Modern polyurethane elastomers modified with polyhedral silsesquioxanes

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Please cite as: CHEMIK 2011, 65, 10, 1035-1040

Introduction

Polyurethanes (PU) are today ranked fifth among polymers in terms of world production volume, being one of the most versatile polymers. They are used in the form of elastomers, foams, coatings, adhesives, fibres, synthetic leather, engineering plastics, aids and other. Polyurethanes are obtained by the polyaddition reaction of isocyanate, polyol and chain extender [1]. Conventional PUs show low resistance to heat, which substantially reduces the area of their possible applications [2].

In recent years nanohybrid polymers with oligosilsesquioxane fragments have become an object of intense interest due to their unique physical, chemical, thermal, mechanical and surface properties. Since the very beginning of research in this field, attention was drawn to the new possibilities of using POSS as a nanofiller in polyurethane plastics widely used as elastomeric engineering materials of improved thermal resistance [3] and reduced flammability [4].

Silsesquioxanes have emerged as an alternative for the siloxane based plastics industry. Silsesquioxanes are polyhedral structures of the general formula (RSiO)$_n$, where $R$ is virtually any organic substituent or a hydrogen atom, and $n$ is an integer, in most cases equal to 6, 8, 10 or 12. The silsesquioxane core is regarded the smallest obtainable fragment of crystalline silica – the dimension of the silsesquioxane molecule is within 3 nm [5]. The name polyhedral oligosilsesquioxanes (POSS) is applied to siloxane molecules combined into a cage-like polyhedral structure. These inorganic cages have in their corners non-reactive groups, which have an effect on the solubility of the compounds in organic solvents and in monomers. One or more of these non-reactive groups may be substituted by a functionality that participates in polymerisation [6].

Synthesis methods of nanohybrid PU/POSS elastomers

POSS molecules can be incorporated in the polymer matrix by copolymerisation, grafting or blending. Many possibilities of chemical transformation of POSS are the reason for the increasingly widespread application of its various types as modifiers of the polyurethane structure. POSS may be incorporated in macro chains as pendant groups, network nodes or fragments of the main chain [7].

Examples of introducing POSS molecules as pendant groups in the chain

Among the first papers on polyurethane nanocomposites with POSS nanoparticles in their structure were the articles by an Air Research Laboratory team led by J. Schwab [8, 9]. They have reported on a method of diol incorporation of POSS directly into rigid polyurethane segments. To this end they used POSS functionalised with bisphenol A (BPA-POSS), which acted as a chain extender. The isocyanate reagent was 4,4’-disocyanatodiphenylmethane (MDI), the elastic component was polyoxytetramethylenediol (PTMG) with an average molecular weight of 2000. The catalyst of the reaction between isocyanate and hydroxyl functionalities was dibutyltin dilaurate (DBTDL). The research was continued by B. Fu and collaborators, who determined the effect of BPA-BOSS on the strengthening of rigid segments of polyurethane elastomers [10, 11]. The content of BPA-POSS in the elastomers they had obtained was 21% and 34%.

Bulk polymerisation reaction was carried out by B. Janowski and K. Pielichowski, who obtained segmented nanohybrid polyurethanes [12, 13]. In their investigations they used 1-[1-(2,3-dihydroxypropoxy)butyl]-3,5,7,9,11,15-heptaisobutylpentacyclo[9.5.1.1(3,9).1(5,5).1(7,13)]octasiloxane (PHIPOSS). The disiocyanate component was MDI, while the diol flexibleising agent was PTMG with an average molecular weight of 1400. In this process PHIPOSS replaced partly the chain extender: 1,4-butanediol. This way, without using any solvents, a series of nanohybrid polyurethanes was obtained containing up to 10wt.% octasilsesquioxane (Fig. 1).

S. Zhang et al. were the first to use 1-(2,3-propanediol)propoxy-3,5,7,9,11,13,15-isobutylpentacyclo[9.5.1.1(3,9).1(5,5).1(7,13)]octasiloxane (POSS diol) to replace part of diol monomers in the synthesis of hybrid POSS-containing polyester resins, which were subsequently crosslinked with isophorone disiocyanate (IPDI), to obtain the hybrid polyurethanes. POSS content in the hybrid polyester resins ranged from 1% to 8.5wt.% [14].

R. Kannan et al. have reported on a method of applying polycarbonate urethanes (PCU) with incorporated polyhedral oligosilsesquioxanes in the fabrication of heart valves and artificial blood vessels [15]. The poloy substrate used was polycarbonate polyol with an average molecular weight of 2000, the isocyanate component was MDI, whereas the nanofiller was 1-(2-trans-cyclohexanediol)ethyl-3,5,7,9,11,13,15-heptaisobutylpentacyclo[9.5.1.1(3,9).1(5,5).1(7,13)]octasiloxane, taken in amounts of 2 and 6 wt.% . The prepolymer was dissolved in N,N'-dimethylacetamide.

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Fig. 1. Synthesis of polyurethane containing oligosilsesquioxane pendant groups [13]
Examples of introducing POSS molecules as network nodes

The first paper presenting a synthesis of POSS-containing polyurethane networks was published in 2005. H. Liu and S. Zheng described a method of obtaining crosslinked PUs, wherein part of the crosslinking agent, aromatic amine 4,4′-methylenebis(2-chloroaniline) (MOCA), was replaced with octa(aminophenyl) polyhedral silsesquioxane (Oap-POSS) [19]. The prepolymer method of synthesis was applied, wherein the isocyanate component was 2,4-diisocyanatotoluene (TDI), and the flexible component was polyoxypropylenediol (Fig. 2). Oap-POSS was introduced into the prepolymer in the form of a solution in DMAC. The process of obtaining the polyurethane network, and their content was maintained at a level between 0 and 52%. All PU/POSS hybrids obtained were homogeneous and transparent. The rigid segments of the system comprised IPDI, while the flexible segments comprised PPG with an average molecular weight of 1000. The organic solvent which facilitated the polymerisation reaction was N,N′-dimethylacetamide (DMAC).

Examples of introducing POSS molecules as parts of macro chain

Yet another type of synthesis of nanohybrid polyurethanes, where polyhedral silsesquioxanes form part of the macro chain, has been described by K. Madhavan [23]. The author presented a new way of incorporating completely or incompletely condensed POSS into the polyurethane matrix (Fig. 3). Using an aliphatic HDI and hydroxyl-terminated polydimethylsiloxane (PDMS), a hybrid PU/POSS structure was obtained, wherein the heptacyclokynyl tricycloheptasiloxane triol (CyPOSS) became part of the main chain, and octakis(hydridodimetylosiloxy)octasilsesquioxane (POSS-H) became the node of the polyurethane network. The entire process was catalysed by DBTDL.

The process of obtaining polyurethanes with incorporated POSS cores in the main chain was also investigated by M. Oaten and N. Choudhury [24]. They used POSS with an open cage structure, containing three hydroxyl functionalities. The synthesis of nanohybrid polyurethane consisted in direct reaction between aliphatic disocyanate (HDI) and trisilanlo isobutyl POSS in toluene. The catalyst was DBTDL.
**Summary**

All the research reports and papers cited here show that in recent years POSS has become a very attractive inorganic-organic nanofiller for polyurethane matrices. Due to its versatile structure and functionality, it is readily soluble in many organic solvents and monomers, enabling introduction thereof into the polymer already at the stage of synthesis. Embedding POSS in polyurethane by way of a chemical reaction improves many basic properties of PU and eliminates its drawbacks. This is associated with the ability of the molecules of polyhedral silsesquioxanes to nucleate aggregation and crystallisation in the polymer matrix, leading to formation of stable morphological forms, reduction of segmental vibrations by large POSS substituents, as well as with possible occurrence of advantageous second order interactions between POSS-containing macro chains.

**Literature**


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Dr. Bassam Shakhashiri is a Professor of Chemistry at the University of Wisconsin-Madison and is the William T. Evjue Distinguished Chair for the Wisconsin Idea. Professor Shakhashiri has captivated audiences with his scientific demonstrations at a variety of locations, including Boston’s Museum of Science, the National Academy of Sciences and the Smithsonian’s National Air and Space Museum in Washington. Admission to the museum is required. Free tickets to Dr. Shakhashiri’s show will be available on a first come, first serve basis. Tickets are available via advance reservation. To reserve tickets, please contact the NESACS secretary either via email secretary@nesacs.org (preferred) or by phone 1-781-272-1966 before October 20, 2011. Tickets will be available for pick-up in the lobby of the museum at the ACS table. (http://www.chemistry2011.org/participate/events.6.09.2011)