Effect of silica nanoparticles on polyurethane foaming process and foam properties

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Abstract. Flexible polyurethane foams (FPUF) are commonly used as cushioning material in upholstered products made on several industrial sectors: furniture, automotive seating, bedding, etc. Polyurethane is a high molecular weight polymer based on the reaction between a hydroxyl group (polyol) and isocyanate. The density, flowability, compressive, tensile or shearing strength, the thermal and dimensional stability, combustibility, and other properties can be adjusted by the addition of several additives. Nanomaterials offer a wide range of possibilities to obtain nanocomposites with specific properties. The combination of FPUF with silica nanoparticles could develop nanocomposite materials with unique properties: improved mechanical and thermal properties, gas permeability, and fire retardancy. However, as silica particles are at least partially surface-terminated with Si-OH groups, it was suspected that the silica could interfere in the reaction of polyurethane formation. The objective of this study was to investigate the enhancement of thermal and mechanical properties of FPUF by the incorporation of different types of silica and determining the influence thereof during the foaming process. Flexible polyurethane foams with different loading mass fraction of silica nanoparticles (0-1% wt) and different types of silica (non treated and modified silica) were synthesized. PU/SiO₂ nanocomposites were characterized by FTIR spectroscopy, TGA, and measurements of apparent density, resilience and determination of compression set. Addition of silica nanoparticles influences negatively in the density and compression set of the foams. However, resilience and thermal stability of the foams are improved. Silica nanoparticles do not affect to the chemical structure of the foams although they interfere in the blowing reaction.

1. Introduction
Polyurethanes are polymeric materials that have a wide range of applications in industry and households because of their numerous valuable properties and the ability to control many of their parameters during preparation. Flexible polyurethane foams (FPUF) are widely used in many industries, including the furniture, construction and automotive fields. These materials are also commonly used in mattresses and upholstery foams. FPUF have many advantages, such as a wide range of flexibility and hardness, good cushioning, high durability during use, low price and low density [1-4].

The main reaction in polyurethane foaming process is the polycondensation of poly-hydroxy compounds (polyols) with disocyanates. Foaming phenomenon occurs when a small amount of blowing agent (water) is added during polymerization process. Water reacts with isocyanate groups giving carbamic acid, which spontaneously lose CO₂, generating the foam bubbles [1].
FPUF are formed as a result of the chemical reactions between components. The urethane linkage is formed as a result of the exothermic reaction between the isocyanate groups with the hydroxyl groups from polyol [3].

The reaction between water and the isocyanate leads to the production of carbon dioxide, which causes foaming of the mixture. The scheme of the foaming reaction is as follows:

![Reaction scheme]

When the isocyanate component is mixed with the polyol component the chemical reaction starts. The reaction is exothermic meaning it produces heat. As the chemical reaction progresses the viscosity of the mixture will also increase. This increase continues during the foaming process until the reacting liquid turns into the polyurethane solid at the end of the reaction.

This foaming process was controlled by measuring different times, usually measured in seconds, with the time beginning as soon as the isocyanate and polyol components are first mixed together. Concepts such as cream time, gel time, rise time and tack-free time were taken into account.

- **Cream time** - this is the first event measured, and is the time interval between the mixing of all the foam ingredients and the time at which the clear mixture turns creamy and starts to expand.
- **Rise time** - this is when the reacted foam has reached its largest volume, or maximum height. It is the time between the start of the finale mixing and the time of complete expansion of the foaming mass.

In recent years, polymer nanocomposites have attracted much attention because of their high potential to achieve great improvement in properties including dimensional stability, gas permeability, flame retardancy, and mechanical and physical properties by adding a small amount of nanoparticles in the polymer matrices [1,5-6]. Furthermore, it has been shown that incorporation of nanoparticles with their large surface area and fine dimensions as well as very close contact between particles and the polymer matrix could alter foam morphology and properties.

## 2. Experimental

### 2.1. Materials

FPUF were prepared by the one-step method. The polyol used to produce the FPUF was Alcupol F-4811 from Repsol. Toluene diisocyanate (TDI T80) from Perstorp was used as an isocyanate. Water was used as a blowing agent. Four types of FPUF were tested in this study. The first foam was pure flexible polyurethane foam (FPUF), and the others were made with the addition of silica nanoparticles and modified silica nanoparticles as fillers. Silica nanoparticles of 12 nm size were obtained from Sigma Aldrich, whereas modified silica nanoparticles were obtained from Wacker Silicones (HDK H2000).

### 2.2. Foam preparation

Polyurethane foam were prepared by one-step and free-rising method. The experiments were as following: weight the polyol, catalysts, surfactant and blowing agent and mix them with a mechanical
stirrer at 2200 rpm for 60 seconds. Then, rapidly add TDI into the mixture and continue to stirring for another 7-10 seconds at the same speed. Pour the mixture into a mold and allow the foam to rise and set at room temperature for 24 hours. Sonication and mechanical stirring were used to aid SiO$_2$ nanoparticles thoroughly mixed with the polyol before adding the other chemicals.

2.3. Formulation of foams

For this work, varying concentration of silica and modified silica nanoparticles ranging from 0 to 1 wt% respect polyol weight were introduced into the formulation as shown in Table 1:

| Samples | SiO$_2$ nanoparticles dispersed in polyol (%wt) | SiO$_2$ nanoparticles dispersed in isocyanate (%wt) | Treated SiO$_2$ nanoparticles dispersed in polyol (%wt) |
|---------|-----------------------------------------------|-----------------------------------------------|---------------------------------------------------|
| 0       | 0                                             | 0                                             | 0                                                 |
| 0.1S    | 0.1                                           | 0                                             | 0                                                 |
| 0.5S    | 0.5                                           | 0                                             | 0                                                 |
| 1S      | 1                                             | 0                                             | 0                                                 |
| 0.1Si   | 0                                             | 0.1                                           | 0                                                 |
| 0.5Si   | 0                                             | 0.5                                           | 0                                                 |
| 1Si     | 0                                             | 1                                             | 0                                                 |
| 0.1SH   | 0                                             | 0                                             | 0.1                                               |
| 0.5SH   | 0                                             | 0                                             | 0.5                                               |
| 1SH     | 0                                             | 0                                             | 1                                                 |

2.4. Characterization

2.4.1. Physical and mechanical properties measurements. The apparent density tests were carried out according to ISO 845:2010. The samples were measured and weighted. The value of the apparent density was calculated as a mass/volume ratio. Set compression tests were conducted according to ISO 1856:2001. Three samples of 100x100x50 mm of each foam were compressed to 75% of its original height for 22 hours at 70ºC, and the compression set is the permanent deformation remaining when the force is removed. Resiliencie was determined according to ISO 8307:2008 by ball rebound test.

2.4.2. Thermogravimetric analysis (TGA). TGA was used to analyse the thermal stability of the prepared foams. The TGA were performed using a TA Instruments Q500. Samples of ~5 mg were heated to 800 ºC at a heating rate of 20 ºC/min in a nitrogen atmosphere.

2.4.3. Fourier transform infrared spectroscopy (FT-IR). FT-IR was performed using a Bruker Tensor 27 equipped with an ATR accessory with diamond crystal. The samples were scanned 100 times with a resolution of 4 cm$^{-1}$ over the wavenumbers range from 4000-400 cm$^{-1}$.

3. Results and discussion

3.1. Reaction times

Figure 1 illustrates the cream time and the rise time variation for the flexible polyurethane foam containing silica nanoparticles obtained.
Variation of cream and rise time shows a uniform increment in rise time while silica nanoparticles concentration increases until 0.5% wt. This implies that the foam rises slower when the filler composition increases indicating that the blowing reaction between TDI and water occurs slower. It could therefore be due to the reaction between silanol groups from the silica nanoparticles and the NCO groups from the isocyanate. This effect is less pronounced in the case of the addition of modified silica nanoparticles in which silanol groups have been eliminated. When the concentration of silica nanoparticles added is over 0.5% wt, agglomerates are formed so they no react with the NCO groups.

3.2. Physical and mechanical properties

Samples from foam produced were cut into various sizes suitable for their respective tests. Figure 2 presents the physical and mechanical properties of the studied foams. In general, the addition of fillers into a flexible polyurethane foam caused an increase in its apparent density. The resilience increased in all foams containing non treated silica nanoparticles. However, the addition of modified silica nanoparticles did not present any effect in the resilience of the foams. The addition of only 0.1% wt silica and modified silica nanoparticles to the flexible polyurethane foam raised the compression set value higher than that of foam without any filler.
Summarizing, addition of fillers to the flexible polyurethane foam, led to deterioration in the physical and mechanical properties. It indicates that the presence of fillers in foams causes some inappropriate changes in the structure of flexible polyurethane foam. This may be related to the changes in foaming process, occurring as a result of the presence of fillers.

3.3. Thermogravimetry

TGA was performed to assess the effect of the addition of silica nanoparticles and hydrophobic silica nanoparticles on the thermal stability of the flexible polyurethane foams.

The decomposition of polyurethanes occurs in two well-defined stages. The temperature corresponding to 5% mass loss is considered to be the initial temperature of the sample’s decomposition process. The temperature of 50 % mass loss corresponds to the temperature range of the decomposition of soft segments. $T_{\text{max} 1}$ is defined as the temperature of the maximum rate of decomposition of rigid segments in polyurethane. $T_{\text{max} 2}$ corresponds to the temperature of the maximum rate of decomposition of soft segments of the polyurethane [3]. Table 2 summarizes the results of the selected parameters obtained from the TGA thermograms.

| Sample | 5% mass loss (ºC) | 50% mass loss (ºC) | $T_{\text{max} 1}$ (ºC) | $T_{\text{max} 2}$ (ºC) |
|--------|--------------------|--------------------|----------------------|----------------------|
| Ref    | 241.9              | 351.8              | 286.8                | 370.3                |
| 0.1S   | 244.6              | 356.4              | 287.1                | 374.5                |
| 0.5S   | 246.3              | 360.3              | 288.1                | 375.4                |
| 1S     | 247.1              | 364.4              | 289.0                | 380.4                |
| 0.1Si  | 242.9              | 351.9              | 286.4                | 371.1                |
| 0.5Si  | 246.0              | 359.1              | 288.2                | 374.5                |
| 1Si    | 249.0              | 360.6              | 289.4                | 379.0                |
| 0.1SH  | 235.3              | 351.0              | 283.1                | 373.6                |
| 0.5SH  | 238.8              | 359.4              | 283.5                | 375.1                |
| 1SH    | 237.0              | 356.5              | 283.8                | 371.5                |

Temperature at which a 5% wt mass loss is produced increased in the foams with the addition of silica nanoparticles in comparison to the value for FPUF without fillers when they are dispersed both in polyol and isocyanate. Higher values of this temperature were observed in foams with the addition of silica nanoparticles. However, this value decreased with the addition of modified silica nanoparticles.

The temperature of 50% mass loss increased with the presence of each investigated nanoparticle. The largest increase was observed in the foam with silica dispersed in polyol in concentration of 1%.

The addition of polyol and isocyanate dispersed silica nanoparticles increased the value of $T_{\text{max} 1}$, but the addition of hydrophobic silica caused this value to reduce lower than the value of FPUF without fillers.

The addition of any filler led to an increase in the value of $T_{\text{max} 2}$.

The results obtained from TGA indicate that the thermal stability of the foams modified with the addition of researched fillers is higher than that of foams without modification. The addition of silica nanoparticles dispersed into polyol produced the best results for the thermal stability. This result indicates that this type of modification could be an effective way to improve the thermal stability of FPUF. Furthermore, it should be noted that these changes are not large, and it is possible that higher contents of fillers should be examined to assess the influence of filler content on the properties of FPUF, and, if it is necessary, adjust the formulation of the foam to improve its physical and mechanical properties.
3.4. ATR-FTIR spectroscopy

FT-IR is a research technique that allows the chemical structure of a tested material to be analysed. In this study, the influence of the added fillers on the chemical structure of the tested foams was investigated. Typical peaks observed in polyurethanes are discussed below. The peak at 3294 cm\(^{-1}\) is assigned to the N-H stretching vibrations. The peaks at 2973 and 2869 cm\(^{-1}\) are from the asymmetric and symmetric stretching vibrations of CH\(_2\) respectively. The peak at 2276 cm\(^{-1}\) is assigned to the N=\(\equiv\)C=O group. The peak at 1717 cm\(^{-1}\) is assigned to the stretching vibrations of hydrogen-bonded C=O groups. The peak at ~1530 cm\(^{-1}\) is from amide II (urethane N-H bending + C-N stretching). The peak at 1080 cm\(^{-1}\) is assigned to the C-O-C stretching vibrations. Figure 3 presents the FT-IR spectra of the foams containing silica nanoparticles dispersed in the polyol studied. The addition of this type of nanomaterials to FPUF does not cause changes in their chemical structure.

![FT-IR spectra of the foams containing silica nanoparticles](image)

Figure 3. FT-IR spectra of the foams containing silica nanoparticles

4. Conclusions

This study has shown that silica nanoparticles addition in foam formulation decrease the rate of the blowing reaction between TDI and water with increase rise time. However the density and set compression properties of foam are worsened. On the contrary, resilience of foam which contain silica nanoparticles is improved. Moreover, silica do not affect to the chemical structure of the foams.

Silica nanoparticles dispersed in polyol caused the best improvement in the thermal stability of the foams. Improvement in the thermal properties is sometimes associated with a better fire behaviour and perhaps the silica could act as a good flame retardant in flexible polyurethane foam formulations.

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