

Thermal decomposition studies on polyurethane elastomers reinforced with polyhedral silsesquioxanes by evolved gas analysis



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ABSTRACT

In this work, we report on the thermal stability of nanohybrid polyurethane (PU)/polyhedral oligomeric silsesquioxanes (POSS) elastomers analyzed by evolved gas analysis (EGA). Functionalized POSS were chemically introduced into PU structure as pendant groups (1,2-propanediolizobutyl POSS (PDI-POSS), disilanolisobutyl POSS (DSI-POSS)) or as chemical crosslinks (octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS (OCTA-POSS)).

EGA results of the thermal degradation of the PU/POSS hybrid elastomers have demonstrated that the hybrid systems are slightly more thermally stable when compared to the unmodified PU matrix, as evidenced by reduced amounts of volatile degradation products. It was found that the thermal decomposition of polyurethane materials reinforced with POSS starts from about 300 °C via urethane bonds breakage. In lower temperature region the modified polyurethanes decompose to some low molecular weight compounds and intermediates with hydroxyl and amine groups. At temperatures above 350 °C evolution of hydrocarbons, aldehydes, alcohols, amines, cyclic species and low molecular weight compounds - carbon monoxide, carbon dioxide, water and ammonia was recorded.

Furthermore, the inclusion of POSS in the PU network directly influences the degradation pathways of both the soft and hard block components of the elastomers – it has been observed that the POSS/PU hybrid systems show reduced levels of CO₂ and changed levels of characteristic ion fragments, e.g. *m/z* 42 related to hydrocarbons and THF.

1. Introduction

Polyurethane elastomers are a class of polymers with a versatile properties that bridges the gap between rubber and plastics. Polyurethane elastomers market during last few years has showed notable development and interest which will lead to a future considerable growth in the market. These days, almost over one-third of the global application of PU elastomers is the production of footwear followed by the furniture and automotive industry. Nowadays, a special attention is paid to high performance elastomeric polyurethanes with specific properties such as reduced flammability, high mechanical and thermal stability or biodegradability. To impart these properties physical additives are applied or modifications of PU structure by chemical methods are performed [1,2]. The type of inorganic filler in hybrid polymeric materials affects not only the price of the final product but also its characteristics, which derived from inorganic component itself

and polymer-filler interactions.

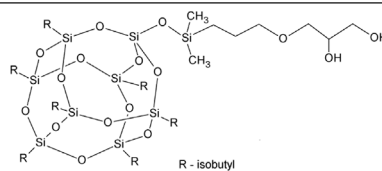
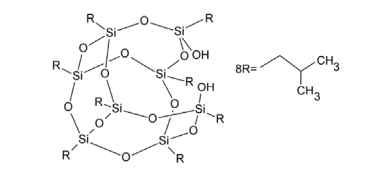
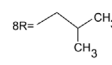
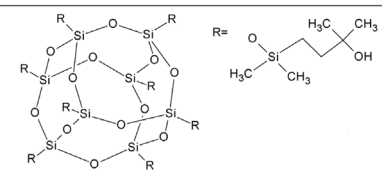
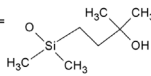
Among inorganic fillers, polyhedral oligomeric silsesquioxanes (POSS) represent unique nanobuilding blocks in the form of silicate cages with sizes of 1–3 nm that can be used to obtain hybrid materials with specific properties [3,4]. Nano-scale POSS particles can be readily modified with a wide range of organic substituents, which makes them nano-scale modifiers of physical and chemical properties in polymeric systems. Different methods are used for POSS nanoparticles incorporation into polymeric matrices, such as copolymerization, grafting or reactive blending [5–7]. It was already proved that combining polymer with an inorganic component on the molecular level lead to materials which are promising candidates to replace conventional composites in e.g. biomedical field [8–11], and the presence of POSS strongly affects mechanical, thermal and barrier properties of polymeric matrices [12–17].

The effect of POSS addition depends strongly on its structure, which

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Table 1
Chemical composition and structures of POSS materials.

<p>PDI-POSS 1,2-Propanediol-Isobutyl-POSS $C_{34}H_{76}O_{15}Si_8$</p>	 <p>R - isobutyl</p>
<p>DSI-POSS DiSilanollsobutyl POSS $C_{32}H_{74}O_{13}Si_8$</p>	 <p>8R= </p>
<p>OCTA-POSS Octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS $C_{56}H_{136}O_{28}Si_{16}$</p>	 <p>R= </p>

may contain non-reactive or reactive organic groups and on the size of POSS cage, the nature of organic part, and the concentration and solubility of POSS in polymer system [18,19]. For example Fu et al. [20] characterized PU materials with diol functionalized POSS cages, where POSS formed microcrystalline domains within polymer matrix and enhance the microphase separation between the hard and soft segments. In another study of Bliznyuk et al. [21], crystalline nanometric species enriched with inorganic silica, were identified. Each time when crystallization of POSS into PU system occur, also a significant improvement in mechanical stability was observed [22].

Noteworthy, the POSS presence not only physically re-enforces the PU matrix but also increases thermal stability and reduces evolution of gaseous degradation products, what can be attributed to suppression of the molecular mobility in polymer system. Such behavior was already proved for different polymeric systems, such as PS nanocomposites [23], Fe_3O_4 /PU composites [24], and HDPE filled with silicon powder [25].

The incorporation of organic substituents to the POSS cages changes their thermal properties, like thermal stability [26]. Detailed studies on the thermal stability of different substituted POSS were performed by Fina et al. [27], who found that the nature of compounds linked to the silicon cages determines the compatibility of POSS with polymer matrices, what in turn affects the final nanocomposites' properties. Phenyl POSS show higher thermal stability and lower solubility than aliphatic ones. Besides, the presence of cyclic/aromatic groups in POSS promotes formation of a thermal barrier that hinders heat transfer through the material, what can improve the overall resistance of polymer matrices [28]. Spolrajic in his work [29] investigated hyperbranched polyester-modified POSS as fillers in linear PU elastomers, and found that this dendritic polyester and POSS provide a synergistic effect in increasing the thermal stability of thermoplastic PU.

PU thermal degradation leads to various volatile products which can participate in secondary reactions such as chain breaking, isomerization and dehydrogenation [30–35]. It was proved [36] that the complex nature of PU degradation processes originates from various reactions, such as dimerization (isocyanate to carbodiimide), crosslinking (carbodiimide with urethane groups) and dissociation through six-membered ring transition state or intramolecular displacement of carbon dioxide with a four-membered ring transition state. On the other hand the results of investigations of thermal properties of segmented PU-POSS hybrid systems are not consistent [37–39] as they vary with POSS structure and its load in the polymer matrix. Zhang et al. [40] suggested that the existence of POSS moieties did not significantly alter the

degradation mechanism of the polymers, while Liu and co-workers [41], who replaced a part of the aromatic amine with octa(aminophenyl)-POSS and crosslinked the PU macrochains, obtained materials with highly enhanced thermo-mechanical properties. PU/POSS composites can be also fabricated by processing methods, e.g. Bourbigot et al. [42] melt mixed thermoplastic PU with POSS- poly(vinylsilsesquioxane) using Braebender mixer. It was postulated that reaction of oxygen with degradation products stabilizes them and slowing down further degradation.

There are few papers from our group concerned on the thermal degradation of PU elastomers reinforced by POSS particles by Lewicki et al. [39,43] and Janowski et al. [44]. Here, we investigate the thermal decomposition behavior of polyurethane elastomers reinforced with different types of POSS, studied by TGA/FTIR/QMS hyphenated technique in inert and oxidative atmosphere. Based on analysis of the evolved gaseous products under different atmospheres decomposition mechanisms of PU/POSS hybrid materials are proposed.

2. Experimental

2.1. Materials

For synthesis of polyurethane/POSS nanohybrid elastomers 4,4'-diphenylmethane diisocyanate (**MDI**) (Sigma Aldrich), polytetramethylene glycol (**PTMG**, M_w 1400, Terathane[®] 1400 Invista), and 1,4-butanediol (**BD**) (Sigma Aldrich), were used. Three different nanofillers obtained from Hybrid Plastics[®] were applied: 1,2 - propanediolizobutyl POSS (**PDI**), disilanollsobutyl POSS (**DSI**) and octa (3-hydroxy-3-methylbutyldimethylsiloxy) (**OCTA**) – Table 1.

2.2. Synthesis

Polyurethane/POSS elastomers were prepared by two-step method to yield macromolecular systems with POSS nanoparticles incorporated as (i) pendant group, (ii) part of the main chain and (iii) cross-link (Scheme 1).

Linking process of POSS with two hydroxyl groups in the structure was realized by a prepolymer method which allowed to effectively disperse POSS and help to control the reaction between isocyanates and hydroxyls. First, MDI was melted at 70 °C in a 100 ml three-necked round-bottomed flask, equipped with a mechanical stirrer and nitrogen inlet. A solution of POSS in a suitable amount of PTMG was then added in one portion. The POSS mixture in PTMG was prepared by heating to

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