

Thermoplastic Polyurethanes-Fumed Silica Composites: Influence of NCO/OH in the Study of Thermal and Rheological Properties and Morphological Characteristics

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1. Introduction

Thermoplastic polyurethanes (TPU's) are a multipurpose group of phase segmented polymers that have good mechanical and elastic properties and hardness. Usually, TPU's 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 (Oertel, 1993). Many factors influence in the separation of phases as the molecular weight, the segmental length, the crystallizability of the segment, the overall composition and the intra- and inter-segments interactions. Fumed nanosilicas are added to increase the thermal, rheological and mechanical properties of TPU's (Maciá-Agulló et al., 1992; Jaúregui-Belogui et al., 1999; Jaúregui-Belogui et al., 1999; Torró-Palau et al., 2001, Péres-Limaña et al., 2001).

When hydrophilic fumed nanosilica is added, the degree phase separation increases due to the interaction hydrogen-bonded between silanol groups on the nanosilica surface and soft segments of the TPU. Therefore, the segmental incompatibility on the TPU is increased with the presence of the hydrophilic nanosilicas. Recent studies have demonstrated that the use of this kind of materials able to form hydrogen-bonds result in less direct interactions between phases, causing a higher phase separation. Furthermore, the interactions between silanol and carbonyl groups are weaker than those between NH and ester carbonyl groups, then silica addition increases the polyester chain mobility and, it allows to become more ordered in relation to the TPU without silica (Sánchez-Adsuar et al., 2000; Tien et al., 2001; Nunes et al., 2000; Nunes et al., 2001).

The aim of this paper is to study the effect of incorporating hydrophilic fumed nanosilica in the formulation of polyurethane adhesives with different NCO/OH to improve its thermal, rheological and adhesive properties. The hypothesis is that the degree of polyurethane

phase segregation was affected by the presence of silica and the formation of hydrogen bonds. Therefore, there should be a variation of properties in polyurethanes in response to the presence of dispersed silica.

In recent papers are showed the results of evaluating these samples using thermal, rheological and mechanical analysis, and adhesion tests (Vega-Baudrit et al., 2006; Navarro-Bañón et al., 2005; Vega-Baudrit et al., 2008; Vega-Baudrit et al., 2009).

2. Materials and methods

Fumed silica (nanosilica HDK N20) was manufactured by Wacker-Chemie (Burghausen, Germany). The nominal primary particle size in all nanosilicas was 7 nm. According to Wacker-Chemie, the nominal specific surface area of all nanosilicas was 200m²/g and 100% of silanol groups.

The TPU was prepared using the prepolymer method. The prepolymer was obtained by reacting the polyadipate of 1,4-butanediol ($M_w = 2440$ Daltons) with 4,4-diphenyl methane diisocyanate - MDI; using different isocyanate/macroglycol equivalent ratios (1,05; 1,15; 1,25). 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 hours 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 crosslinking 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 with the necessary stoichiometric amount of 1,4-butanediol. The reaction time was 2 hours.

TPU solutions were prepared by mixing 20 wt% solid polyurethane and 2 wt% nanosilica with 2-butanone in 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 adhesives. This preparation was carried out in two consecutive stages: *i*) the nanosilica was mixed for 15 min at 2500 rpm with 1/3 butanone volume required. *ii*) the TPU and 2/3 butanone volume were added to the previous solution, stirring the mixture for 2h at 2000 rpm. TPU solutions were kept in a hermetic container until use. A TPU solution without silica was also prepared as control. Most of the properties of the polyurethanes were measured using solid films, which were prepared by placing about 100 cm³ of solution in a mould and allowing a slow evaporation of the solvent at room temperature during 2 days. The polyurethane films obtained were about 0.7 to 0.9 mm thick. The nomenclature of the polyurethane-nanosilica mixtures were PU105, PU115 and PU125 (according with NCO/OH, respectively).

2.1 Experimental techniques

Samples were characterized by FTIR with Attenuated Total Reflectance (ATR), Differential Scanning Calorimetry DSC, Dynamic Mechanical Thermal Analysis DMTA, Transmission Electronic Microscopy TEM and X-ray Diffraction XRD.

The IR spectra of the polyurethane films were obtained in the transmission mode using a Bruker Tensor 27 spectrophotometer. Under the experimental conditions used, the signal/noise ratio of the equipment was 0.04% transmittance (at 2000 cm^{-1}). The resolution was 4 cm^{-1} and 80 scans were recorded and averaged.

DSC experiments were carried out in a TA instrument DSC Q100 V6.2. Aluminium pans containing 12–15 mg of sample were heated from -80°C to 80°C under nitrogen atmosphere. The heating rate was $10^\circ\text{C}/\text{min}$. The first heating run was carried out to remove the thermal history of the samples. From the second heating 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.

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 $5^\circ\text{C}/\text{min}$, a frequency of 1 Hz and a strain of 64 mm peak-peak.

A JEOL JEM-2010 instrument was used to analyze the morphology of the nanosilicas; an acceleration voltage of 100 kV was used. The nanosilicas were placed directly into the grid specially design for TEM analysis.

The polyurethane crystallinity was determined using Seifert model JSO-DEBYEFLEX 2002 equipment. This equipment was provided with a copper cathode and a nickel filter, and the monochromatic radiation of copper ($K\alpha$) was used as the X-ray source ($\lambda=1,54\text{\AA}$). A range of diffraction angles (2θ) from 5° to 90° were used in the experiments.

3. Results and discussion

Recent studies (Nunes et al., 2000; Nunes et al., 2001; Vega-Baudrit et al., 2006; Navarro-Bañón et al., 2005; Vega-Baudrit et al., 2008; Vega-Baudrit et al., 2009) have demonstrated that the addition of fillers as silica 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 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.

3.1 Characterization of polyurethanes with different NCO/OH

Synthesized thermoplastic polyurethanes (TPU) with different NCO/OH were characterized by IR-FTIR spectroscopy (Figure 1). No significant differences among the TPU, except for a higher intensity of the bands between 900 and 1300 cm^{-1} , which increases with increasing the NCO/OH. Similarly, there is no characteristic band of the isocyanate groups ($-\text{NCO}$) close to 2250 cm^{-1} , indicating that the reaction was complete.

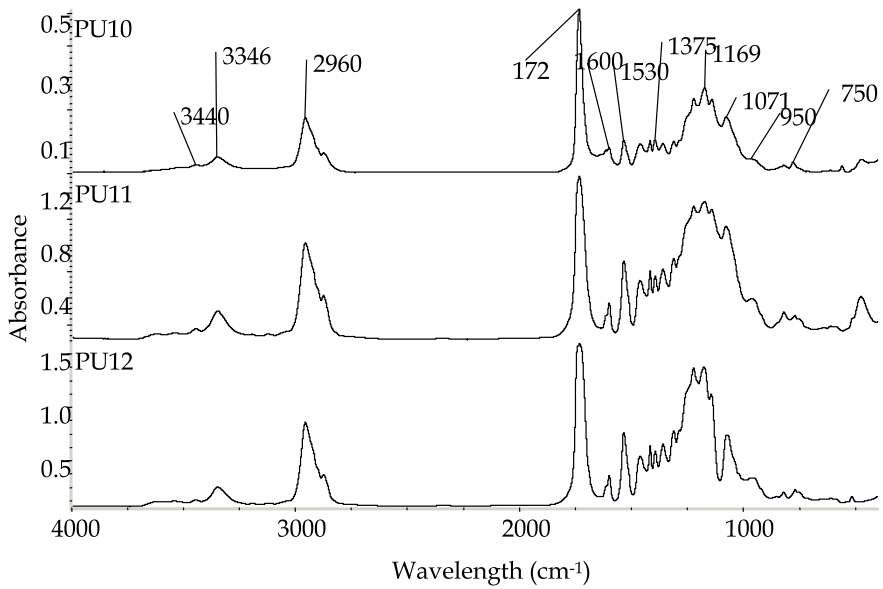


Fig. 1. FTIR of synthesized thermoplastic polyurethanes (TPU) with different NCO/OH.

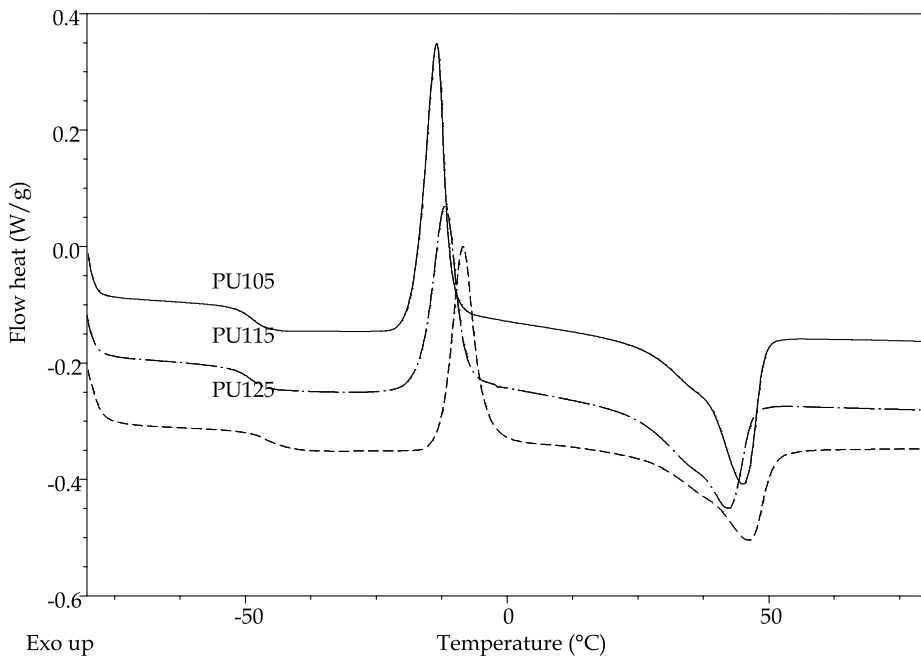


Fig. 2. DSC thermograms of synthesized thermoplastic polyurethanes (TPU) with different NCO/OH

In DSC thermograms (Figure 2), first glass transition temperature (T_{g1}) is close to $-48\text{ }^{\circ}\text{C}$ and is associated with soft segments of TPU. From -8 to $-13\text{ }^{\circ}\text{C}$ is showed the crystallization of soft segments, with an enthalpy of crystallization located between -20 and -26 J/g . Also, close to $46\text{ }^{\circ}\text{C}$, it shows the melting temperature of soft segments, with a melting enthalpy of approximately 26 J/g . Finally, a second DSC thermogram carried out up to $300\text{ }^{\circ}\text{C}$ shows a second glass transition temperature (T_{g2}) close to $250\text{ }^{\circ}\text{C}$, which corresponds to the hard segments. Figure 3 shows parallel plate rheology - storage modulus (G') and loss (G'') as a function of temperature - of sample PU105.

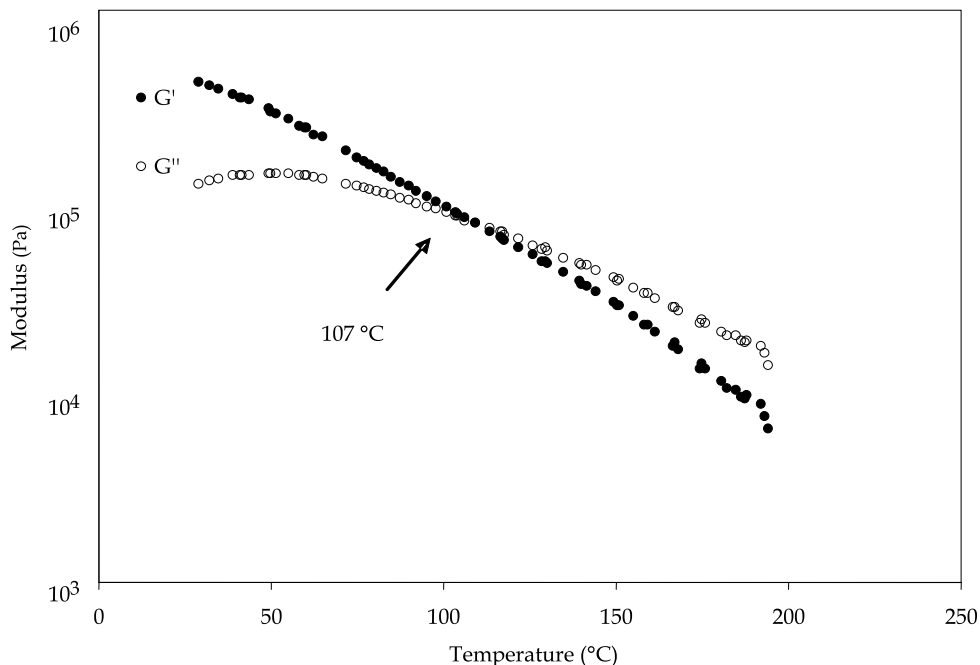


Fig. 3. Storage modulus (G') and loss (G'') of sample PU105.

Figure 4 shows the storage modulus G' for samples with different NCO/OH. For G' , there was an increase in the entire temperature range with increasing NCO/OH. The same situation occurs with the loss modulus throughout the temperature range, the material with an NCO/OH of 1.05 has the lowest value. It is noted that increasing this ratio increases the value of the temperature of crossover between the modules, due to higher content of hard segments in TPU. Also, the higher modulus crossover between G' and G'' is presented by the polyurethane with the NCO/OH of 1.25. The difference between the two polyurethanes in the form of crossing is not significant.

It is expected that the sample with the highest ratio NCO/OH, - which has the highest hard segment content- present the greatest values in the storage and loss modules, and an increase in temperature and modulus of softening due to mixture of phases. As determined by IR-FTIR spectroscopy (Table 1), with increasing NCO/OH increases the degree of phase

separation (DPS), is a greater mobility of the polymer chains, so it is more ordered, crystalline, and both thermal and rheological properties are improved.

NCO/OH	1,05	1,15	1,25
DPS	83,3	86,4	88,6

Table 1. Degree phase separation (DPS) for samples with different NCO/OH.

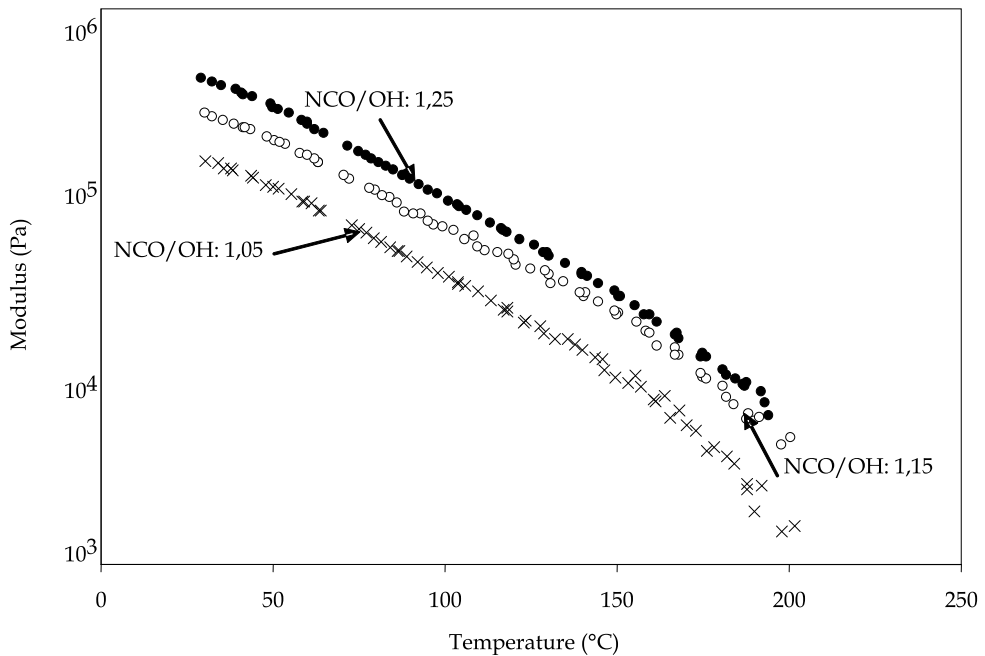
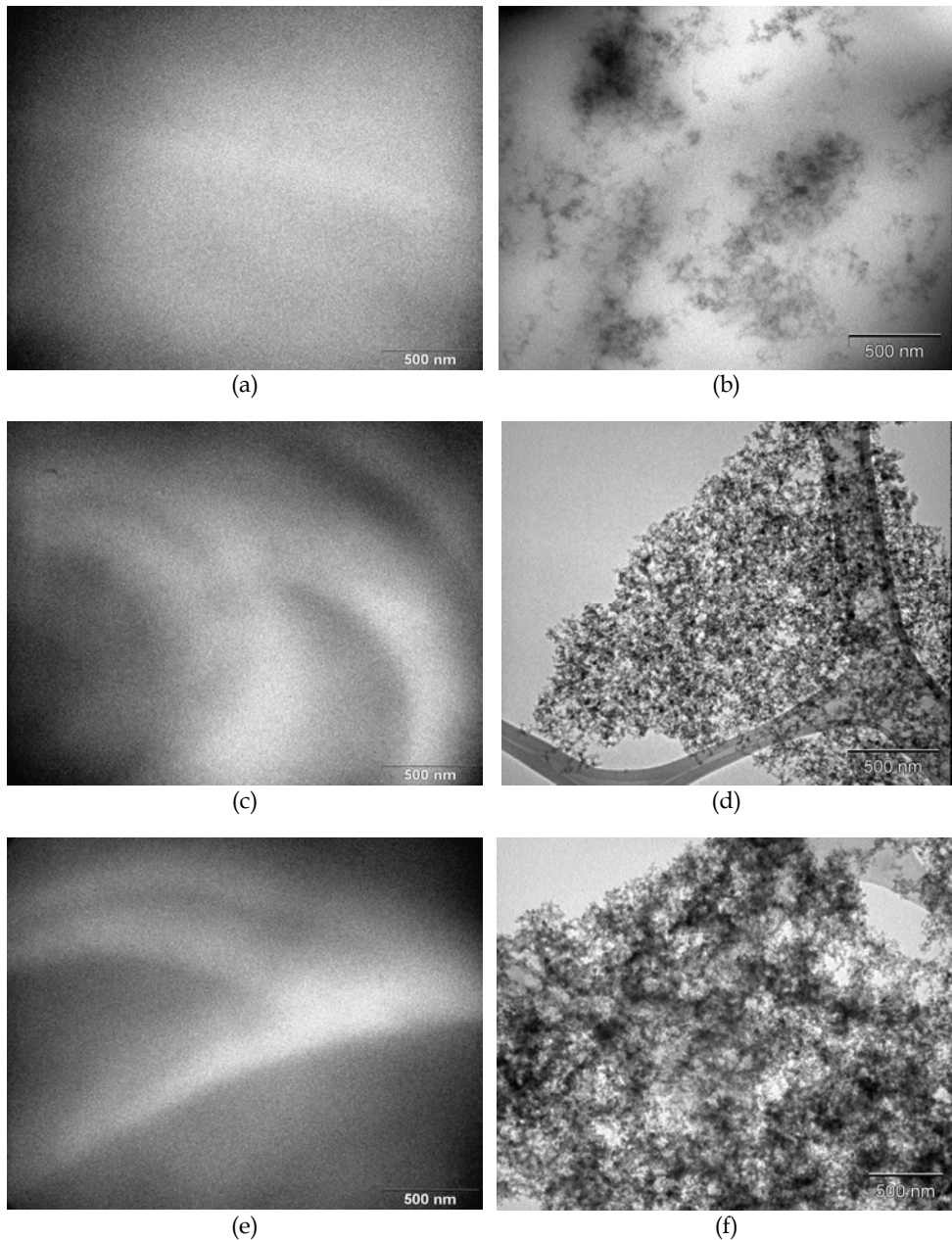


Fig. 4. Storage modulus G' for samples with different NCO/OH.

3.2 Characterization of polyurethane adhesives containing fumed silica

TPU's with different NCO/OH and containing fumed silica were analyzed by transmission electron microscopy-TEM (Figure 5). When NCO/OH is increased, DPS in TPU's is increased, too. Samples with fumed silica (PU105, PU115, and PU125) show an increase of DPS (Figure 6). This effect, as expected, is less evident in samples with lower NCO/OH, where there are light and dark areas, corresponding to the phases of hard and soft segments, respectively. That is, the material is less affected by the presence of fumed silica, and has the lowest phase segregation. Moreover, the degree of aggregation of silica increases with increasing the NCO/OH in the TPU's.



(a) TPU with NCO/OH of 1,05 without silica, (b) PU105, (c) TPU with NCO/OH of 1,15 without silica, (d) PU115, (e) TPU with NCO/OH of 1,25 without silica, (f) PU125

Fig. 5. TEM of TPU with different NCO/OH.

To quantify the effect of phase segregation, we used the IR-FTIR spectroscopy. We calculated the degree of phase segregation (DPS) and the degree of phase mixing (DPM) (Torró-Palau et al., 2001, Péres-Limaña et al., 2001). The addition of fumed silica does not alter the chemical structure of TPU.

TPU's without silica, with increasing of NCO/OH, DPS is increased, although it increases the content of hard segments of polyurethane. With the addition of silica to polyurethane, the DPS is favored in all samples. Silanol groups increases the possibility to produce hydrogen bonds in polymer, so the links inter-urethane, more favored energetically, interact to a greater extent and promotes greater interaction between the polyurethane soft segments, resulting in increased segregation phase between hard and soft segments of TPU.

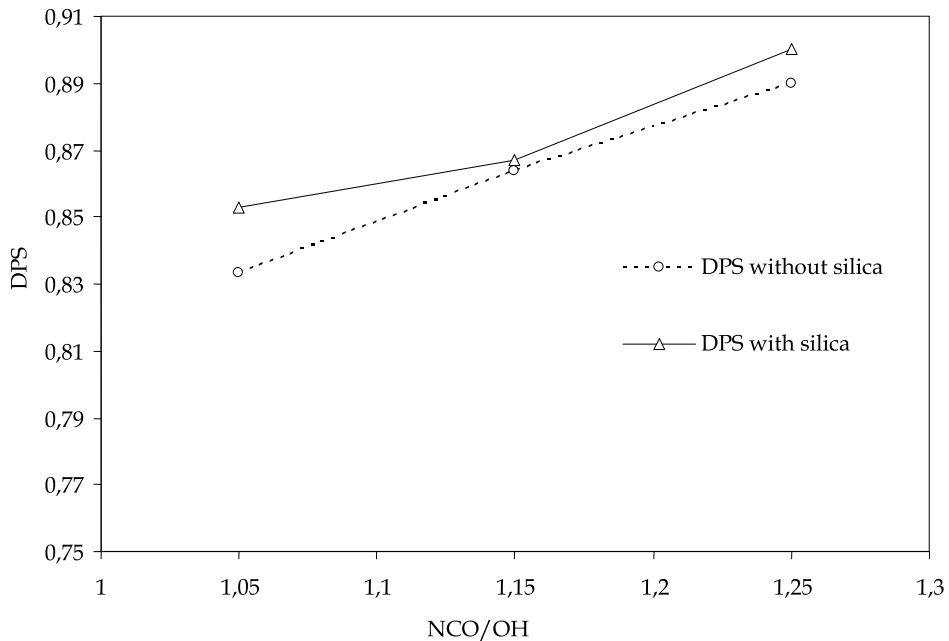


Fig. 6. Samples with and without silica with different NCO/OH

To study the interaction between TPU with different NCO/OH and silica, thermal properties and crystallinity were studied. Differential scanning calorimetry (DSC) and the X-ray diffraction were used (Figures 7 to 12).

As mentioned, the first glass transition is associated with soft segments of polyurethane. For the TPU synthesis, we used a polyol whose chains are less polar. It is expected that as the NCO/OH, increase the repulsion between hard and soft segments, and increase DPS. TPU's will present a greater order and therefore will be more crystalline. TPU's without silica, show an increase of T_{g1} as a response of increased in DPS (Figure 8). By incorporating fumed silica, the values of the glass transition temperature decrease over the polyurethanes do not contain silica.

In TPU's with silica, the association-dissociation equilibrium of the hydrogen bond is favored toward the formation of more hydrogen bonds, specifically towards the formation of more interactions between the hard segments at the expense of the rupture of interactions between hard and soft segments. These interactions are stronger than interactions between soft segments themselves and silanol groups, so that TPU, despite the establishment of interactions between soft segments, they are less energetic than those between hard and soft segments, so that the polymer need less energy to reach the glass transition, crystallization or melting, these phenomena occur at lower temperatures.

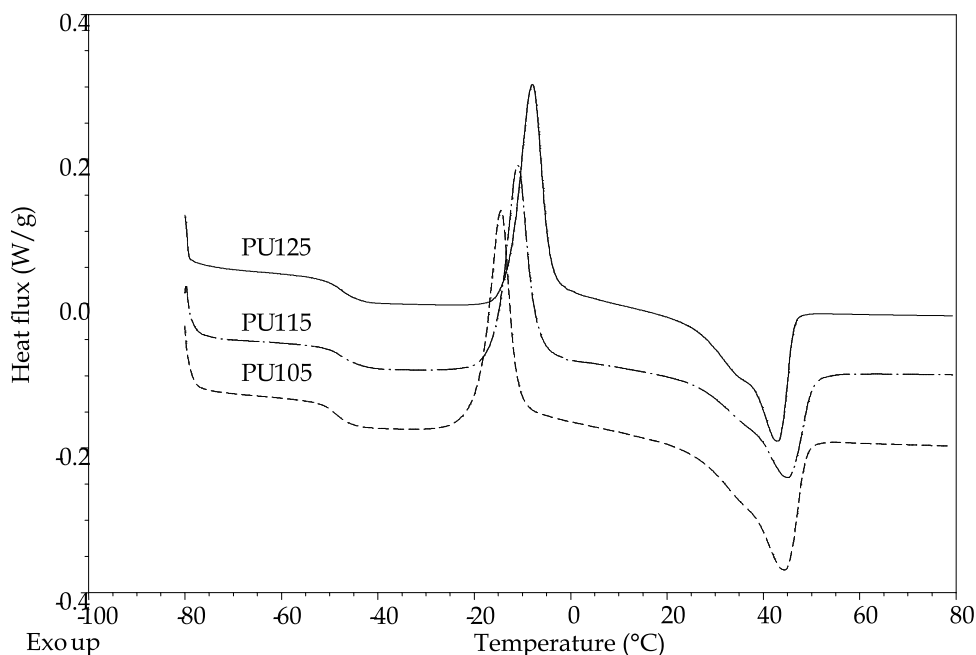


Fig. 7. DSC thermograms of synthesized thermoplastic polyurethanes (TPU) with different NCO/OH and silica.

Other properties affected by the presence of fumed silica are the enthalpy and crystallization temperature (Figures 9 and 10). During the first scan of DSC, the material is softened to 80 °C and is then rapidly cooled to -80 °C to fix the polymer chains, so that during the second sweep of temperature changes can be observed related energy with the crystal structure of the material.

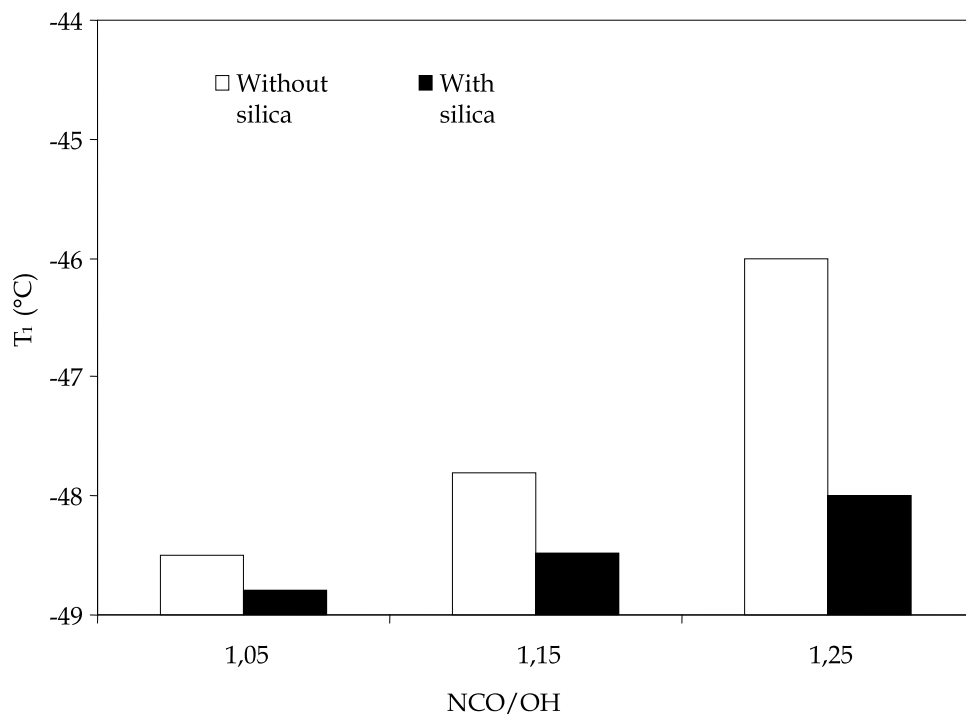


Fig. 8. Tg values of samples with different NCO/OH and with –without silica.

To compare TPU's without silica, when NCO/OH is increased, crystallization enthalpy decreases. Also, cold crystallization process occurs at higher temperatures. PU105 without silica has highest enthalpy of crystallization, -the crystallization process is more exothermic and it occurs at a lower temperature-. In TPU, to have a lower DPS, are favored interactions between hard and soft segments, which are energetically more favorable than those observed between the soft segments themselves. By increasing the NCO/OH in TPU's without silica, the DPS increase and establish more interactions between soft segments, which have less power than earlier, and the crystallization enthalpy decreases relative to that of PU105 without silica, and the process crystallization is observed at higher temperatures. PU125 sample without silica has therefore lower enthalpy of crystallization and the crystallization process is observed at higher temperatures.

Also, samples containing fumed silica, with increasing NCO/OH increase the enthalpy of crystallization and cold crystallization process is observed at lower temperatures. This is because the main interactions that are established in polyurethanes with silica correspond to soft segment-soft segment due to increased phase segregation with respect to TPU's without silica, which affects the association-dissociation equilibrium of hydrogen bonding. So polyurethane sample with higher DPS is more affected by the presence of silica (PU125) and has the highest enthalpy of crystallization temperature and crystallization occurs at lower values for PU115 and PU105. Finally, we observe that TPU's without silica, release more energy during heating process comparing with samples with silica. Also, the cold

crystallization process of polyurethane is observed at a lower temperature. This is because the samples without silica have a lower DPS.

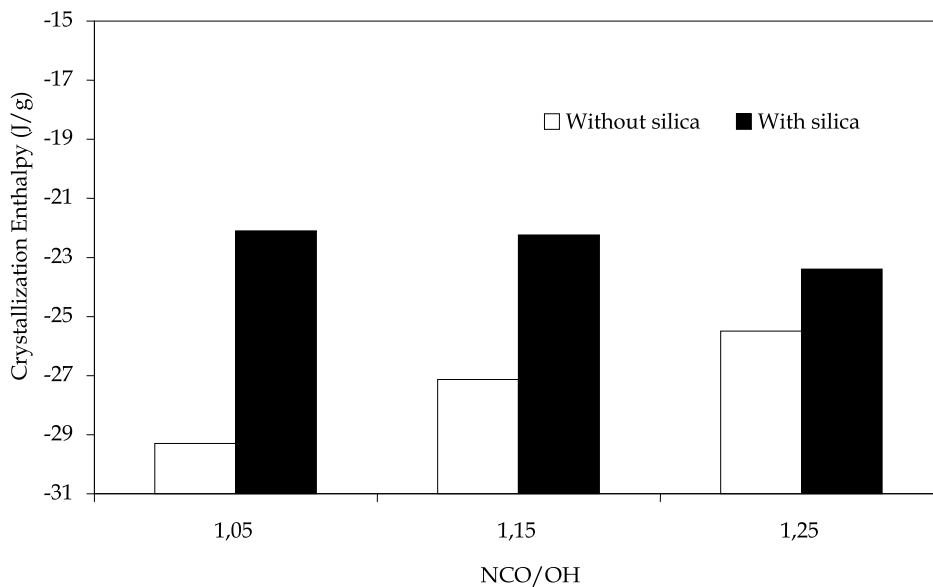


Fig. 9. Enthalpy of crystallization and cold crystallization of samples with different NCO/OH and with -without silica.

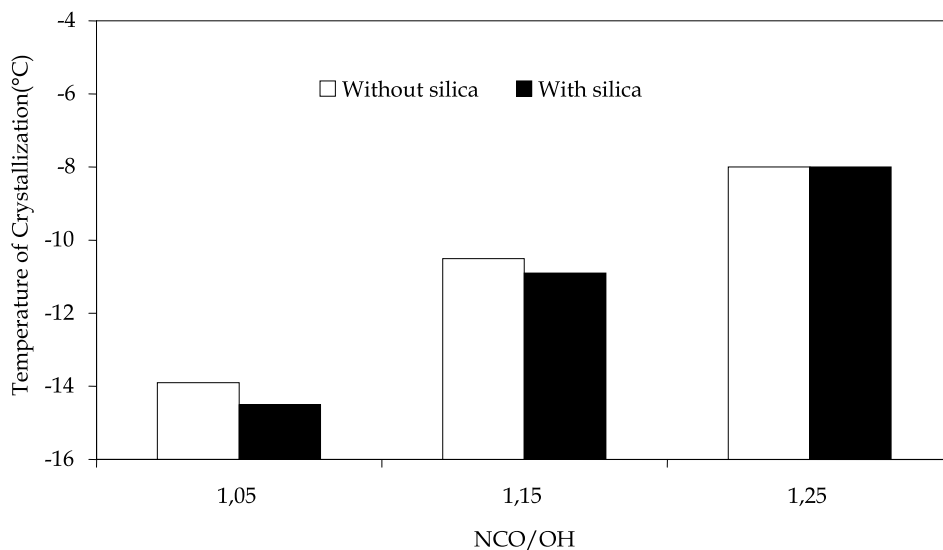


Fig. 10. Temperature of crystallization of samples with different NCO/OH and with -without silica.

During fusion enthalpy (softening) in TPU's without silica, the melting enthalpy decreases with increasing NCO/OH, as a result of increased phase segregation of polyurethane, and it is necessary to apply a lower energy content to achieve softening of the polyurethane. PU105 without silica has the highest melting enthalpy, - process that needs more energy to soften the polymer - and as expected, there is a greater melting temperature. In TPU's with lower DPS, are favored interactions between hard and soft segments, which are energetically more favorable than those, observed between the soft segments themselves. By increasing the NCO/OH in TPU's without silica, DPS increase and establish more interactions between soft segments, which have less energy than before, and so the melting enthalpy decreases and the melting process occurs at lower temperatures. PU125 sample without silica has therefore lower enthalpy of fusion. In this case, the difference between the melting temperatures in TPU's without silica with different NCO/OH is not significant.

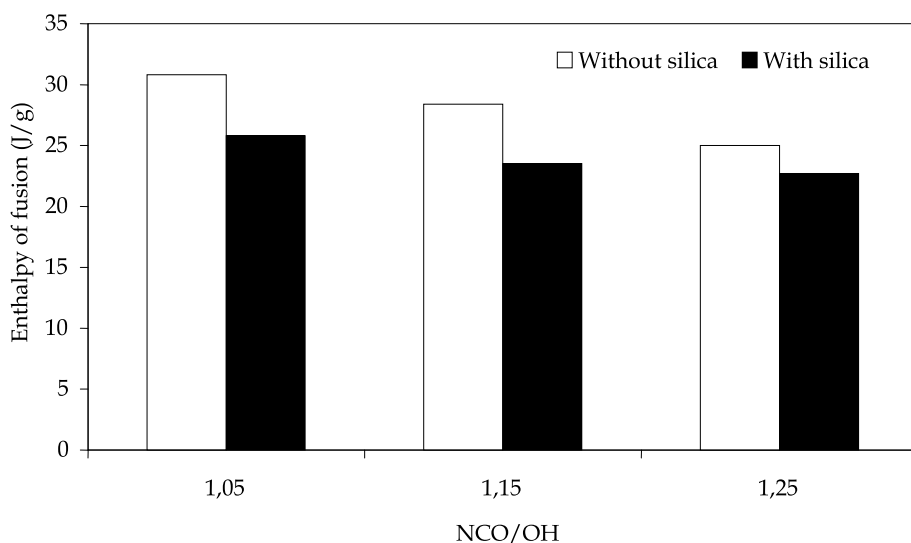


Fig. 11. Enthalpy of fusion of samples with different NCO/OH and with –without silica.

In polyurethanes containing fumed silica, with increasing NCO/OH, the melting enthalpy decreases and the softening process occurs at lower temperatures. This is because the main interactions that are established in TPU with silica correspond to the soft segments themselves, due to increased phase segregation due to the effect of the presence of silica on the association-dissociation equilibrium hydrogen bond. So, TPU with higher DPS, is more affected by the presence of silica (PU125) and has the lowest melting enthalpy and melting temperature is observed at lower values for other TPU's with silica.

Finally, polyurethanes do not contain silica; require more energy during the heating process to melt for TPU's with silica. Also, the merger of polyurethane without silicon is observed at a higher temperature than the samples containing hydrophilic silica. This is because the samples without silica have a lower DPS, thus favoring interactions between hard and soft segments, which are energetically stronger than those, observed between the soft segments in TPU's themselves with silica, as required more energy for melting.

Also, It was used X-ray diffraction (XRD). Results show -as in previous studies-, significant diffraction peaks at $2\theta = 20^\circ$ and $2\theta = 25^\circ$ (without silica). TPU's with silica present three main reflections at 2θ : ($21.2^\circ - 21.7^\circ$), 2θ : ($22.2^\circ - 22.4^\circ$) and 2θ (24.1° to 24.6°). Some reflections of (101) are insignificant, so it was not possible to quantify.

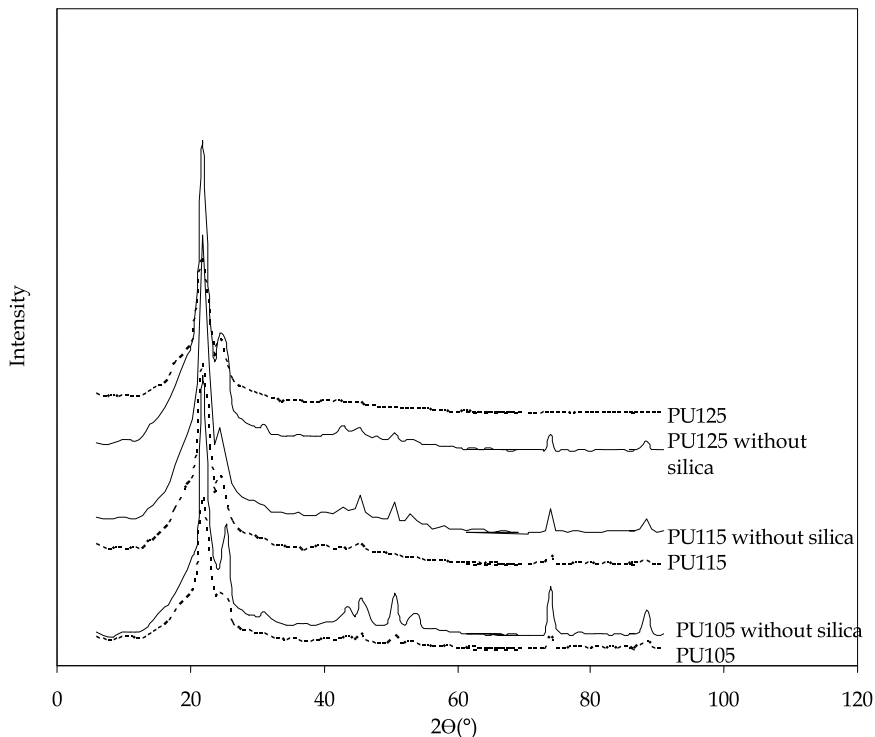


Fig. 12. X-ray diffraction (XRD) of samples with different NCO/OH and with -without silica.

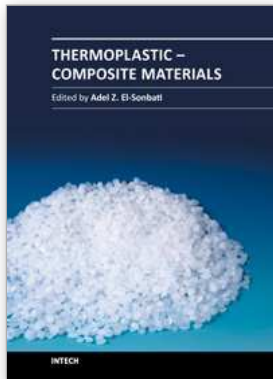
4. Conclusions

The morphological study of polyurethanes without silica indicates that the increase of NCO / OH increases the degree of phase segregation (DPS), due to the effect of repulsion that exists between the polar hard segments of polyurethane and non-polar chains polyol. With the addition of hydrophilic silica to polyurethane, the degree of phase separation is favored in all polyurethanes, indicating a possible interaction of silica silanol groups by hydrogen bonds with the polymer.

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Composite materials often demand a unique combination of properties, including high thermal and oxidative stability, toughness, solvent resistance and low dielectric constant. This book, "Thermoplastic - Composite Materials", is comprised of seven excellent chapters, written for all specialized scientists and engineers dealing with characterization, thermal, mechanical and technical properties, rheological, morphological and microstructure properties and processing design of composite materials.

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