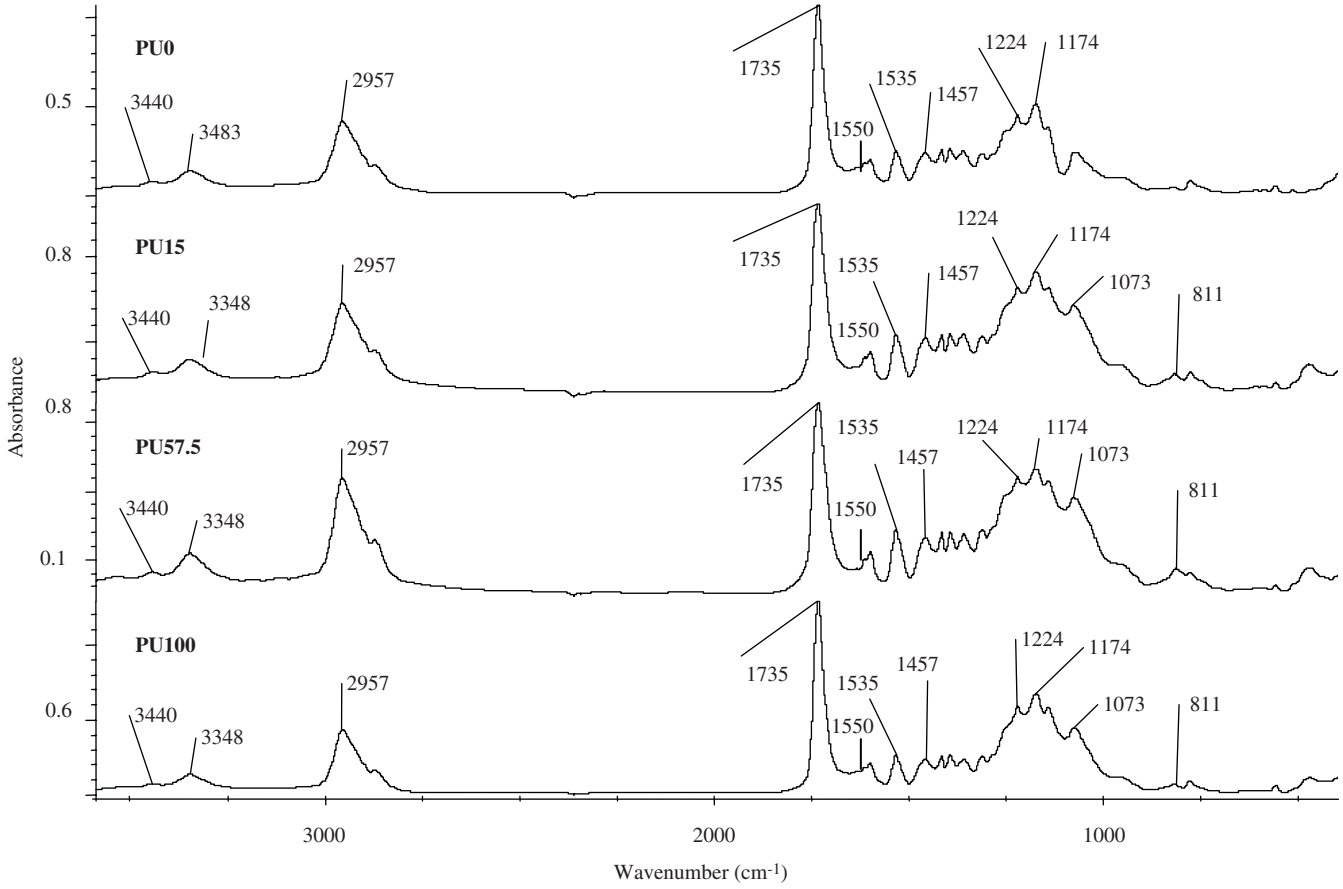


Fig. 4. IR spectra of the polyurethane–nanosilica mixtures.

DPS such as the molecular weight, the segmental length, the crystallizability of the soft segments, the overall composition and the intra- and inter-segments interactions [1,9,10]. The DPS in the polyurethanes is affected by adding nanosilica likely due to the hydrogen-bond interactions created between the silanol groups on the nanosilica surface and the C = O groups in the polyester (i.e. soft segments) of the polyurethane. Therefore, the segmental incompatibility in the polyurethane increases by adding hydrophilic nanosilicas; the higher the silanol content on the surface of nanosilica, the higher the DPS. Recent studies [9,10] have demonstrated that the addition of materials able to form hydrogen bonds result in less direct interactions between phases, causing a higher degree of phase separation in the polyurethane. On the other hand, the interactions between the silanol groups and the ester carbonyl groups in the polyurethane are weaker than those between the N–H and ester carbonyl groups, and therefore the silica addition increases the polyester chain mobility in the polyurethane allowing the creation of more ordered phases, with respect to the polyurethane without silica.

DPS in the polyurethanes was also studied by DSC. Fig. 6 shows the DSC thermograms of the polyurethanes with and without nanosilica. The DSC curves

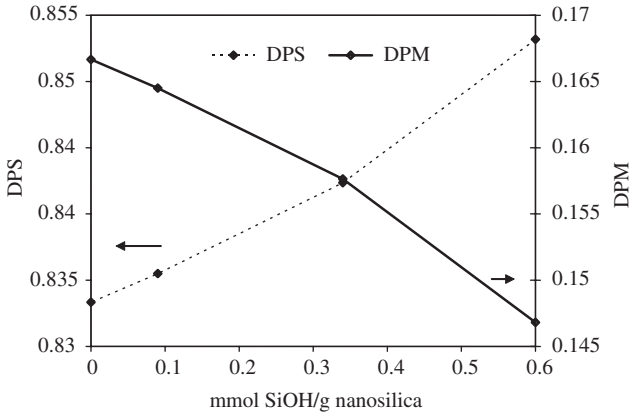


Fig. 5. DPS and DPM values for the polyurethane–nanosilica mixtures as a function of the silanol content on the surfaces of nanosilicas.

show one T_g value due to the soft segments located at low temperature followed by the cold crystallization of the soft segments (i.e. an exothermal peak), as well as the melting of the soft segments (located at higher temperature). The glass transition temperature (T_g) shifts to lower temperature in the polyurethanes containing nanosilicas, as compared to that without

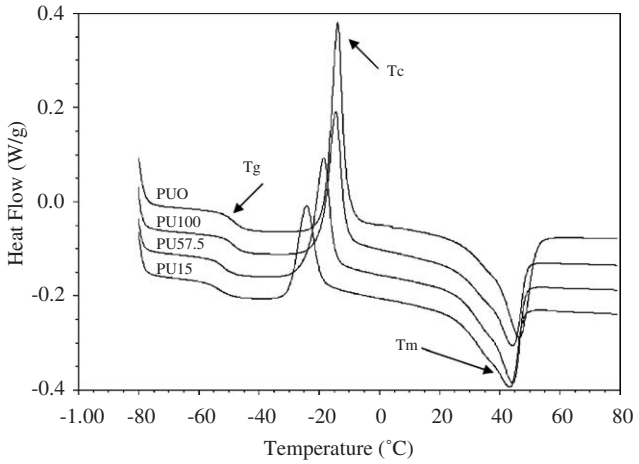


Fig. 6. DSC thermograms of the polyurethane–nanosilica mixtures.

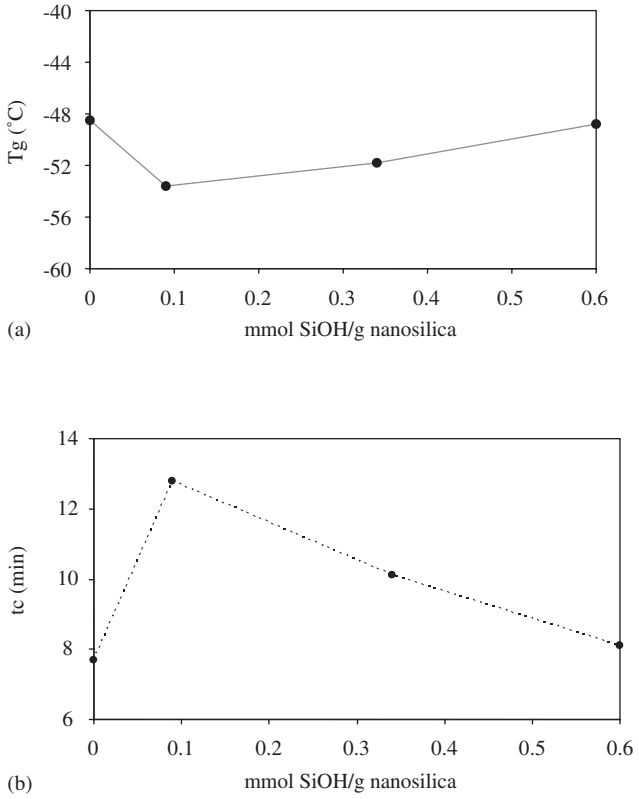


Fig. 7. (a). Glass transitions temperature (T_g) and (b). crystallization time (t_c) of the polyurethanes with and without nanosilicas as a function of the silanol content on the surfaces of nanosilicas.

nanosilica (Fig. 7a), and thus the rotational movement of the soft segments is produced at lower temperature, indicating a higher degree of phase separation between the hard and soft segments in the polyurethanes containing nanosilica. On the other hand, the higher the silanol content in the nanosilica, the higher the T_g value of the polyurethane–nanosilica mixture, and therefore smaller the degree of phase separation. This is in agreement with the increase in the DPS value in the polyurethanes containing nanosilicas with higher amount of silanol groups, and therefore, the formation of hydrogen bonds between the soft segments in the polyurethane and the silanol groups on the nanosilica surface is favoured. The formation of hydrogen bonds contributes to increase in interactions between the soft segments and then they become more organized giving an increase in crystallinity (which is due to the soft segments in TPUs [1]).

Table 4 shows a summary of the parameters obtained from the DSC thermograms. When the silanol content on the nanosilica surface increases, the crystallization temperature, the crystallization enthalpy, and the melting enthalpy of the soft segments in the polyurethanes increase due to the creation of hydrogen bonds between the silanol groups on the surface of nanosilica and the ester carbonyl groups in the polyurethane. The polyurethane without nanosilica shows the highest crystallinity and the smallest DPS value, i.e. it has the lowest DPS between the hard and soft segments. Furthermore, the time of crystallization (t_c) of the polyurethane at 25 °C (Fig. 7b) increases by adding nanosilica due to the increase in DPS. On the other hand, the time of crystallization decreases when the percentage of silanol groups on the nanosilica surface increases, i.e. the highest time of crystallization corresponds to the polyurethane containing the nanosilica with the lowest silanol content.

The rheological behaviour of the polyurethane–nanosilica mixtures was studied by plate–plate rheometry. Fig. 8a shows the variation of the storage modulus (G') as a function of the temperature for all polyurethanes and Fig. 8b shows the variation of the storage (G') and loss (G'') moduli as a function of the temperature for PU0 and PU57.5. There is a continuous decrease in the storage and loss moduli by increasing the temperature due to the rupture of the physical interactions between the polyurethane chains. When the nanosilica is added to the polyurethane, G' and G'' increase, the increase is more noticeable by increasing the temperature. This is due to the creation of hydrogen bonds between the nanosilica and the soft segments and thus, the higher the silanol content on the surface of nanosilica, the higher the storage modulus of the polyurethane. On the other hand, the polyurethane without nanosilica (PU0) shows a cross-over between the storage and loss moduli at 85 °C (Fig. 8b), i.e. at low temperature the storage modulus is higher than the loss modulus, but at higher temperature the loss modulus is higher. The addition of nanosilica removes the cross-over and always the storage modulus is higher than the loss modulus. Therefore, the incorporation of nanosilica makes the polyurethane more resistant to flow, more markedly by increasing the silanol content. The differences in the rheological behaviour of the polyurethanes

Table 4
Some parameters obtained from the DSC curves of the polyurethanes with and without nanosilicas

Polyurethane	Crystallization temperature (°C)	Crystallization enthalpy (J/g)	Melting point (°C)	Melting enthalpy (J/g)
PU0	−14	−29.3	47	30.8
PU15	−24	−19.4	44	24.8
PU57.5	−18	−21.7	44	25.3
PU100	−15	−22.1	44	25.8

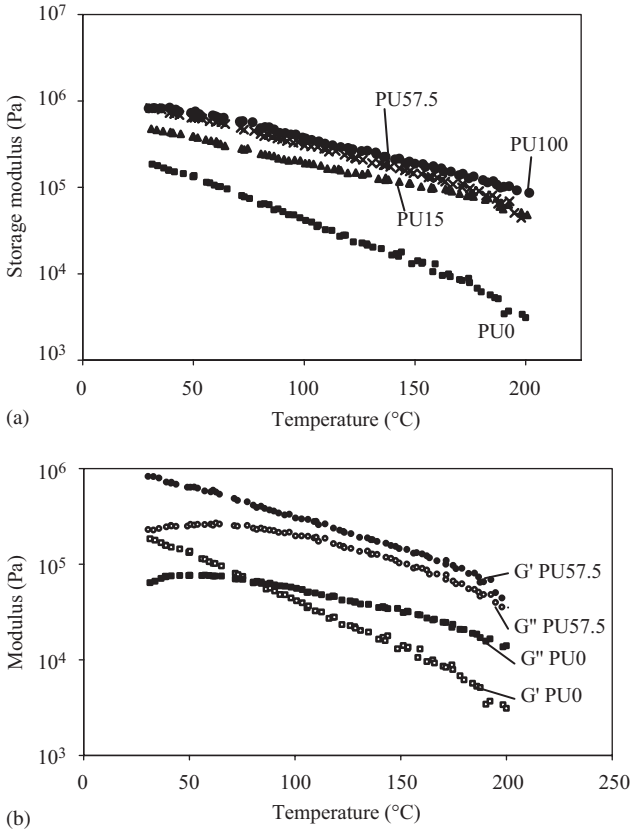


Fig. 8. (a) Variation of the storage modulus (G') as a function of the temperature in the polyurethanes with and without nanosilica. (b) Variation of the storage (G') and loss (G'') modulus as a function of the temperature for the polyurethanes without (PU0) and with HDK H20 nanosilica (PU57.5).

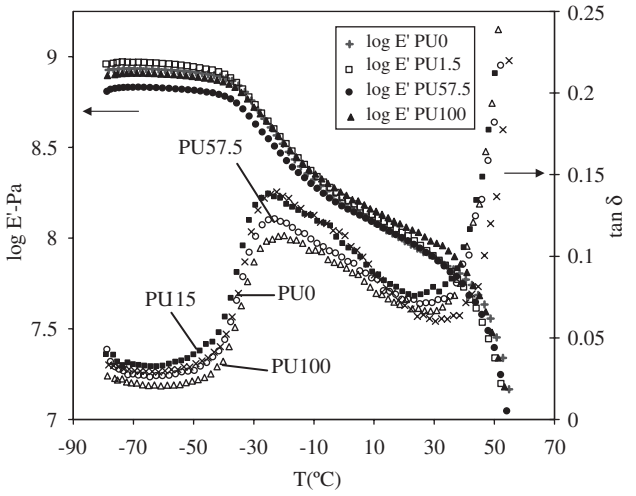


Fig. 9. Variation of the storage modulus (E') and tan δ as a function of the temperature for the polyurethanes with and without nanosilicas. DMTA curves.

seem to be in good agreement with the results obtained using DSC.

DMTA experiments allowed to obtain the viscoelastic properties of the polyurethanes in the region of low temperature where the glass transition temperature (T_g) is found. Fig. 9 shows the variation of the storage modulus (E') and tan δ as a function of the temperature for the polyurethanes without and with nanosilicas. Below the glass transition, the storage modulus (E') does not vary with the temperature, and it is higher for the polyurethanes containing nanosilicas. The glass transition is more clearly evidenced as a maximum in the curves of tan δ. The T_g value of the polyurethane without silica is located at -22 °C and increases by increasing the silanol content of the nanosilica indicating a greater DPS in the polyurethanes with nanosilicas. This trend in T_g value is more marked in PU100 indicating the interaction between the nanosilica and the polyurethane which is responsible for the rotational movement of the polymer chains at higher temperature. This trend is in agreement with that found with DSC. Furthermore, because of the maximum tan δ and the area below the glass transition curve in Fig. 9 decrease by increasing the silanol content on the surface of nanosilica, stronger interactions between the nanosilica and the polyurethane are produced, i.e. higher number of hydrogen bonds are produced. Thus, PU100 has the smallest area under the tan δ curve and PU0 the largest one.

Fig. 9 shows that after the glass transition, a rubbery plateau is produced. In the rubbery plateau, the storage modulus of the polyurethanes slightly increases by increasing the silanol content in the nanosilica. Therefore, the higher the silanol content, the greater interactions with the ester carbonyl in the soft segments (physical cross-links are produced, i.e. hydrogen bonds), and the higher the crystallinity of the polyurethane. At

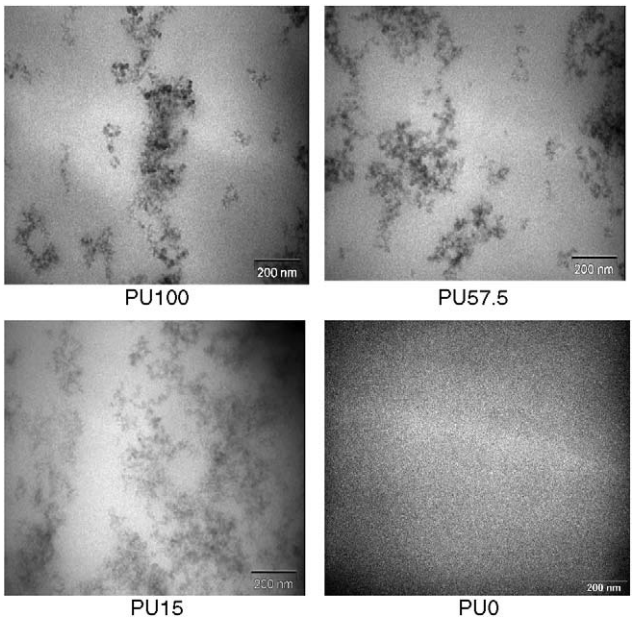


Fig. 10. TEM micrographs of the polyurethanes with and without nanosilicas.

about 35 °C, a sudden decrease in the storage modulus occurs (or a sudden increase in tan δ—Fig. 9) produced because of the softening of the polyurethanes.

The morphology of the polyurethanes was analysed by TEM (Fig. 10). TEM micrographs show the globular shape of the nanosilica-aggregated particles. PU15, PU57.5 and PU100 show the nanosilica-aggregated particles extended within the soft segments (lighter zones) of the polyurethane. PU0 is more uniform, probably due to the smaller phase segregation. The degree of nanosilica agglomeration is more important in PU15 because it contains the nanosilica with lower amount of silanol groups.

The mechanical properties of the polyurethanes were measured by stress–strain tests. Fig. 11a shows the tensile strength and Fig. 11b includes the elongation at break of the polyurethanes as a function of the silanol content of the nanosilicas. The tensile strength increases by adding nanosilica to the polyurethane and the trend is more marked by increasing the silanol content of the nanosilica. The elongation at break of the polyurethanes slightly decreases by adding nanosilica. These results can be explained as a favourable orientation of the polyurethane chains produced during the mechanical test. Therefore, the interactions between the silanol groups on nanosilica and the ester carbonyl groups in the soft segments allow a reduction in the distance between polyurethane chains favouring the crystallization of the soft segments [16].

The peel strength values of PVC/polyurethane adhesive joints as a function of the time after bond formation are given in Fig. 12. The immediate peel strength (measured 30 min after joint formation) of the joint

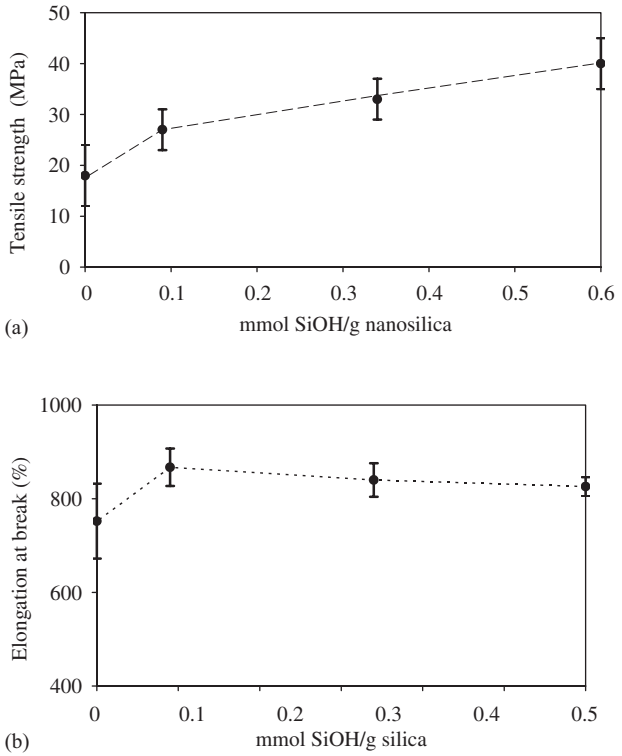


Fig. 11. Variation of (a) tensile strength and (b) elongation at break for the polyurethanes with and without nanosilicas as a function of the silanol content on the surfaces of nanosilicas.

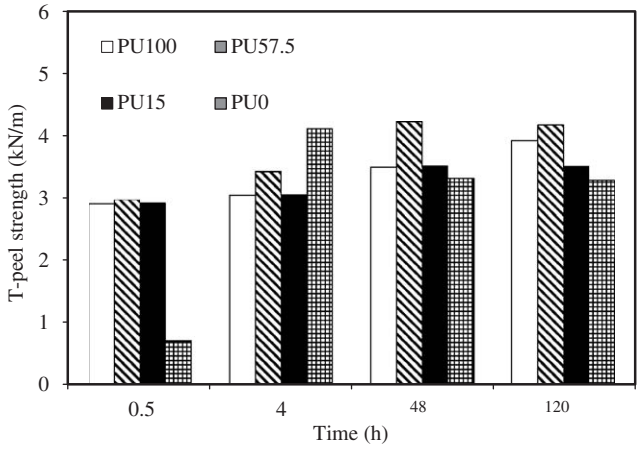


Fig. 12. T-peel strength values of PVC/polyurethane adhesive joints as a function of the time after joint formation.

produced with the polyurethane without nanosilica is low and the addition of nanosilica noticeably increases the immediate peel strengths, irrespective of the silanol content on the surface of nanosilica. Because an interfacial failure between the PVC and the adhesive is always obtained, the differences in the rheological and mechanical properties among the polyurethanes containing nanosilicas with different silanol content do not become relevant.

The T-peel strength increases 4 h after joint formation because the crystallization of the polyurethanes is produced (Fig. 12). Small differences in peel strength values are obtained by increasing the time after joint formation up to 120 h. The final adhesion is somewhat higher in the joints produced with the polyurethane adhesives containing nanosilicas, and mainly for the joint produced with the polyurethane with higher silanol content nanosilica likely to be due to the differences in the mechanical and rheological properties of the polyurethanes containing different nanosilicas.

4. Conclusions

The addition of nanosilicas improved the thermal, rheological, mechanical and adhesion properties of thermoplastic polyurethanes, due to the creation of hydrogen bonds between the silanol groups on the nanosilica surface and the ester carbonyl groups in the soft segments of the polyurethane. As a consequence, the storage modulus, the crystallinity, the tensile strength and the immediate peel strength values increased. Nanosilica disrupted the compatibility between the hard and soft segments favouring some degree of phase separation in the polyurethane. The higher the silanol content on the surface of nanosilica, the higher the degree of phase separation in the polyurethane. Final peel strength values of PVC/polyurethane adhesive joints could be related to the rheological and mechanical properties of the nanosilica–polyurethane mixtures.

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