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Application of SiO_2 Nanoparticles for Thermophysical Improvement of Integral Skin Polyurethane Elastomers

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Abstract
A dramatic improvement has been achieved by reinforcement of integral skin polyurethane elastomers, using SiO_2 nanoparticles. Ultrasonification and high rate mechanical stirring were utilized to disperse the nano filler in polyether polyol matrix. A silane-based coupling agent was also used to ensure the interaction of nanoparticles with polymer, improving the homogeneity. This was monitored by scanning electron microscope. Physical properties of the prepared elastomers, e.g., tensile strength, elongation at break, elasticity modulus and abrasion resistance, were investigated. Also, thermomechanical characterization techniques, e.g., dimensional mechanical analysis, thermal mechanical analysis and thermal gravimetric analysis, were applied for evaluation of nanocomposite elastomers. Effect of nano filler on polyurethane segments and probable phase separation was also studied.

Keywords
Polyurethane, integral skin elastomer, nano SiO_2, thermomechnical, phase separation

1. Introduction

Polyurethane (PU) is globally consumed on a huge scale as sealant, foam, adhesive, coating, casting elastomer, molded product, etc., due to its excellent properties for such applications and wide range of structures. There are several industries that use PU-based products that contain inorganic fillers. The phase separation between inorganic and organic components may take place and will deteriorate the properties of the materials [1, 2]. High-performance polyurethane nanocomposites are emerging as a new class of materials for their demanding applications in many industries. During the few past years, material research specialists have shown great interest especially in the field of nano filled elastomers, since their application has dramatically improved the materials' properties [3–5]. Attractive

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improvement of these materials in different characteristics, e.g., thermal resistance and mechanical strength, is due to polymer–filler interaction. In order to achieve the expected improvement by adding nano materials to elastomers, it is important to understand how these nanoparticles influence the organic matrix. Investigating the interaction between polymer and inorganic phases, nanoparticle doped elastomers would be classified as: (a) structures involving physical interactions through van der Waals forces, hydrogen bonds and mechanical dispersion; (b) chemical interactions through covalent and ionic–covalent bonding. In order to provide the chemical interaction conditions, most of researches have focused on the sol–gel technique. This would produce high-performance composites. There are also many reports that involve the physical mixing of nano material and polyol as the synthesis route. The main problem in these kinds of prepared nanocomposites is the heterogeneous dispersion of the nanoparticles [6–10].

While it can be expected that nano SiO_2, with extremely large surface area, would affect the PU properties much more than regular fillers, it is noticeable that the dispersion of nano filler in polyol matrix is quite effective. The main objective of this research was to investigate the effect of nano SiO_2 on thermal and physical properties of integral skin PU elastomers. A coupling agent was also added to the elastomer formulation in order to provide the compatibility between nano SiO_2 and polyol. The effect of well dispersed nano filler on thermal and physical properties of PU was monitored.

2. Experimental

2.1. Materials

Daltorim® EK 20350 polyether polyol from Huntsman (appearance: white viscous liquid; viscosity at 25°C: 1740 mPa s; specific gravity at 25°C: 1.025 g/cm^3; flash point: 265°C; fire point: 290°C) containing surfactants, catalysts and other additives was dried and degassed under vacuum at 40°C. Suprasec® 2082 MDI (appearance: brown liquid; viscosity at 25°C 340 mPa s; specific gravity at 25°C: 1.23 g/cm^3; burning point: 220°C) was also from Huntsman. The polyol:MDI ratio was 100:41 parts by weight (pbw) in synthesis of polyurethane elastomer samples. Nano-sized SiO_2 was Aerosil® 200 with specific surface area of 200 m^2/g and average particle size of 12 nm, from Degussa. Amino A-100 coupling agent from Silquest® Chemicals with γ-aminopropyl triethoxysilane-based structure was added 3 pbw to the polyol. Merck® water free acetone was used as dispersion media.

2.2. Synthesis of Polyurethane Nanocomposites

SiO_2 nanoparticles and γ-aminopropyl triethoxysilane were added to water-free acetone (50 ml). Mechanical mixing would provide the medium for interaction between OH functional groups of Aerosil and the amine group of the coupling agent. This would be the starting step for achieving the better dispersion of nano filler in polyol matrix. Then polyether polyol (200 g) was mixed with this suspension.

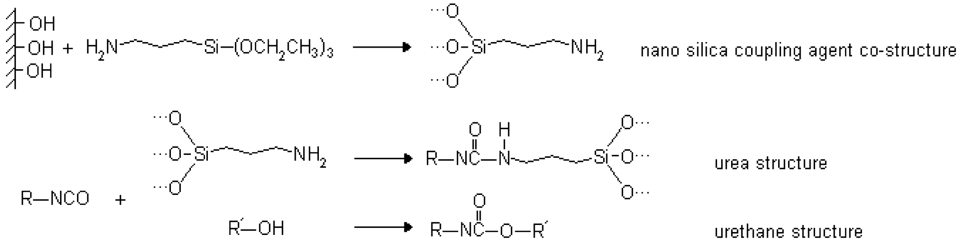

Figure 1. Mechanism of nano SiO_2 interaction in presence of silane-based coupling agent.

Table 1.
Amount of SiO_2 nanoparticles in prepared integral skin polyurethane elastomers

Sample	SiO_2 (wt%)
IS-0	0.0
IS-1	0.5
IS-2	1.0
IS-3	1.5
IS-4	2.0
IS-5	2.5
IS-6	3.0

A high shear mechanical stirrer (15 min) and ultrasonic homogenizer (20 min) were used to perform the mixing process. In the next step, acetone was removed under vacuum at 20°C. The MDI portion was then added to the mixture, being well homogenized by ultrasonification (30 min). The nanocomposite was cured as a sheet at 25°C under vacuum for 16 h the schematic mechanism of reactions and interactions are shown in Fig. 1. Table 1 shows the nano SiO_2 content of each sample. Test specimens for mechanical analysis were provided, punching the cured PU sheets by a standard dimension punching die cut system.

2.3. Investigating the Thermophysical Characteristics of Prepared Nanocomposites

The tensile properties of cured elastomers were determined according to ASTM D-412 by an Instron-1122 tensometer. The standard die's dimensions were according to type C in the D-412 test method. The cross-head speed was 50 mm/min and the test was conducted at room temperature. Five specimens of each sample were tested. Abrasion resistance of integral skin PU elastomers was determined according to DIN 53516 (applied weight: 10 N; path length: 350 mm; rate: 2 mm/s; sample diameter: 10 mm; sample thickness: 10 mm). Thermal gravimetric analysis (TGA) was performed using a DuPont instrument (heating rate: 5°C/min) using about 15 mg of each sample. Linear expansion coefficient (α) of samples was measured by a DuPont thermal mechanical analysis (TMA) apparatus (sample dimensions: 5 × 5 × 10 mm). A dynamic mechanical analyzer (DMA) was used to investigate the glass transition temperature (T_g) of nanocomposite samples (mode: three-point bending; atmosphere: N_2; temperature range: −20 to 200°C; scanning rate: 5°C/min; frequency: 10 Hz). Samples' dimensions were 2 × 10 × 50 mm. Three specimens of each prepared PU sample were tested in abrasion, TGA, TMA and DMA experiments. In order to inspect the dispersion quality in synthesized elastomers, a Cambridge (UK) scanning electron microscope, model 5360, was used. The fracture surfaces were sputter coated with gold prior to scanning. The distribution of nanoparticles in the polymer matrix was then investigated.

3. Results and Discussion

3.1. Dispersion Quality of Nano Filler in Polymer Matrix

It is of great importance to inspect the dispersion of nanoparticles in the polymer matrix, which has been reported to have a significant impact on the mechanical properties of nanocomposites [11–13]. As mentioned before, nano SiO_2 tends to be agglomerated extensively. This would greatly affect the homogeneous dispersion of the nanoparticles in the polyol, making it a difficult process. In this work, a silane-based coupling agent was added to modify the surface of the nanoparticles. As shown in Fig. 1, the presence of γ-aminopropyl triethoxysilane in the dispersion step would cause better dispersion of SiO_2 nanoparticles. As a result of the interaction between γ-aminopropyl triethoxysilane, polyol and inorganic nanoparticles, the proposed homogeneity is achieved. On the other hand, the amine functional group of the coupling agent would react with MDI, producing urea structures which are highly compatible with a urethane-based polymer network and would assist the homogenizing process. SEM images of prepared composites confirm the well dispersed situation in all samples (Fig. 2). This would be one of the most effective parameter in further improvement of integral skin PU nanocomposites. The SEM images presented in Fig. 2 are of fractured surface of each sample. It is commonly known that heterogeneous dispersion of filler in polymer matrix or any probable agglomeration would cause a non-uniformity which would act as a local stress aggregating sector, demonstrating some defective parameters, e.g., failure in physical properties prior to achieving the real load. As observed in Fig. 2 the fracture surface of prepared samples (the weakest point of samples during the physical testing) possess a good filler distribution, which may confirm the acceptable dispersion in other regions, but it is impossible to be assured of this quality all around the sample.

3.2. Physical Properties

As shown in Figs 3 and 4, the tensile strength and elongation at break of integral skin polyurethane would be improved in accordance with nano filler content. This is an evident result in polymeric systems, reinforced by nano fillers [12, 13]. SiO_2 nanoparticles inherently possess high modulus and would strengthen the PU matrix

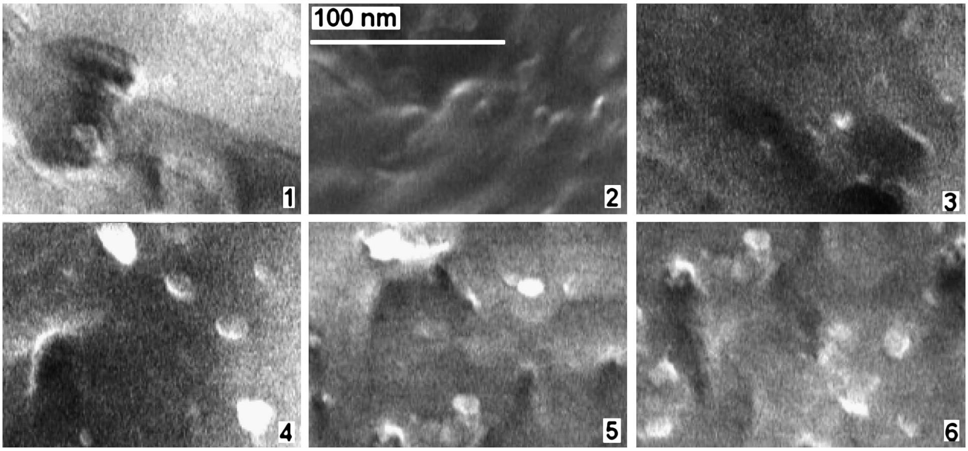

Figure 2. SEM images of prepared nanocomposites.

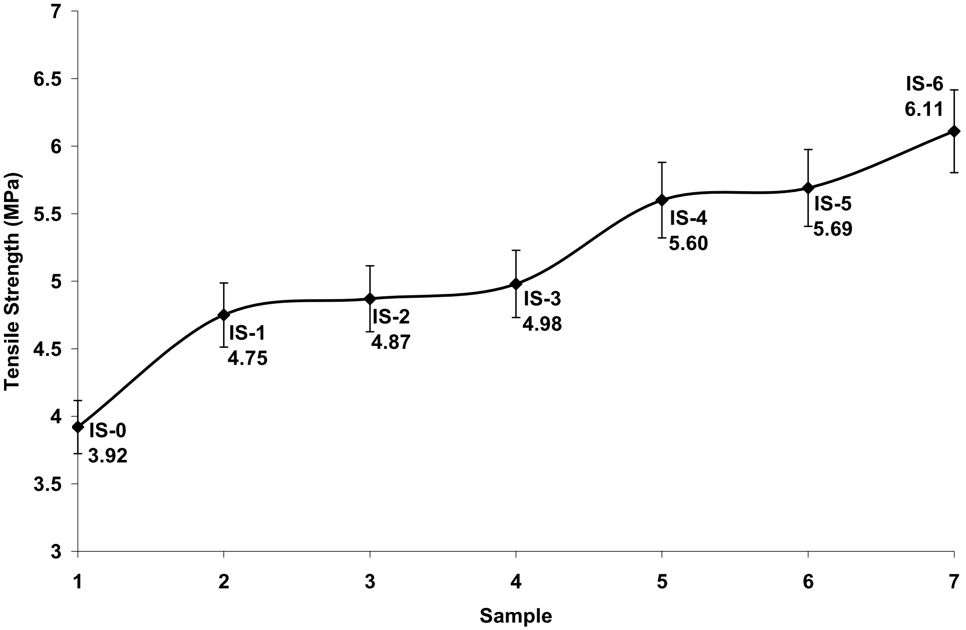

Figure 3. Effect of SiO_2 nanoparticles on tensile strength of integral skin PU elastomers.

(dispersed in nano scale). As mentioned before, the vacuum cure condition was provided for synthesis of integral skin polyurethane nanocomposites. This would prevent the bubble trap which has been reported as one of the main causes of failure in tensile properties. On the other hand, acetone assisted dispersion of nano SiO_2 and coupling agent treatment would reduce the possible heterogeneity of network which causes a negative effect [14–16]. Acetone would enable us to overcome the

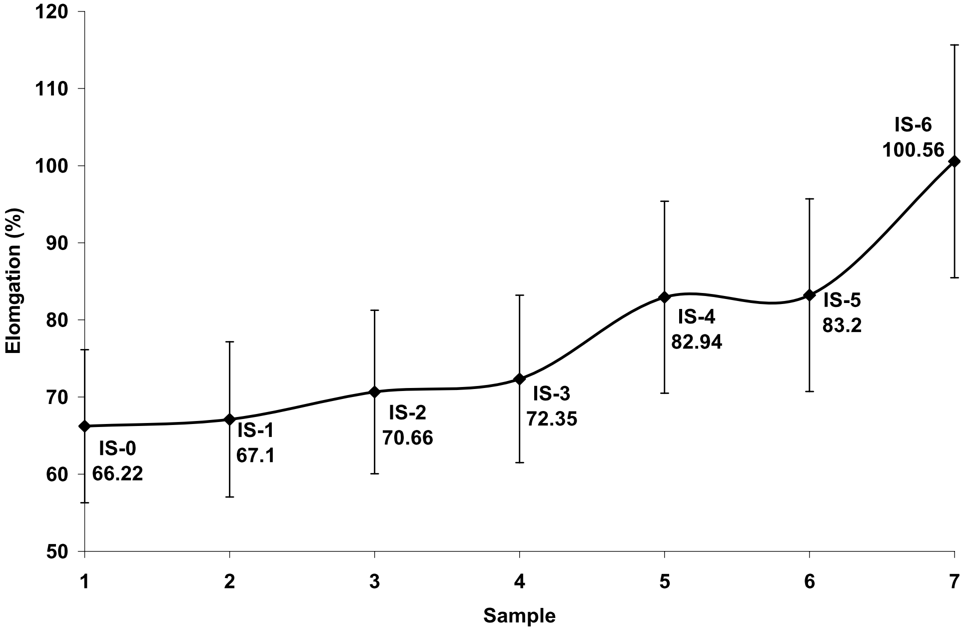

Figure 4. Increment in elongation at break of integral skin PU–SiO_2 nanocomposites.

problem of high viscosity, which would introduce high viscosity in the nano filler containing samples.

Abrasion resistance of the elastomers was defined as the mass loss during the contact friction to the grit abrasive sheet. Abrasion resistance of PU samples is also improved due to nano SiO_2 content. This is because of high stability of SiO_2 against friction forces which is dependent on surface area and would be dramatically increased in accordance with reduction in its particle size. Decrease in abrasion resistance of IS-6 may be in accordance with high amount of nano SiO_2, which would damage the cross-link density of the polymer network because of its high surface area (Fig. 5).

3.3. Thermal Properties

The thermal expansion coefficient (α) of prepared nanocomposites is increased in most of the samples according to nano SiO_2 content. It is desirable according to the presence of an inorganic phase which provides higher expansion in high temperature conditions. The thermal conduction of inorganic material would provide better distribution of thermal energy, leading to higher α. Failure in this coefficient for some of the samples would be in accordance with small size of the sample, which is somehow influencing the results (Fig. 6).

DMA results show that nano SiO_2 affects the glass transition temperature (T_g) of nanocomposites (Fig. 7). Increment in the T_g of soft segments indicates that SiO_2 nanoparticles have been in a very tight correlation with polymer network because of their high surface area. On the other hand, as shown in Fig. 1, the sur-

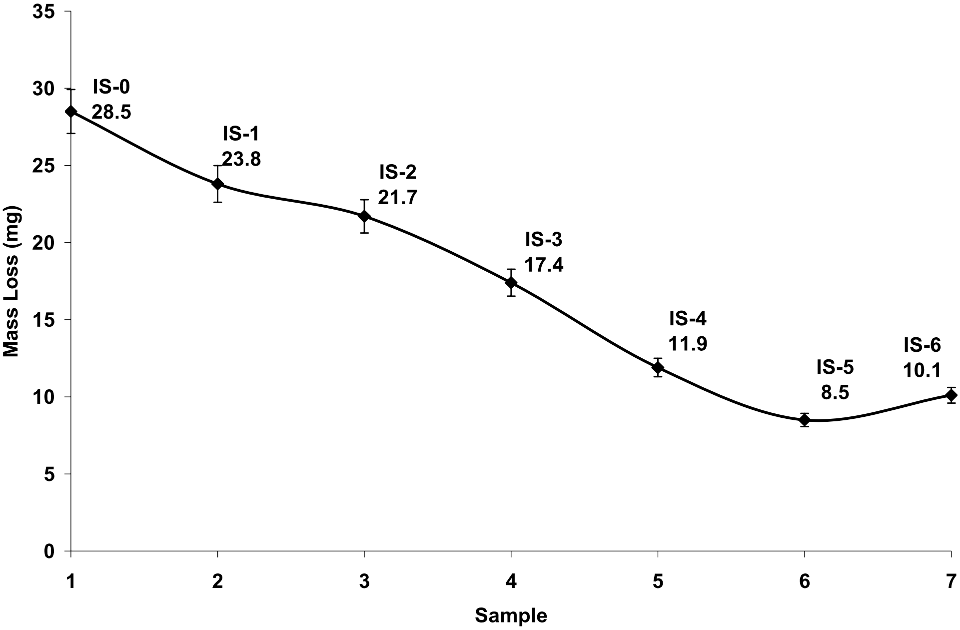

Figure 5. Mass loss of integral skin PU–SiO_2 nanocomposites in abrasion resistance test.

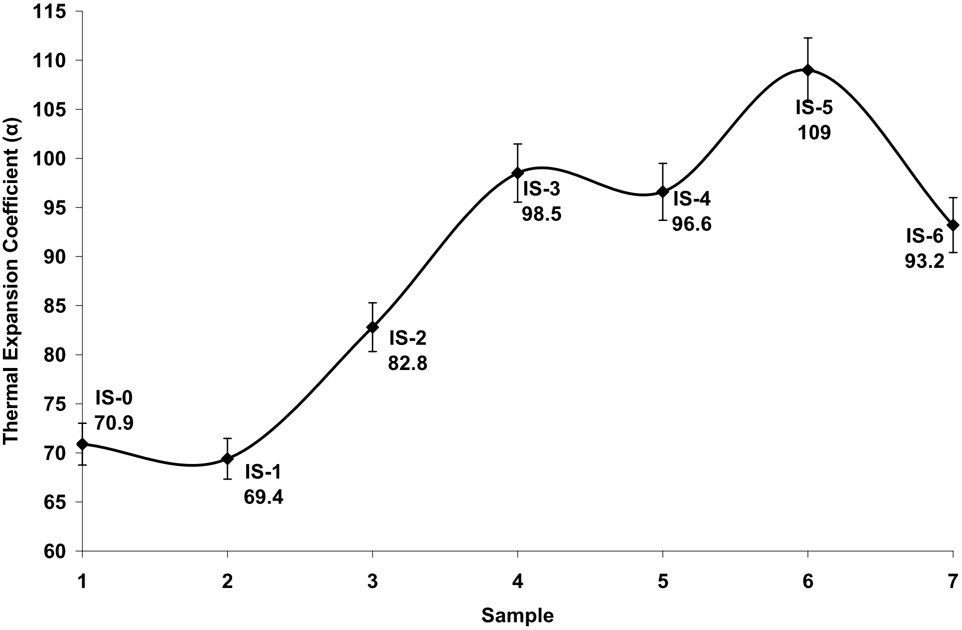

Figure 6. Thermal expansion coefficient of integral skin PU elastomers reinforced by nano SiO_2.

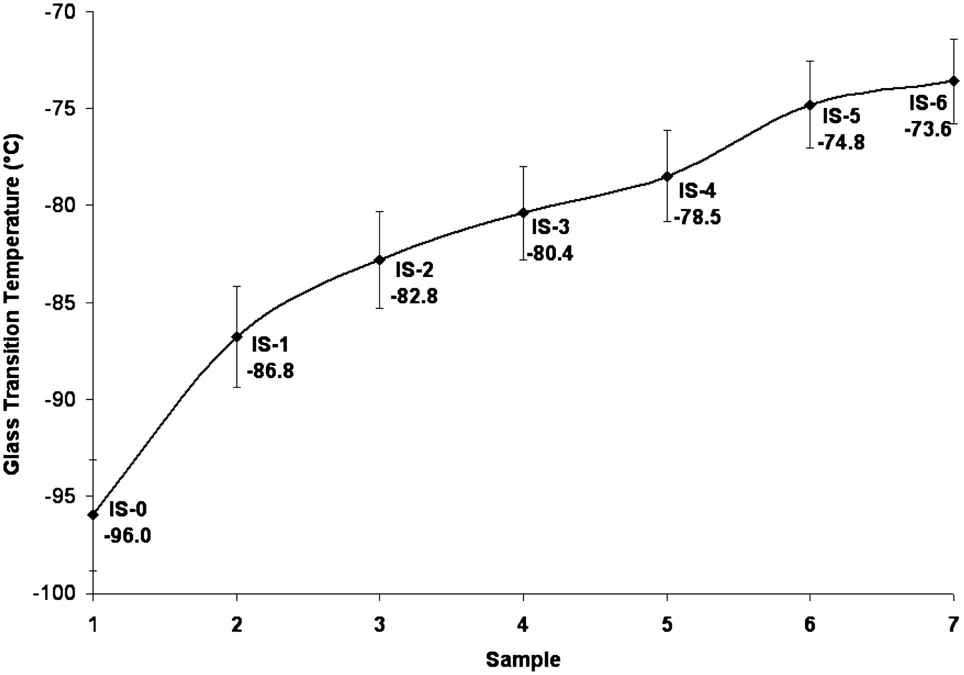

Figure 7. Glass transition temperature of PU elastomers affected by SiO_2 nanoparticles.

face hydroxyl groups of nano SiO_2 would strongly interact with a cross-linking polymer network in the presence of a silane coupling agent, which leads to hindered relaxational mobility in the polymer segments near the interface, increasing the T_g. Figure 8 shows the variations of $\delta_{\tan}$ *versus* amount of nano filler. The $\delta_{\tan}$ would increase with addition of nanoparticles. This is due to the high mobility of integral skin PU segments because of nanoparticle–macromolecule network interaction. Interactions of the segments would result in chain mobility by improving the homogenized dispersion. Better dispersion in the presence of a coupling agent would reduce the distance between nanoparticles providing better interaction with each other and also with polyurethane matrix. Thus, the storage modulus is higher in comparison with non-filled integral skin elastomer and the reverse is true for the loss modulus. As described before, formation of urea structure during the synthesis procedure and distribution of urea network besides the polyurethane cross-linking would also be effective in increasing the T_g of nanocomposite.

Thermal gravimetric analysis (TGA) of prepared nanocomposites demonstrates that the presence of heat resistant inorganic filler would also improve the thermal stability of nanocomposites. Segmented polyurethane structures are mostly synthesized by long chain polyols, using diamines as chain extenders. The study of micro structures in segmented polyurethanes is interesting for polymer researchers. It has been demonstrated that phase separation is depended on preparation procedure.

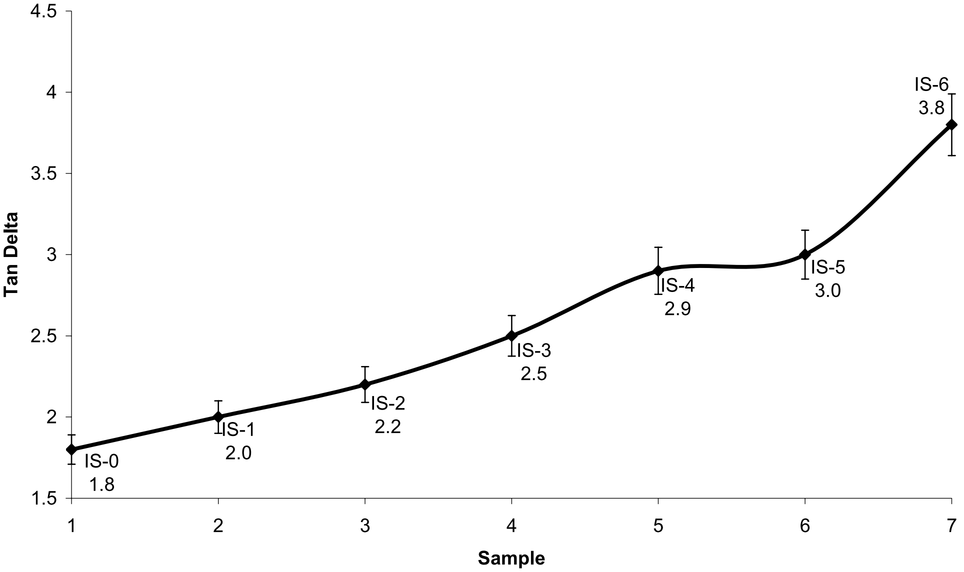

Figure 8. $\delta_{\tan}$ of integral skin PU elastomer reinforced by nano SiO_2.

Table 2.
Amount of soft and hard segments in TGA thermogram of integral skin PU–nano SiO_2 composites

Temperature region	IS-0	IS-1	IS-2	IS-3	IS-4	IS-5	IS-6
320–400°C	14.72	11.43	9.61	9.32	10.01	7.32	7.27
590–640°C	9.80	10.15	12.27	12.92	13.21	10.79	14.38

There are two main mass loss signals in the TGA thermogram of each nanocomposite. The mass loss located in the lower temperature region (320–400°C) is related to soft segments and the signal located in the higher temperature region (590–640°C) is due to hard segments (Table 2). Hard segment domains play the role of physical cross-linker acting as a high modulus filler in combination with nano SiO_2, whereas the soft segment provides extensibility and elasticity. As shown in Fig. 9, the amount of the fraction related to soft segment is decreased due to infusion of nano SiO_2, while the reverse is true for the hard segment related content. This would be attributed to the morphology of the segments which, in polyurethane elastomers, depends on the relative amount of the soft and hard phases [2]. Reinforcement of integral skin PU structures with low amount of soft segments by nano SiO_2 provides the previously discussed improvements, especially for elongation at break. Higher amount of hard segments means that there are fewer soft domains and, thus, the nano filler, which is conducted to the silane coupling agent, would be highly effective in providing the modified characteristics. The modifying role of nano SiO_2 in integral skin PU would be quite desirable due to the presence of coupling agent. The silane coupled nano SiO_2 interacts with both hard and soft segments. As de-

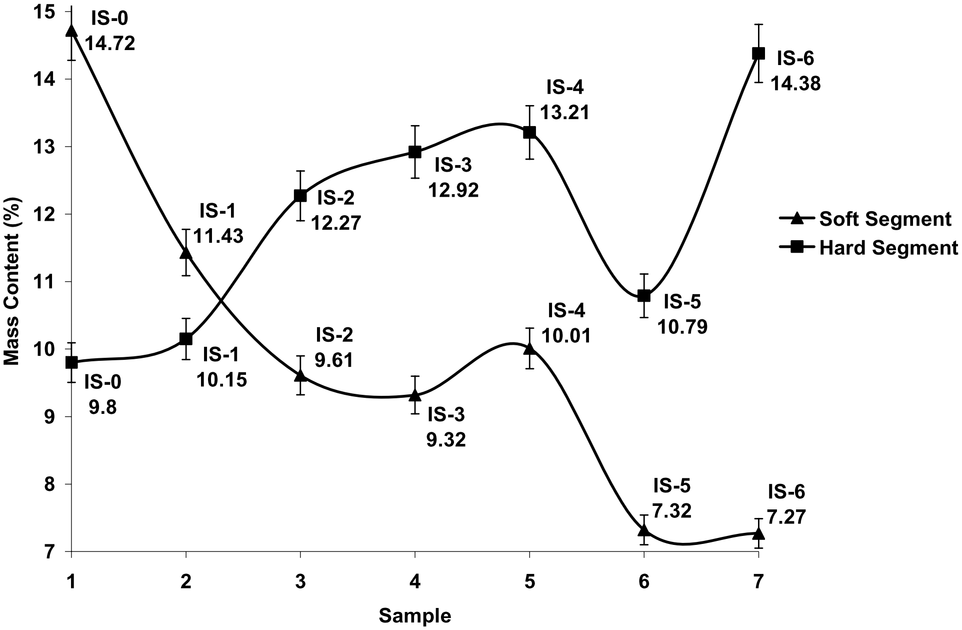

Figure 9. Quantitative effect of nano SiO_2 on amount of segments and their thermal stability in TGA graph of integral skin polyurethane elastomers.

tailed before, OH groups of nano SiO_2 react with isocyanate and may interact *via* hydrogen bonding in polyurethane structure. Accordingly the effect of nano SiO_2 on integral skin polyurethane elastomers is defined through the adsorption of both PU segments on the particle surface and chemical bonding, potentially affecting the structure of both phases. It is also noticeable that a high amount of nano SiO_2 would cause the phase separation in the polyurethane structure. It has been previously reported that SiO_2 would disrupt the short scale phase separated morphology, which is attributed to phase separation in unfilled PU [17]. This has also affected the physical properties especially in IS-5 sample which contains 2.5 wt% of nano SiO_2.

4. Conclusion

Chemically modified SiO_2 nanoparticles which have been homogenously dispersed in the integral skin polyurethane samples would improve their physical and thermal characteristics. Coupling agent would provide the interaction between urethane chain and SiO_2 molecules. High surface area: particle size ratio of nano SiO_2 would be the main reason which influences the excellent properties.

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