Polyurethane/POSS Hybrid Materials

Edyta Hebda and Krzysztof Pielichowski

Abstract Organic–inorganic hybrid materials, prepared via chemical synthesis or physical blending of functionalized nanofillers within polymer matrix, have gained an increased attention in the recent years. Polyhedral oligomeric silsesquioxane (POSS) nanoparticles, due to their nanometer size and functionalization possibilities, are applied as effective modifiers—both chemical and physical, for polymer matrices, including polyurethanes (PU). Research efforts focused on polymers incorporating polyhedral oligomeric silsesquioxane (POSS) have intensified in recent years, revealing new synthetic routes and interesting features of these composite materials. This chapter describes polyurethane/POSS systems with different architectures—with POSS molecules as pendant groups in the polyurethane chain, incorporated in the main chain and as cross-linking agents. The methods of incorporation of POSS into polymer matrices via covalent bonds or physical blending have been presented, and the influence of preparation conditions on the structure and properties of nanocomposites was discussed. Application fields, such as gas membranes or biomedical implants, have been outlined.

Keywords Polyurethane · POSS · Hybrid materials · Nanocomposites · Synthesis Modification · Properties

1 Introduction

Polyurethanes (PU) are an important group of polymers with a wide range of applications in industry and technology. They are obtained by polyaddition reactions of isocyanates with compounds containing reactive hydrogen atoms, such as alcohols or amines. The group of polyurethane materials includes foams, varnishes, adhesives, fibers, and elastomers [1, 2].

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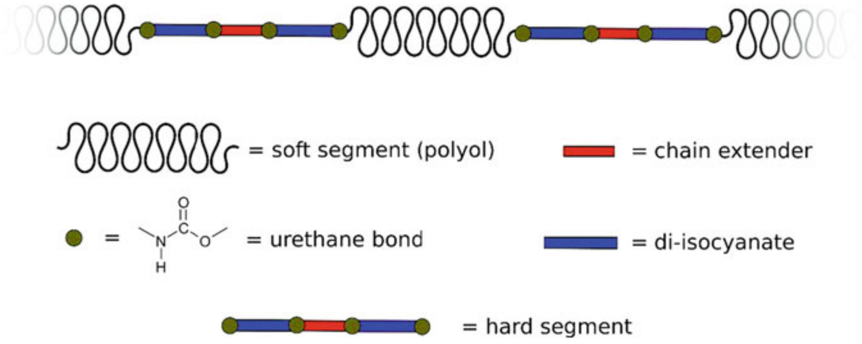


Fig. 5.1 Segmental construction of polyurethanes; adopted from [5]

Elastomers are characterized by a large modulus of longitudinal elasticity, tearing module, compressibility, very high resistance to scratches and attrition, and excellent elastic properties. They are resistant to aging, weathering, typical solvents, and oils. They can be manufactured in a very wide range of hardness, but—in contrast to hydrocarbon rubber—remain elastomers even at high hardness. Considering the processing, polyurethane elastomers can be divided into three main groups—cast, rolled, and thermoplast elastomers. Cast polyurethane elastomers are obtained with a ratio of isocyanate to hydroxyl and possibly amino groups nearing to stoichiometric. Because this provides the highest molecular weight of linear polyurethane, their physical properties are best among all polyurethanes [3].

Linear polyurethanes are segmented polymers consisting of rigid and flexible segments. There is a close relationship between the properties of segment polyurethanes and their chemical structure and physical structure. Rigid segments are formed by the reaction of isocyanate groups with chain extenders and consist of isocyanate residues, extenders, urethane, and possibly urea groups. On the other hand, the flexible segments are built from polyol chains and consist of methylene and ether groups or ester groups. Rigid segments are joined together via polyol flexible segments. The polyurethanes therefore resemble block copolymers with a structure of the type $(AB)_n$, which are constructed from alternating repetitive rigid and flexible blocks (Fig. 5.1). This type of segment construction is a key feature distinguishing polyurethane elastomers from other such materials and is the main reason for the favorable mechanical properties of these materials in a wide range of temperatures [4].

The polar and hard-to-melt rigid segments interact strongly with each other, in particular through hydrogen bonds between the NH groups and the oxygen atoms of the ether or ester group and usually do not mix homogeneously at temperatures below 120 °C with less polar, easily meltable flexible segments. This leads to their separation and formation of the so-called rigid domains, resulting in polyurethane becoming diphase and microheterogeneous. In polyurethanes with 10% of rigid segments, phase separation takes place before the start of the reaction. If the polymer is obtained below the miscibility temperature with the chain extender—glycol, the resulting macromolecules show a higher degree of self-association than the polyurethane obtained in a homogeneous system or solution. In rigid domains, there is physical cross-linking; thus, they fulfill a function similar to the function of the polymer reinforcing filler. At room temperature, almost all NH groups in polyurethanes are bound by hydrogen bonds, therefrom only 30–60% with carbonyl groups of urethane groups. Rigid domains are the phase of ordered rigid segments, permeating with the phase (usually continuous) of flexible segments [3]. Even in the case of very good phase separation, interfacial areas can be distinguished which at the border between soft and hard domains. These areas have intermediate properties between flexible and rigid properties, and their dimensions are a measure of the degree of phase separation [1].

Due to stronger interaction with the urethane groups of segments of rigid ester groups of oligoester chains than with ether linkages of oligoether chains, the microphase separation takes place to a greater extent in polyetherurethanes than in polyesterurethanes. Flexible segments in the non-deformed state are distributed statistically, as a result of which the soft domains are isotropic and amorphous. The flexible segments are arranged approximately perpendicular to the longitudinal axis of the hard domains, which makes these domains locally anisotropic. Because rigid domains are also statistically arranged, the polymer as a whole exhibits mechanical isotropy and optical isotropy.

Rigid polyesterurethane domains are 3–10 nm in size and polyetherurethane 5–10 nm and consist of 2–4 repeating segments. Rigid domains both of polyether and polyesterurethane have a fringed-layered structure with a thickness equal to the length of the rigid segment, the average distance between the centers 10–25 nm and the width below several dozen nanometers. Such domains act as cross-linkers bond; they limit chain relaxation and allow crystallization of the segments after application of stress, thereby increasing the tensile strength of the polymer and its thermal resistance. In many polyurethane systems, in addition to the microphase structure, the oriented domains also form a super spherulitic structure. The spherulite radius is proportional to the size of the rigid segments, and the bigger is the radius, the larger the phase separation. In the center of the spherulite, the content of rigid segments is very large and decreases in the radial direction. The spherulites in polyetherurethanes made of 4,4′-methylenediphenyl diisocyanate (MDI) have a diameter of 1–10 μm and an open fiber structure [3].

The occurrence of a two-phase domain structure causes high strength of polyurethanes. The presence of resistant to sticky flow of rigid domains in which the rigid segments strongly interact with each other, in particular the formation of hydrogen bonds, reduces the intensity of the stress line due to domains deflection, forking of their cracks and their plastic deformation. The domains of the flexible segments additionally strengthen the polymer as a result of viscoelastic dissipation of energy in the immediate vicinity of the fractured blade, and thanks to the progressive ordering and crystallization during deformation. With the increase in the content of rigid segments, the degree of phase separation increases and the mechanical properties improve. The content and structure of flexible segments also significantly affect the properties of polyurethanes. Polyestroles provide excellent mechanical proper-

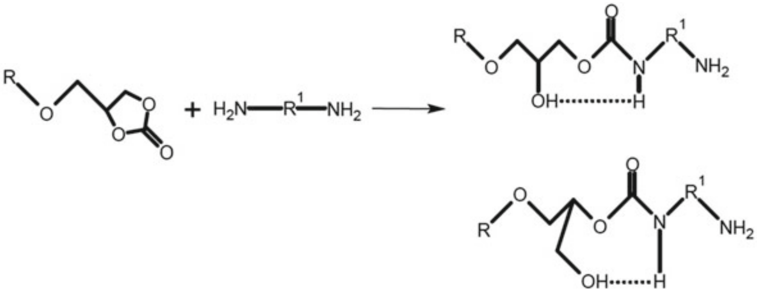


Fig. 5.2 Reaction of cyclic carbonate with amine; adopted from [9]

ties, while polyetheroles have better microbial resistance and hydrolysis. On the other hand, increasing the molecular weight of the elastic segment causes increase in the glass transition temperature of the obtained polyurethanes. Polyethers have poorer miscibility with MDI than polyesters; the elastomers obtained from them show a higher degree of phase separation, moreover the rigid domains forming in them are larger and their structure is more complex than in the case of polyestroles. The phase separation tendency also increases as the hydrocarbon chain length increases in polyetheroles and polyestroles due to the decreasing polarity of the polyol [4, 6].

As commonly used diisocyanates—(MDI) and toluene 2,4-diisocyanate (TDI) are reported to exert harmful effects if they enter the body through inhalation, skin (open wounds) or eye contact [7], and their production process is based on the reaction of toxic phosgene with amines, alternative synthetic routes have been proposed that do not require the use of diisocyanates. Three approaches have been applied for the synthesis of non-isocyanate PU (NIPU)—by step-growth polyaddition, polycondensation, and ring-opening polymerization. From industrial perspective, synthesis of polyurethanes in the reaction of multifunctional cyclic carbonates with aliphatic primary diamines or polyamines proceeding via step-growth polyaddition is the most viable option [8]. In the polyaddition reaction, two isomers are formed, one with a secondary β-hydroxyl group and the other possessing a methylol group, which form intramolecular hydrogen bonds with the urethane group—Fig. 5.2.

NIPU show relatively low sensitivity to moisture in the surrounding environment, and the hydroxyl groups formed at the β-carbon atom of the urethane group cause an increase in adhesion properties. The presence of intra and intermolecular hydrogen bonds [10] as well as the lack of unstable biuret and allophanate units [11] lead to an improved thermal stability and hydrolytic stability/chemical resistance of NIPU to nonpolar solvents, as compared to conventional PU.

The properties of polyurethanes can be changed by using different types of fillers that do not mix homogeneously with the polyurethane components. Classic powder or fibrous fillers increase the hardness and improve the mechanical properties of polyurethanes; however, they significantly increase the density of the material. In recent years, polyurethane/nanofiller composites have been extensively studied in which the particles of the reinforcing phase have nanometric dimensions. At this length scale, significant improvements of some polymer properties with a relatively low content of the nanofiller can occur. As nanoadditives metal nanoparticles, organophilized layered silicates, including montmorillonite, zinc oxide, aluminum oxide, titanium oxide, silica or carbon nanotubes have been applied [12–16].

A new and promising group of materials are hybrid polyurethane/functionalized polyhedral oligomeric silsesquioxane (POSS) materials, which, due to the possibility of chemical bonding of nanoparticles with organic matrix, show improved properties compared to classical polymer/nanofiller systems.

The dimensions of POSS molecules do not exceed a few nm; therefore, they are classified as 0-D nanofillers with a spherical structure. Many POSS derivatives containing reactive functional groups attached to corners of Si-O cage have already been synthesized. The presence of such groups makes POSS capable of reacting with traditionally used monomers. Materials created in this way can be included in the group of (nano) hybrid materials in which oligosilsesquioxane molecules are covalently bound to organic polymers. POSS derivatives containing hydroxyl, amino, or isocyanate groups can be used for chemical modification of all kinds of polyurethane materials, such as elastomeric, foamed, and coating materials [17].

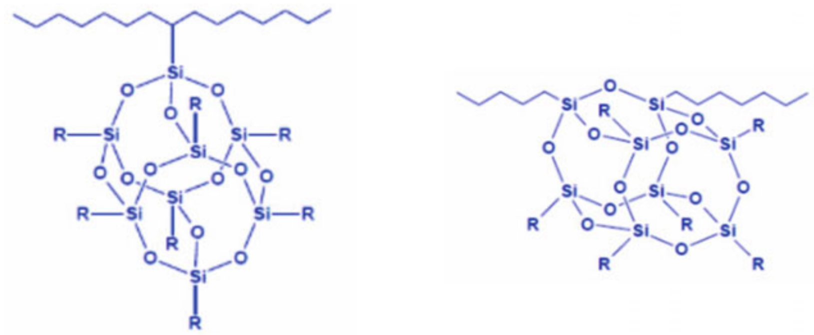
The number and functionality of the substituents attached to the POSS cage determine the way of incorporation of these compounds into the PUR structure as:

- a side group of the main chain or end group terminating the polymer chain (monofunctional POSS),
- a main chain fragment (di-functional POSS), or
- a network node (multifunctional POSS).

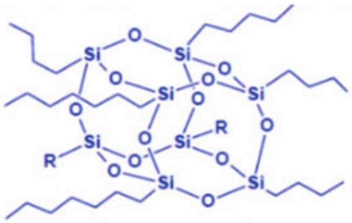
For the synthesis of hybrid polyurethanes, numerous POSS have been used, including POSS monofunctional compounds with isocyanate or amino substituents, POSS compounds with one dihydroxyalkyl and dihydroxyaryl reactive group, difunctional POSS compounds with two hydroxyl substituents, and multifunctional POSS with a partially caged structure or a fully condensed cage with isocyanate, hydroxyl, or amino substituents [17, 18].

2 Chemical Modifications

POSS molecules can be incorporated in the polymer matrix by copolymerization, grafting, or reactive blending. Numerous possibilities of chemical decoration of POSS molecules with organic substituents open up new perspectives for synthesis of organic–inorganic polyurethane hybrid materials in which silsesquioxanes can be incorporated in the macrochains as pendant groups, network nodes, or fragments of the main chain. This gives the opportunity to design novel materials with a broad spectrum of known and yet unknown properties [19]. Therefore, for several years, a significant increase in the use of POSS compounds as an inorganic nanoadditive in polymeric materials has been observed.



(a) side group of the main chain (b) polymer backbone fragment



(c) polymer network node

Fig. 5.3 Location of POSS moieties in the polymer structure

Polyhedral silsesquioxanes can be incorporated into the polymer chain chemically by several methods [18, 20–23]:

- copolymerization of organic monomers with POSS compounds having at least two reactive functional groups—hybrid polymers are obtained with covalently bound POSS nanoparticles as a side group of the macrochain (Fig. 5.3a), a polymer backbone fragment (Fig. 5.3b), or a polymer network node (Fig. 5.3c),
- chemical modification of polymers by grafting them with POSS molecules with one reactive group—systems with a covalently bond POSS molecule constituting a side group of the main chain of macromolecules or telechelic polymers terminated with POSS molecules are obtained.

2.1 POSS Molecules as Pendant Groups in the Polyurethane Chain

One of the first papers dealing with the subject of polyurethane hybrid materials, containing POSS compounds in their structure, were prepared by Schwab et al. [24, 25] Diol (bisphenol A—BPA)-POSS was used as a chain extender, the isocyanate component was 4,4′-diphenylmethane diisocyanate (MDI), and soft segments were composed of flexible polyoxytetramethylene diol (PTMG) with an average molecular weight of 2000. The catalyst for the reaction between isocyanate and hydroxyl groups was dibutyltin dilaurate (DBTDL). Later, these studies were continued by Fu et al. who determined the influence of BPA-POSS on the structure and properties of polyurethane elastomers—Fig. 5.4 [26, 27].

The synthesized materials contained 21 and 34 wt% of BPA-POSS. Structural investigations using the WAXD and SAXS methods revealed that BPA-POSS creates crystallites in the polymer, whose presence is manifested by clear reflections on WAXD patterns. The formation of crystallites is most likely induced by polyurethane phase separation of rigid and elastic domains, which was confirmed by SAXS studies. The value of the great period was 111 Å for hybrids with 34 wt% of POSS and 164 Å for materials containing 21 wt% of POSS. The size of rigid domains determined by the SAXS method was 34 Å for both BPA-POSS loads. When polyurethane/POSS elastomers were subjected to uniaxial deformation, enhanced tensile modulus and strength of the hybrid polymers were recorded. TEM observations on a stretched and relaxed PUR/POSS materials indicated that tensile stretching broke the large hard segment domains into disk-like smaller domains with plane normals almost parallel to the stretching direction, as shown in Fig. 5.5.

Interesting research results were presented in the work of Hoflund and coworkers [28] on the resistance of PUR/POSS coatings used in space satellites for erosion caused by atomic oxygen. Polyurethane nanohybrid systems were prepared using MDI, polytetramethylene diol as an elastic component, and 1,4-butanediol and trimethylpropane substituted with a group containing heptacyclopentyl-POSS (TMP-POSS). XPS surface tests revealed that in the samples exposed to the oxygen atom stream for 63 h, the carbon content on their surface was reduced from 72.5 to 37.8%, while the concentration of oxygen and silicon on the surface increased with prolonged exposure time, from the initial value of 2.28–2.93%. The obtained data suggest that atomic oxygen destroys cyclopentyl rings in POSS-TMP, forming CO and/or CO_2 and H_2O that desorb from the material surface. Extended exposure time results in the formation of a silica layer on the surface of the sample, which favorably protects the inner polymer layers against the influence of atomic oxygen.

POSS nanohybrid polyurethanes for coatings, made of dihydroxy isobutyl-POSS (R = isobutyl), isophorone diisocyanate, dimethylolpropionic acid, and ethylenediamine as a chain extender, have been prepared by Turri [29, 30]. POSS particles easily integrated into the polyurethane structure, and the resulting materials formed stable aqueous dispersions if the POSS content did not exceed 10%. X-ray analysis showed the presence of crystallites in the obtained coatings even at low POSS content. The results of dynamic mechanical analysis show a reinforcing effect, mainly in the case of polytetramethylene diol with a molecular weight of 2000. In addition, polyurethanes with built-in POSS were characterized by lower surface wettability and lower value of the polar surface energy component than pure polymer, even with relatively low silsesquioxane content. This effect may be due to both a stratification of apolar components of the coating close to polymer–air interface and a topographical change of the surface due to formation of nanosized structures.

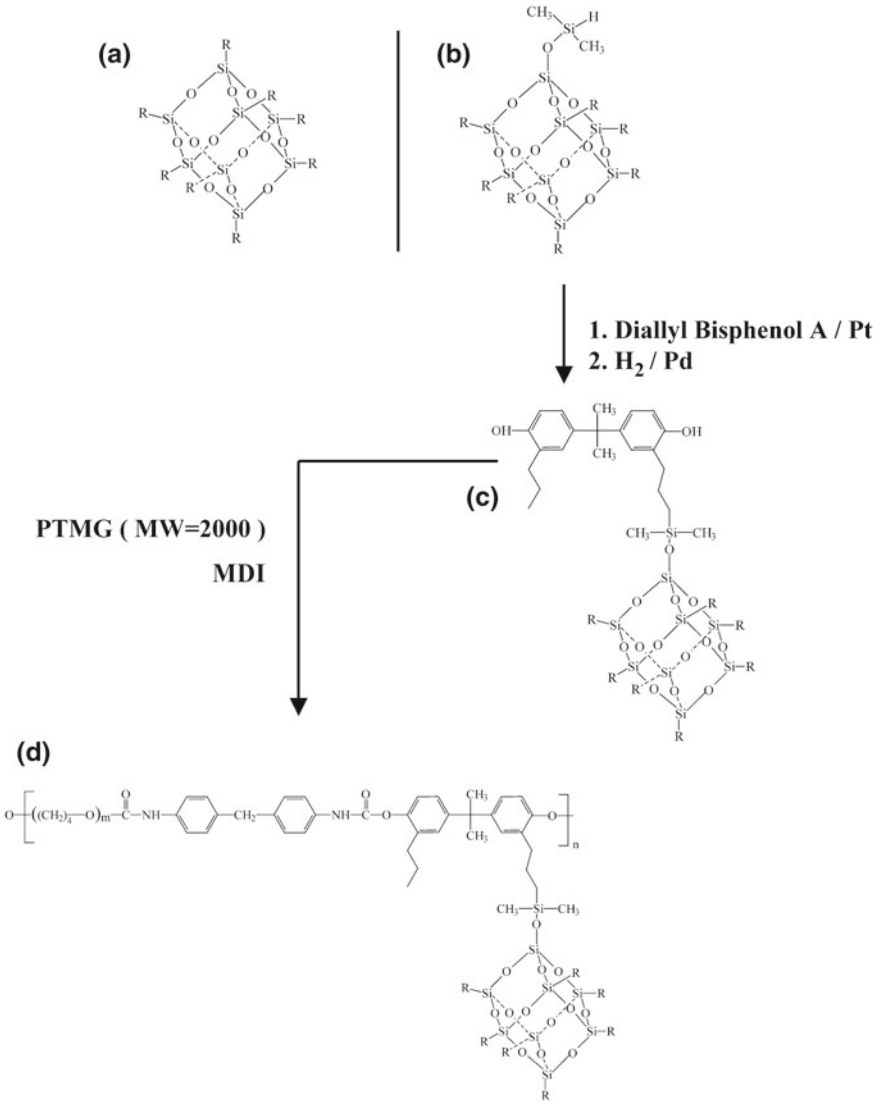


Fig. 5.4 Schematic diagram of the synthesis for POSS-polyurethane: **a** octacyclohexyl-POSS, with R = cyclohexyl; **b** hydrido-POSS; **c** BPA-POSS; and **d** POSS-PU [27]

The phenomenon of wetting the surface of polyurethane composites with 1-(2,3-propanediol)propoxy-3,5,7,9,11,13,15-heptaisobutylpentacyclo-POSS (PHI-POSS)was studied by Zhang et al. [31]. It was shown that the contact angle values increase with the increase of silsesquioxane content, whereas free surface energy decreases more than twice for a sample containing 8.5 wt% of PHI-POSS in oligoestrodiol, compared to unmodified polyurethane. As AFM studies showed, the

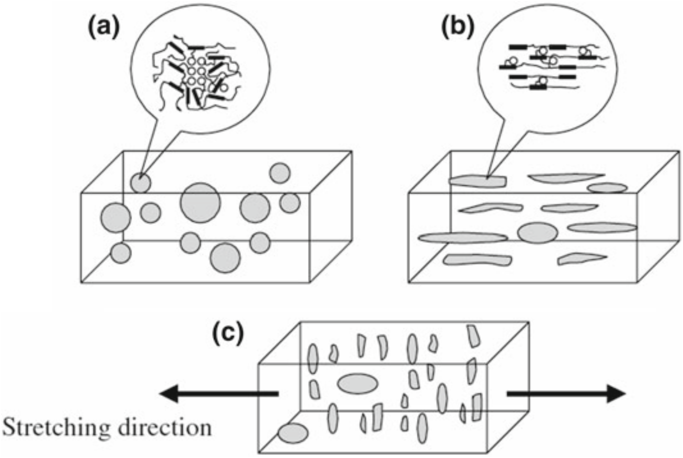


Fig. 5.5 Schematic diagram of microphase changes during stretching: **a** no deformation or low deformation (POSS molecules form nanocrystals in the hard segment domains); **b** intermediate deformation (e.g., 400%) (some POSS crystals are destroyed in the hard segment domains); and **c** large deformation after relaxation (e.g., 700%) as in TEM [27]

average surface roughness (Ra) increased with the increase of silsesquioxane content; however, Ra values were much lower than 100 nm, and thus the impact of roughness on the contact angle value was insignificant. As the reason for the reduction of surface energy of the materials studied, migration of the polyester segments toward the polimer surface was named. This effect intensifies after incorporation of silsesquioxane containing alkyl substituents which strengthen the migration effect of the elastic segments; it leads to a decrease in free energy and to an increase in the contact angle values. WAXD results showed that for lower PHI-POSS contents, the silsesquioxane nanoparticles are well dispersed in the polymer matrix, which limits the tendency to form crystallites. However, for hybrids containing 8.5 wt% of silsesquioxane, PHI-POSS forms crystallites, and there is a tendency for phase separation between the oligoester segments and silsesquioxane moieties. Besides, stiff POSS cages hinder crystallization of oligoestrodiol segments. The DMA analysis revealed an increase in the glass transition temperature of the elastic segments phase with an increase in silsesquioxane content, most likely due to limiting the mobility of oligoester chains by large silsesquioxane side groups. Thermal stability (decomposition onset temperature determined by TGA) under inert gas atmosphere was increasing with an increase of POSS content.

Surface roughness tests of coatings obtained from urethane cationomers synthesized from oligooxypropylene diol and modified PHI-POSS showed that at even a relatively small (1%) PHI-POSS content the roughness increases, as revealed by confocal laser microscopy results [32, 33]. Thermal and rheological properties of poly (urethane–urea) ionomers containing 3-(2-aminoethyl)amino)propylheptaisobutyl-POSS were discussed by Madbouly et al. [34, 35]. It was observed that the depen-

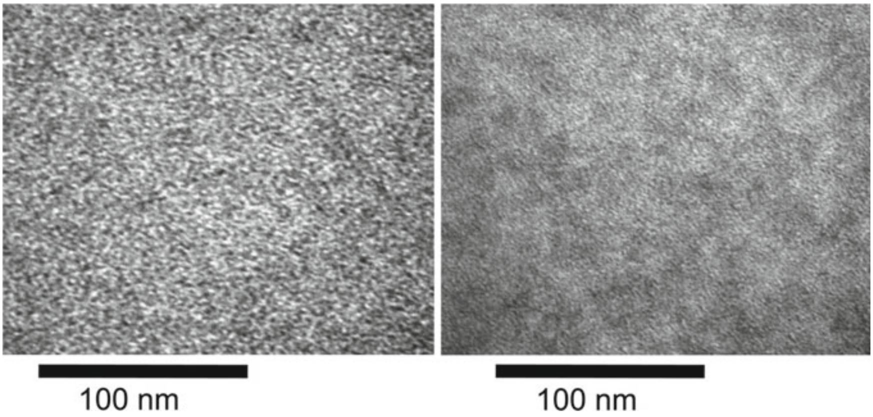


Fig. 5.6 TEM photographs for pure PU and PU/POSS composite (10 wt% POSS). The dark particles represent the hard segments, and the bright matrix represents the polyester soft segments. The sample of 10 wt% POSS shows finer morphology than that of pure PU [34]

dence of the imaginary component of the stiffness modulus versus the vibration frequency deviates from the straight line at 140 and 160 °C for a pristine polymer and polymer containing POSS, respectively. Such deviation indicates that above these temperatures the Williams–Landel–Ferry equation ceases to describe their viscoelastic properties due to the phase separation phenomena of rigid and elastic segments. The increase of this temperature value for nanohybrid polyurethane, as compared to the unmodified polyurethane, demonstrates that POSS has increased the miscibility between rigid and flexible segments, which leads to a material with a relatively higher homogeneity at elevated temperature. The increase in miscibility has also been confirmed by TEM microscopy—Fig. 5.6.

Thermogravimetric analysis of the obtained hybrid ionomers under inert atmosphere showed the beginning of the decomposition process at a temperature of 270 °C, regardless of the content of POSS in the polymer. The authors linked the first stage of thermal degradation of the material with the distribution of elastic segments, whereby in the second stage starting at ca. 350 °C, the rigid segments are decomposed. These results indicate that the presence of silsesquioxane in polyurethane does not significantly increase the polymer resistance to thermodegradation under inert conditions. In the oxidizing atmosphere, nanohybrid polyurethane is more stable at high temperatures compared to the unmodified polymer, and there is more solid (char) residue after decomposition.

Hybrid coatings based on polyurethanes/polyhedral oligomeric silsesquioxanes were investigated by Lai et al. [36]. Hydroxy-terminated polybutadiene (HTPB), isophorone diisocyanate (IPDI), and *trans*-cyclohexane diolisobutyl-POSS were used as precursors for the hybrid coatings which were spin-coated to form films. Electrochemical characteristics showed that the PU/POSS hybrids offer very good corrosion protection. In comparison with the value for the untreated aluminum alloy

(AA) ($2.48–8.22\times10^{-3}$ Acm^{-2}), the measured corrosion electric current (I_{corr}) value decreased significantly for the PU/POSS hybrids on the AA (1.24×10^{-6}–7.61×10^{-8} Acm^{-2}) and was lower than that of the PU film on AA ($1.32–1.37\times10^{-5}$ Acm^{-2}). The result obtained can be explained by the formation of denser hybrid films that were less susceptible to localized pitting.

Hu et al. [37] synthesized POSS molecule with two functional amino groups—3-(2-aminoethylamino)propylheptaphenylPOSS (AA-POSS). Incorporation of AA-POSS to polyurethane matrix causes changes in water uptake and contact angle. With an increase of AA-POSS content, the lower water uptake was observed from 13.6 to 3.2 wt% for pristine PU and PU/POSS (4 wt%), respectively. It was postulated that POSS migrates to the surface, thus preventing the solvent molecules to penetrate into the interior, as well as POSS molecules, as highly hydrophobic, lower the polymer surface–water interactions. DSC data showed increase of Tg from 75 °C (for reference PU) to 99 °C for PU containing 12 wt% of silsesquioxane; chemical incorporation of rigid POSS moieties effectively hinders the macrochains motions. The enhanced thermal stability of AA-POSS-modified polyurethanes, as found by TGA, could be caused by suppressing the molecular mobility of polyurethane chains by bulky POSS substituents which provide additional heat capacity, thereby stabilizing materials during the thermal degradation process.

Nanohybrid-segmented polyurethanes were obtained through solvent-free polymerization in mass by Janowski et al. [38]. 1-(1-(2,3-dihydroxypropoxy) butyl)-3,5,7,9,11,15-isobutyl-pentacyclo [9.5.1.1.(3.9).1(5.5).1(7,13)] octasiloxane (PHI-POSS), 4,4′-diphenylmethane diisocyanate (MDI), 1,4-butanediol (chain extender), and polyoxytetramethylene diol (PTMG) with an average molecular weight of 1000, 1400, and 2000 (soft segment) were used. Schematic route of polyurethane-/POSS-segmented elastomers synthesis is shown in Fig. 5.7.

Thermo (oxidative) stability of novel PU/POSS nanohybrids was investigated by thermogravimetry (TG) [39]—the highest thermal stability, both of inert and oxidative atmosphere, have the PU containing 4 and 6 wt% of PHI-POSS. Temperatures of maximum rate of degradation, defined as the first maximum in DTG curve (T_{DTGmax}), were shifted toward higher temperatures for polyurethanes containing 6 wt% of PHI-POSS (PTMG 1000) and for all nanohybrids based on PTMG 1400. In case of PTMG 2000, a slight decrease of T_{DTGmax} was observed. The results obtained suggest that there is a restricted molecular mobility of PU macrochains in the presence of POSS and reduction of rate of volatile products' emission. Lewicki et al. [40] investigated mechanisms by which POSS influences the molecular dynamics and phase separation behavior of both the hard- and soft-block segments. Different solid NMR techniques were used to probe the segmental dynamics of a model elastomeric system that incorporates POSS (at a range of loadings) into the elastomer hard block. NMR characterization of these novel systems has shown that the incorporation of POSS significantly alters the dynamical behavior of the soft-block interphase region and may be negatively impacting the crystalline order of the nanostructured hard-block domains. The obtained NMR data strongly suggest that at comparatively low polyol molecular weights, where overall phase separation is less favorable, there is an increase in the rigid domain fraction with increasing POSS loadings.

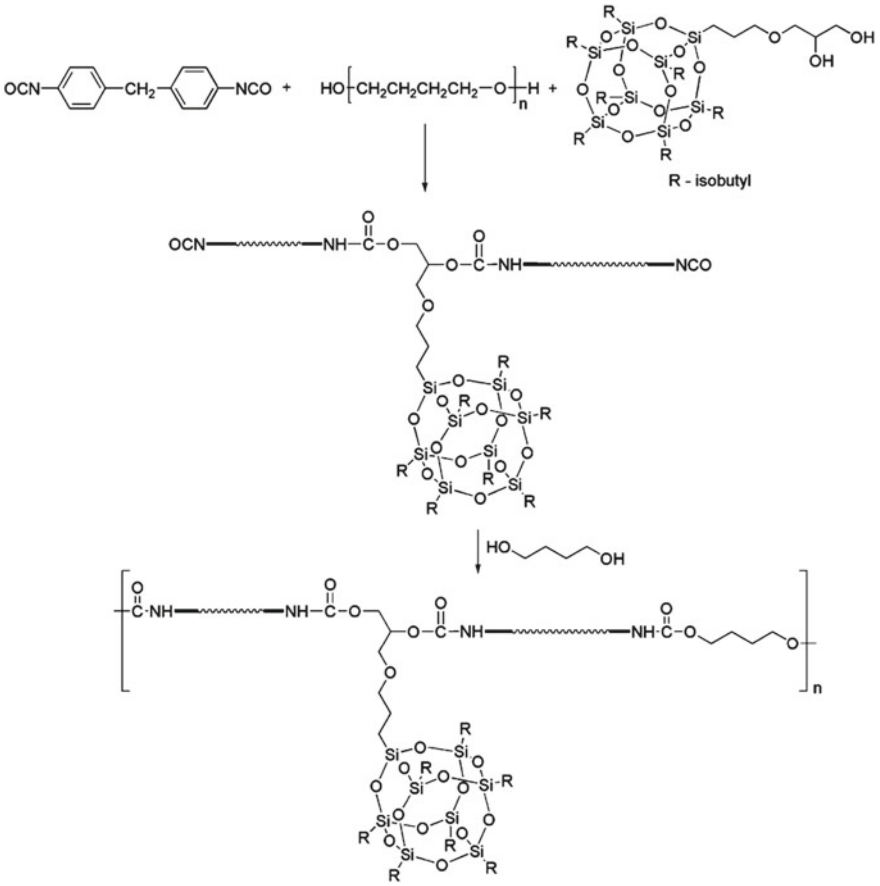


Fig. 5.7 Schematic presentation of the synthesis route for PU-/POSS-segmented elastomers [38]

Raftopoulos et al. [41–43] investigated morphology of a series of PHI-POSS/PU hybrid materials on the basis of poly (tetramethylene glycol) as the soft component, 4,4′-diphenylmethane diisocyanate and 1,4-butanediol as chain extender. AFM measurements indicate the formation of POSS crystallites in the PU matrix, with extended structures at low POSS content and more regular structures at higher POSS content. Figure 5.8 shows lateral force AFM images for polyurethanes with POSS content 4 and 10 wt%. For the PU hybrids with smaller filler content, the POSS molecules aggregate to nanometer-size longitudinal crystallites (about 60–70 nm in length) (Fig. 5.8, top), which form spherulites of several microns average sizes (Fig. 5.8, bottom left). At higher filler content (10 wt%), POSS forms more regular crystallites of ca. 120 nm size diameter (Fig. 5.8, bottom right). PHI-POSS displays tendency to form crystallites in the PU matrix, such as extended structures for lower POSS content and more regular structures for the higher silsesquioxane load (PU10).

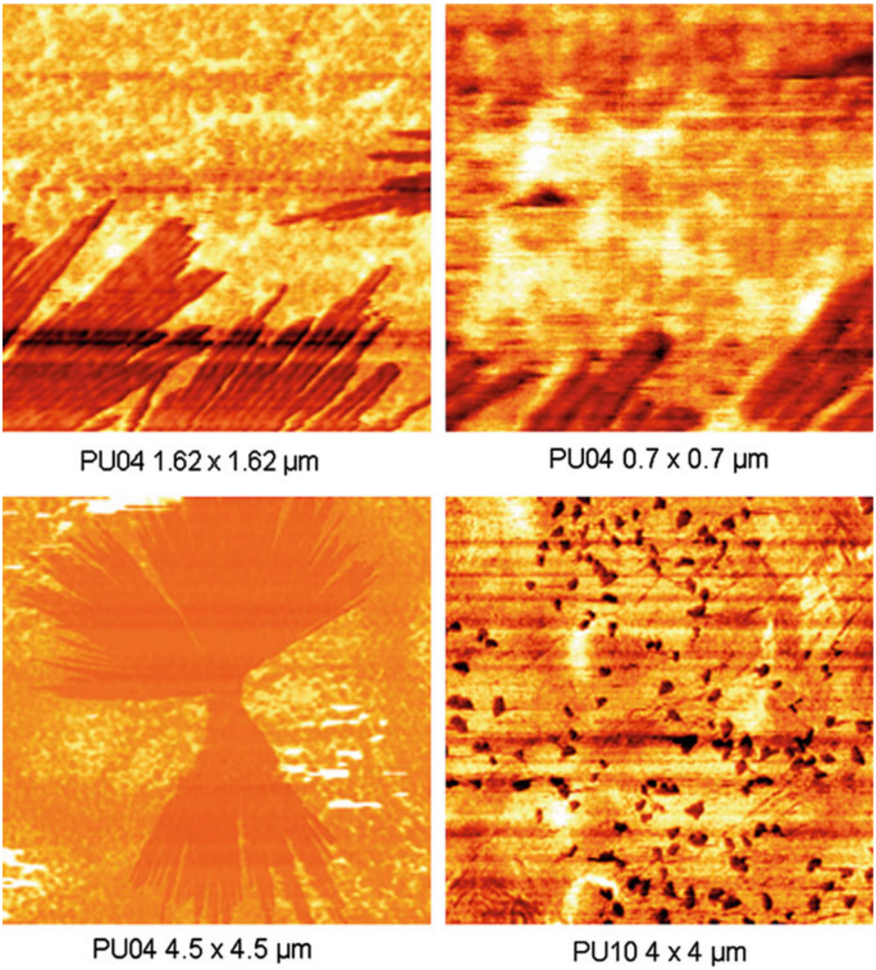


Fig. 5.8 Lateral force atomic force microscope images for PU04 (area 1.62 × 1.62 µm, top left; 0.7 × 0.7 µm, top right; 4.5 × 4.5 µm, bottom left) and for PU10 (4 × 4 µm, bottom right) [41]

The unique POSS cage structure, vast functionalization possibilities, and ease of their chemical incorporation into polymer matrices are the key factors deciding about silsesquioxanes application in the biomedical field. The main features that allow the medical use of POSS additives are biocompatibility, biodegradability, cytological compatibility, as well as no toxicity and thermodynamic stability [44–46].

Recently, numerous works have been devoted to polycarbonate-based materials with POSS molecules built in as pendant groups in the main chain [47–49]. The presence of POSS in the polymer chain results in increased mechanical strength and thermal stability [50]. The hybrid composites are also much more resistant to enzymatic and oxidative biodegradation [51]. Moreover, they suffer from calcination to a much lesser extent than unmodified polycarbonate urethane [52]. Through the incorporation of POSS, a continuous, porous matrix is formed, with a pore size of 150–250 μm [53], which turns out to be an excellent substrate for propagation and cell differentiation [50]. Materials of this kind do not degrade in a living organism, so they can be a better substitute for silicones [54].

Kannan et al. patented a nanocomposite polymer based on poly(carbonate–urea)urethane (PCU) with *trans*-cyclohexanediolisobutylsilsesquioxane as a pendant group [55]. Further developments include poly(carbonate–urea)urethane (PCU)/POSS hybrids for potential use in cardiovascular bypass grafts and as microvascular components of artificial capillary beds [56–58]. A POSS-PCU blood vessel implant with controlled porosity was obtained by foaming extrusion, applying $NaHCO_3$ as the blowing agent [59]. The obtained materials were found to show better resistance to hydrolysis and oxidative degradation, as well as viscoelasticity similar to that of the biological vessels [60, 61]. The PCU-POSS hemocompatibility was also tested, and it was found that silsesquioxane molecules repel platelet and fibrin adsorption because of their variable surface tension, and on a vascular interface, they would contribute to the increased thromboresistance [62–64]. Moreover, POSS cages are thought to exhibit optimal cytocompatibility [65].

Improved biocompatibility and biostability against oxidation, hydrolysis, and enzymatic attack under in vitro and in vivo conditions [66, 67] led to the design of the first artificial heart valve made of PCU-POSS nanocomposite [68]. Surface thrombogenicity and mechanical failure of polymeric heart valves are primarily associated with the choice of valve material. Polymer thicknesses of 100, 150, and 200 μm were selected to investigate the mechanical properties and the suitability of these nanocomposites for valve leaflet application. The mechanical test results (Table 5.1) showed that the tensile strength of POSS-PCU increased as compared to PCU. The Young’s modulus of POSS-PCU was significantly greater in comparison with the control PCU for 100 μm thickness.

POSS-PCU showed no significant difference in tear strength compared to PCU. In addition, POSS-PCU demonstrated comparable tear strength to the commercially available PU materials (Table 5.2).

Since PCU/POSS nanocomposites possess excellent mechanical strength, good surface properties, and resistance to platelet adhesion, they were used to design prototype of an artificial heart valve—Fig. 5.9.

In the course of other studies, Ghanbari and colleagues [69] proved that the presence of POSS compounds in the PCU/POSS nanocomposite reduces the tendency of PCU to calcification and thus extends the duration of use of these materials in vivo.

PCU/POSS hybrid nanocomposites were utilized by Chaloupka et al. [70] for fabrication of lacrimal ducts. Different manufacturing techniques were applied to develop a small diameter conduit for the lacrimal duct reconstruction. The aim was to obtain a conduit with distinct outer and inner wall surfaces, characterized by controlled porosity forfacile integration and regeneration into native surrounding tissue.

Table 5.1 Summary of tensile strength, elongation at break, and tear strength for POSS-PCU (100, 150, and 200 μm thick) and control (100 μm thick PCU) at 25 and 37 °C [68]

Temperature (°C)	Thickness (μm)	Tensile strength (N mm^{-2})	Elongation at break (%)	Young's modulus (N mm^{-2})	Tear strength (N mm^{-1})
25	Control (100)	33.8 ±2.**1**	649.3 ±15	9.1 ±0.9	49.0 ± **1**.3
	100	53.6 ±3.4**	704.8 ± 38	25.9 ±1.9**	50.0 ± **1**.2
	150	54.0 ± 3.2	745.9 ± $10.7^{\#}$	24.9 ± 0.4	55.6 ± 6.4
	200	55.7 ± $1.7^{\#}$	745.8 ± $14.7^{\#}$	17.3 ±0.3*	56.8 ± 3.5
37	Control (100)	24.8 ±3.4	683 ± 62.5	8.4 ±0.5	54.7 ± **1.0**
	100	55.9 ±3.9**	762.7 ± 19.3	26.2 ± 2.0**	50.9 ± 3.3
	150	55,6 ±2.4	845.4 ±21.0^{*}	23.0 ±1.4	56.2 ± **1**.8
	200	31.0 ±0.6*	852.4 ± 4.7*	15.9 ±0.2*	63.4 ± **1**.5*

Data are presented as mean ± SEM, $n = 5$
*$P < 0.05$ compared to 100 μm thickness
**$P < 0.01$ compared to respective control
$^{\#}P < 0.01$ compared to respective thickness at 37 °C

Table 5.2 Mechanical properties of commercially available PU-based polymers and PCU/POSS [68]

Polymer	Hardness (Shore A)	Tear strength (N mm^{-1})	Tensile strength (N mm^{-2})	Elongation at break (%)
Estane® (PEU)	85	55	48.3	570
Chronoflex® C	80	45	37.9–45.5	400–490
Elasteon™	75–90	50–80	20–30	500–750
POSS–PCU	84	50 ± 1.2	53.6 ± 3.**4**	704.8 ± 38

It was found that by using cast PCU/POSS for the inner wall, formation of scar tissue is prevented and drainage is secured. This wall can thereafter be covered with a coagulated layer allowing suturing of the conduit to the residual lacrimal duct and preventing implant displacement.

The research on PCU/POSS nanocomposites was also carried out by Bakhshi et al. [71] As biocompatibility of PCU containing silsesquioxane is much better than this of nickel and titanium alloy used for shape-memory stents fabrication, an attempt was made to electrohydrodynamically sputter of organic–inorganic hybrids on metallic stents. The peel strength of the deposit was studied before and after degradation of the coating. It has been shown that the surface modification increases the peel strength by 300%. It was also shown how the adhesion strength of the PCU/POSS coating changes after exposure to physiological solutions composed of hydrolytic, oxidative, peroxidative, and biological media. Interestingly, it turned out that NiTi alloys coated with the PCU/POSS layer undergo integration with the stent after long-term (70 days) exposure to biological environments. The applied polymer coating also increases the corrosion resistance. Antithrombogenic properties have also been

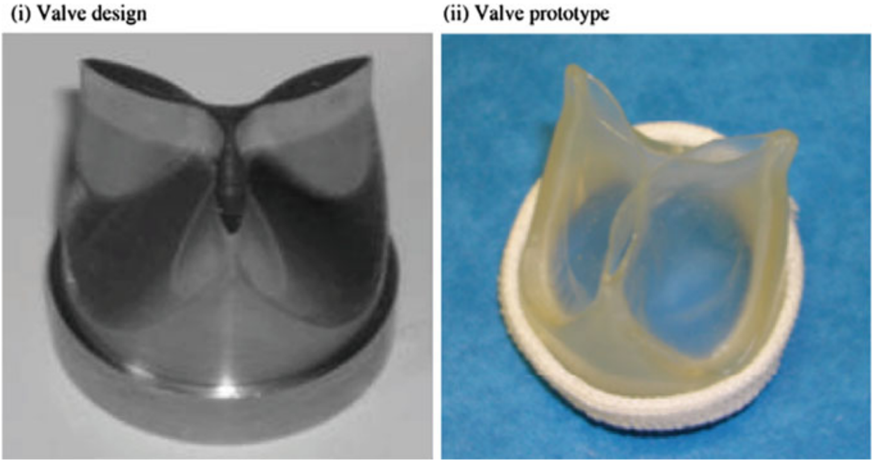


Fig. 5.9 Synthetic heart valve (i) design and (ii) prototype made with the POSS-PCU nanocomposite polymer developed at UCL and currently under investigation [68]

obtained, and facilitated endothelialization has been observed [72, 73]. Coating of NiTi alloys with poly(carbonate–urea)urethane/POSS layer extends the service life of metallic stents by about 10 years [74].

2.2 POSS Incorporated in the Main Chain

The process of obtaining polyurethanes with POSS cores incorporated in the main chain was studied by Oaten and Choudhury [75]. An open cage POSS with three functional hydroxyl groups (trisilanol) was used, and the synthesis of hybrid polyurethane relied on the direct reaction between an aliphatic diisocyanate (HDI) and trisilanolisobutyl-POSS in toluene, catalyzed by dibutyl tin dilaurate (DBTL). The transparent PU-POSS thin films obtained were used as a protective barrier to cover steel. The ^{29}Si NMR and angle-resolved (AR-XPS) investigations showed that PU-POSS forms a 3-D network which consists of polymer chains cross-linked through urethane bridges and due to condensation of free silanol groups from POSS units. Hydrogen bond interactions of the amide groups in the urethanes and the long-range hydrophobic interactions of the hexamethylene and isobutyl groups contribute to the lamellar structure formation—Fig. 5.10. Thermogravimetric studies revealed a three-stage decomposition of the polymers obtained. The first stage begins at a temperature of 200 °C and is related to the breakdown of urethane bonds and degradation of isobutyl groups of trisilanol. The second stage, starting at 415 °C, and the third stage, commencing at 470 °C, are related to the thermal degradation of the Si-O bonds of the silsesquioxane. DSC studies in combination with photoacoustic Fourier transform infrared spectroscopy (PA-FTIR) have revealed the formation of a silica

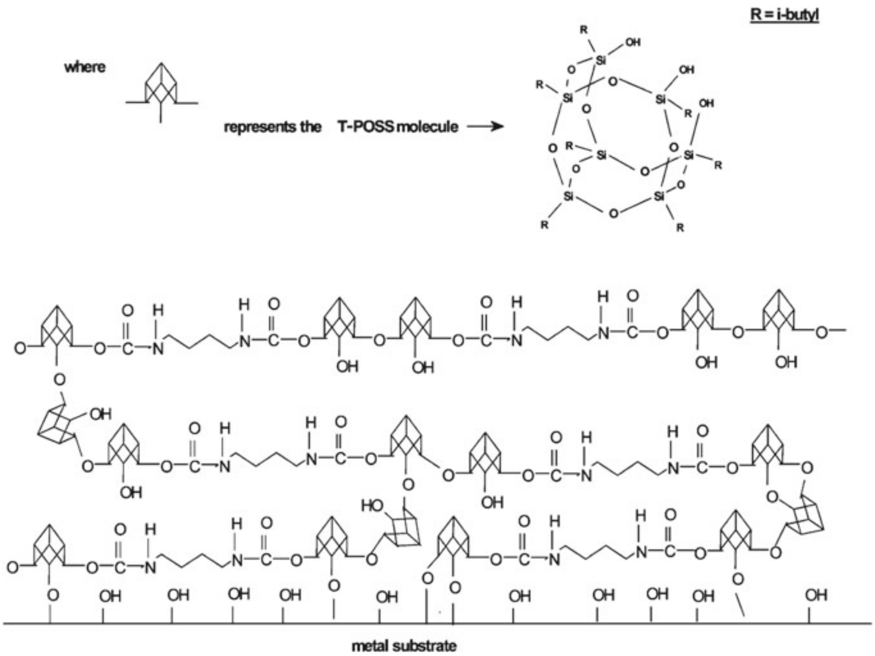


Fig. 5.10 Proposed structure of the hybrid thin film on steel [75]

layer that protects the material onto which the hybrid polyurethane was applied prior to thermal degradation.

Pistor et al. [76] described the effect of isobutyl trisilanol POSS on the crystalline structure of thermoplastic polyurethane. POSS nanocages introduced in the polyurethane matrix tended to form aggregates, and an increase in the rate of crystal formation was observed with the increase of POSS content in the PU matrix. At the content of 1.14 wt% of POSS, there was one crystallization stage, leading to formation of smaller crystals in the form of disks. With an increase of the POSS load, two stages of crystallization occurred. In the first stage, disks were created, while in the second stage, spherulites were formed—Fig. 5.11. The obtained results confirm that POSS nanoparticles have a strong influence on the crystallization mechanism.

Pan et al. [77, 78] obtained polyurethane/trisilanolisobutyl polyhedral oligomeric silsesquioxane (PU/TSI-POSS) hybrid composites using MDI and glycerol propoxylate as the PU components. The chemical structure of TSI-POSS and the synthesized hybrids are shown in Fig. 5.12.

X-ray diffractograms showed that by increasing the content of TSI-POSS in polyurethane matrix (above 22 wt%), larger cluster-like crystallites are formed in rigid segments, increasing thus their volume. Glass transition temperature of hybrid composites was found to increase with TSI-POSS content. Due to the presence of isobutyl groups in the TSI-POSS, which are sensitive to oxygen, a reduction in the

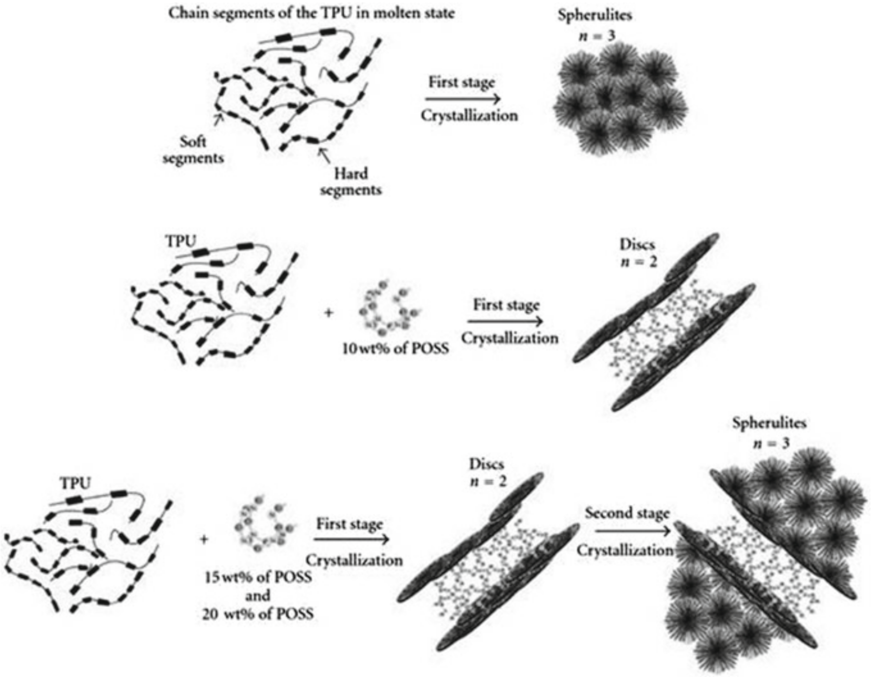


Fig. 5.11 Schematics for the PU and the nanocomposites nucleation and crystal growth phenomena [76]

decomposition temperature of the PU/TSI-POSS composites was observed with an increase of POSS content in the polymeric material [79, 80].

Our research group [81] incorporated disilanol isobutyl-POSS (DSI-POSS) in a PU synthesized using PTMG, MDI, and BD. The obtained hybrid materials were studied toward molecular dynamics behavior, and it was found that incorporation of DSI-POSS does not exert any significant effect on Tg, indicating that incorporation of POSS is practically not affecting the mobility of the soft phase. MDSC results revealed three distinct regions—the first weak and broad endotherm at ca. 70 °C has been associated with the disruption of ordering of short MDI-BD sequences or glass transition of hard segmental microdomains. The next endotherm around 170 °C was due to the main phase separation effect. The last peak commencing at ca. 250 °C was attributed to the thermal decomposition process. By utilizing pyrolysis-GC/MS and DSC methods, we have also studied the effects of DSI-POSS on the mechanisms of thermal degradation of polyurethane matrix [82]. The results of analytical pyrolysis assays of the polyurethane systems demonstrated that low levels of POSS substitution (<10 wt%) lead to a significant increase in both the onset temperature of thermal depolymerization and a reduction in the yield of volatile degradation products [83].

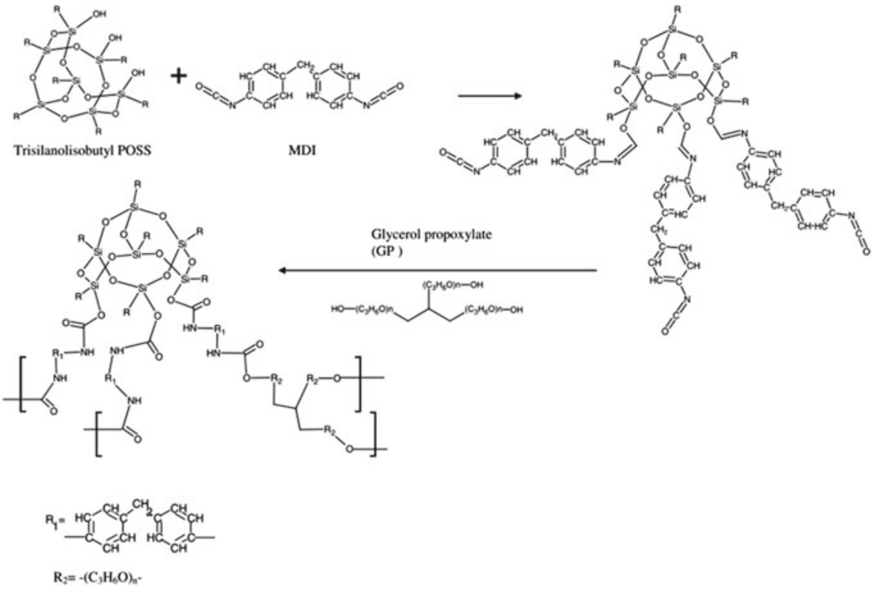


Fig. 5.12 Chemical structures of TSI-POSS monomer and PU/TSI-POSS–hybrid composites [77]

2.3 POSS in a Polyurethane Network Node

POSS can also be used as cross-linkers in polymeric systems. This is accomplished through the functionalization of POSS with eight identical groups that may react to form materials with a high cross-link density. Functional groups that have been employed in the preparation of cross-linked hybrid materials are epoxy, amine, methacryloyl, vinyl, alkyl halide, and hydroxyl groups. Neumann et al. [83, 84] synthesized POSS with eight –NCO groups, using hydrosilylation of octakis (dimethylsiloxy) octasilsesquioxane. As the cross-linking agent, POSS reacted with poly(ethylene glycol) to form cross-linked polyurethane. Nuclear magnetic resonance (^{29}Si NMR) showed that the cage structure of POSS was not damaged after chemical incorporation in the PU matrix [85].

Liu and Zheng [86, 87] used octaaminophenyl polyhedral oligomeric silsesquioxane as a cross-linking agent and 4,4′-methylenebis-(2-chloroaniline) to prepare polyurethane networks containing POSS. DMA investigations showed that in the glassy state ((−75)–(−25) °C), the dynamic storage moduli of all the POSS-containing hybrids are significantly higher than that of the control PU. The TGA results indicated that the thermal stabilities of the nanocomposites were improved, as evidenced by the rate of volatile release from the materials and the enhanced char yields together with ceramic yields. Moreover, contact angle measurements showed that the organic–inorganic nanocomposites with POSS displayed a significant enhancement in surface hydrophobicity. Significant nanoscale reinforcement effect of the POSS cages on the polyurethane matrix and the formation of robust structure of the POSS-containing PU networks were postulated to be the main reasons for properties enhancements caused by silsesquioxanes moieties [88–90].

A functional N-phenylaminomethyl POSS was synthesized by Zhang and coworkers [91] and then used as a cross-linker for polyurethane elastomers—Fig. 5.13. The obtained PU-POSS elastomers showed no macrophase separation up to 52 wt% of POSS load. HRTEM images revealed a well-separated nanostructure of POSS with a typical phase size of 5–10 nm. The storage modulus (DMA), T_g, DSC, and Young modulus (tensile test) were increased with increasing POSS concentration. Thanks to good compatibility of POSS and PU, a cross-linker could be dispersed in PU matrix in nanoscale, restricting efficiently polyurethane chains mobility. As POSS concentration further increased, the cross-linking density also increased, and, when POSS concentration reached 26 wt%, a permanent network was formed.

The same authors studied the process of gelation of cross-linked PU-POSS composites at various curing temperatures, times, and POSS concentration [92]. After the completion of the curing reaction, the critical concentration of POSS beyond which the gelation of PU-POSS composites happens was found around 2.5 wt%. In the materials between 2.7 and 6 wt%, formation of self-similarity network near the critical gel occurred. This revealed that different structures were formed, which are shown in Fig. 5.14.

A new class of ester–amine-functionalized silsesquioxane macromers, synthesized by Madhavan et al. [93–96], was introduced into the polyurethane matrix. DSC showed that the glass transition temperature corresponding to the hard segment increases with an increase in the POSS-amine content as POSS rigid cubes restrict the free rotation of the macromolecular chains. The contact angle measurements revealed its increase with the increase of POSS-amine load for all hybrid materials. This was due to formation of granular POSS aggregates of highly hydrophobic nature on the PU surface. Moreover, permeability coefficient decreases with an increase the POSS concentration, and the selectivities of O_2/N_2 and CO_2/N_2 gas pairs increased with an increase in the POSS concentration.

Hu et al. [97, 98] used octa(aminopropyl) silsesquioxane (OapPOSS) for functionalization of graphene sheets (GO) via amide group formation between the amine groups at the eight vertices of POSS and the oxygen-containing groups of graphene oxide. The obtained functionalized graphene (OapPOSS-GO) was used to reinforce waterborne polyurethane (WPU) to obtain OapPOSS-GO/WPU nanocomposites by in situ polymerization. Morphological studies using field emission SEM (FESEM) showed a faster OapPOSS-GO development in the polyurethane matrix compared to GO and OapPOSS. It may be explained by a synergistic effect: The OapPOSS grafted onto the GO surface can lead to a large interlayer spacing, providing effective physical interactions such as van der Waals forces and hydrogen bonds, thus resulting in a better dispersion; on the other hand, OapPOSS-GO surface can provide abundant amine functional groups for grafting PU chains, thus introducing covalent bonds between OapPOSS-GO and PU chains through in situ polymerization. In addition, a significantly better hydrophobicity was achieved for OapPOSS-GO/WPU (contact angle values of ca. 94^o) compared to the GO/WPU and OapPOSS/WPU matrix.

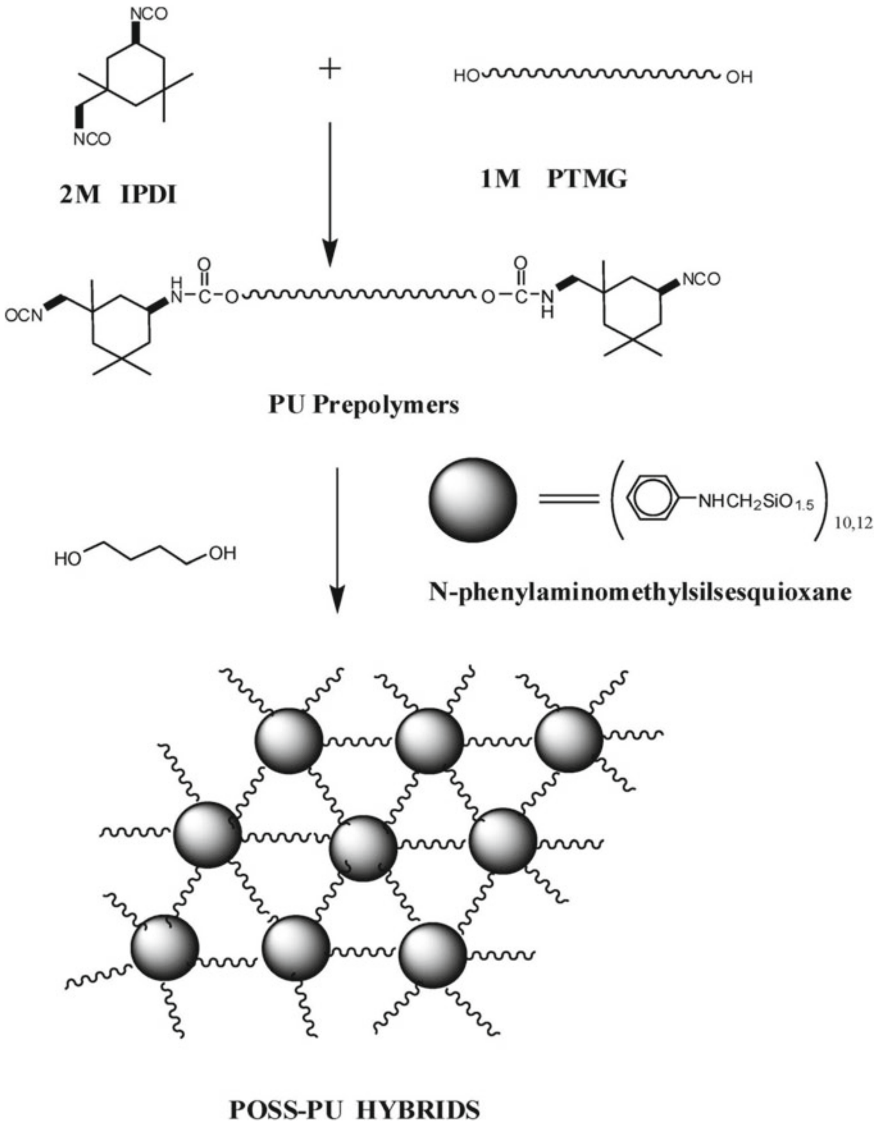


Fig. 5.13 Synthesis of PU-POSS hybrids [91]

Hybrid polyurethane elastomers with octakis [m-isopropyl-α, α’-dimethylbenzylisocyanatodimethylsiloxy]octa silsesquioxane (NCO-POSS) were synthesized by Prządka et al. [99] using IPDI and polyoxypropylene triol. The obtained polyurethane hybrids showed an increase in the M100 module (stress at 100% of the relative elongation) (Fig. 5.15) up to 2.5% mass of NCO-POSS and decrease above this concentration of silsesquioxane.

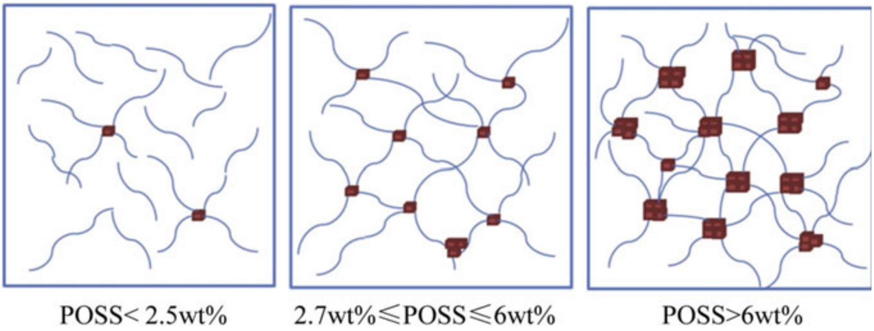
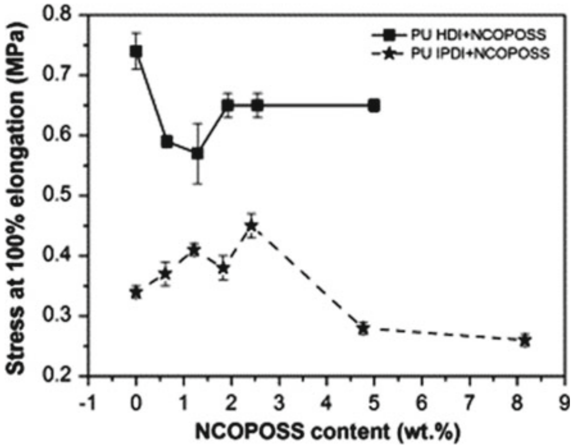


Fig. 5.14 Schematic diagram of PU-POSS composites at different POSS concentration. Cubics represent the POSS; lines represent the strands between POSS [92]

Fig. 5.15 Stress of hybrid polyurethane materials at 100% elongation as a function of NCO-POSS content [99]



NCO-POSS added in a small amount caused an increase in polyurethane stiffness, while its larger load led to excessive cross-linking, which disturbed the formation of hydrogen bonds with carbonyl groups, causing lower separation of rigid and soft segments and consequently reduction in the mechanical properties of polyurethane composites [100–103].

Star-shaped polyhedral oligomeric silsesquioxane-polycaprolactone-urethane hybrid materials were obtained by Teng et al. [104, 105] who used POSS with eight organic, functional arms chemically bonding to the polymer matrix. By incorporating organic groups in the core through extension with PCL and cross-linking with PU, organic–inorganic nanocomposites with enhanced cell attachment profile and biodegradability could be synthesized [106, 107]. The PCL-PU-POSS films revealed a high porosity of >75% and intrinsic nanoscale features that enhance cell attachment and growth. They exhibited negligible weight loss during the initial 24 weeks of degradation, followed by a large increase in the weight loss of 18% in the following 28 weeks. As cell viability is still maintained at >95%, even after 48 h of incubation with the by-products of degradation, one can consider these hybrid materials to be promising candidates for scaffolds in tissue engineering.

Star-like PU hybrid films using functional cubic silsesquioxanes (CSSQ) (with up to eight reactive sites at the corner of POSS) were developed by Mya et al. [108, 109] Octakis-(dimethylsilyloxy) silsesquioxane isopropenyldimethylbenzylisocyanate (OS-PDBI), and octakis-(dimethylsilyloxy) hydroxypropyl silsesquioxane (HPS) were prepared by hydrosilylation reaction and used as nano-cross-linkers. Additionally, different types of PU hybrids were also prepared by using OS-PDBI macromonomer with hexane diol (HD) monomer. AFM images showed that no phase separation in the macroscopic level occurs for PU hybrid films and incorporation of CSSQ in PU structure provides enhanced thermal stability and increased cross-link density, as revealed by TGA and DMA results. Moreover, the presence of cage structure improved oxidation resistance and mechanical strength.

Pielichowski's group [110] incorporated into polyurethane elastomer octa-OH-functional POSS as a relatively massive and robust three-dimensional cross-linking core—Fig. 5.16. The influence of this cross-linking moiety on the morphology and molecular dynamics of the PU system was studied. AFM images for a polyurethane matrix showed numerous globules and spherulites of rigid segment domains dispersed in a flexible continuous phase with dimension 3–6 μm. After introducing the POSS molecules embedded as nodes of the polymer network, the globules sizes have decreased, and they assumed more spherical shapes ranging from 10 to 300 nm. On the phase images of hybrid elastomers with POSS, rigid spherical structures with softer center were observed. These new structures have been interpreted as forms consisting of POSS molecules connected to MDI, which have become soft cores surrounded by rigid segments. Additionally, despite extensive chemical cross-linking, the rubbery mechanical modulus decreased on addition of POSS, confirming that hard microdomains reinforce the matrix to a greater extent than chemical cross-links [111].

Blattmann and Mülhaupt [112] reported on the synthesis of novel multifunctional polyhedral oligomeric silsesquioxane (POSS) cyclic carbonates and their cure with diamines to produce POSS/NIPU nanocomposites with variable POSS content—-Fig. 5.17.

Authors found that Young's modulus and tensile strength were improved with an increase of POSS content as a result of higher cross-link density and silica content. Moreover, the incorporation of POSS considerably improved scratch resistance of optically transparent and colorless NIPU/POSS coatings as evidenced by the surface gloss and SEM images.

A series of NIPU coatings was prepared by Liu et al. through the ring-opening polymerization of rosin-based cyclic carbonate with amines, then the NIPUs were modified with epoxy and cyclic carbonate-functionalized POSS to form NIPU/POSS coatings [113]. Incorporation of POSS moieties into the NIPU networks caused an improvement in thermal stability, water tolerance, and pencil hardness of the hybrid coatings with an increase of the POSS content, whereby the impact strength, adhesion, and flexibility of the coatings were not observed to be affected to a significant extent. In an another development, this research group has obtained biomass-based

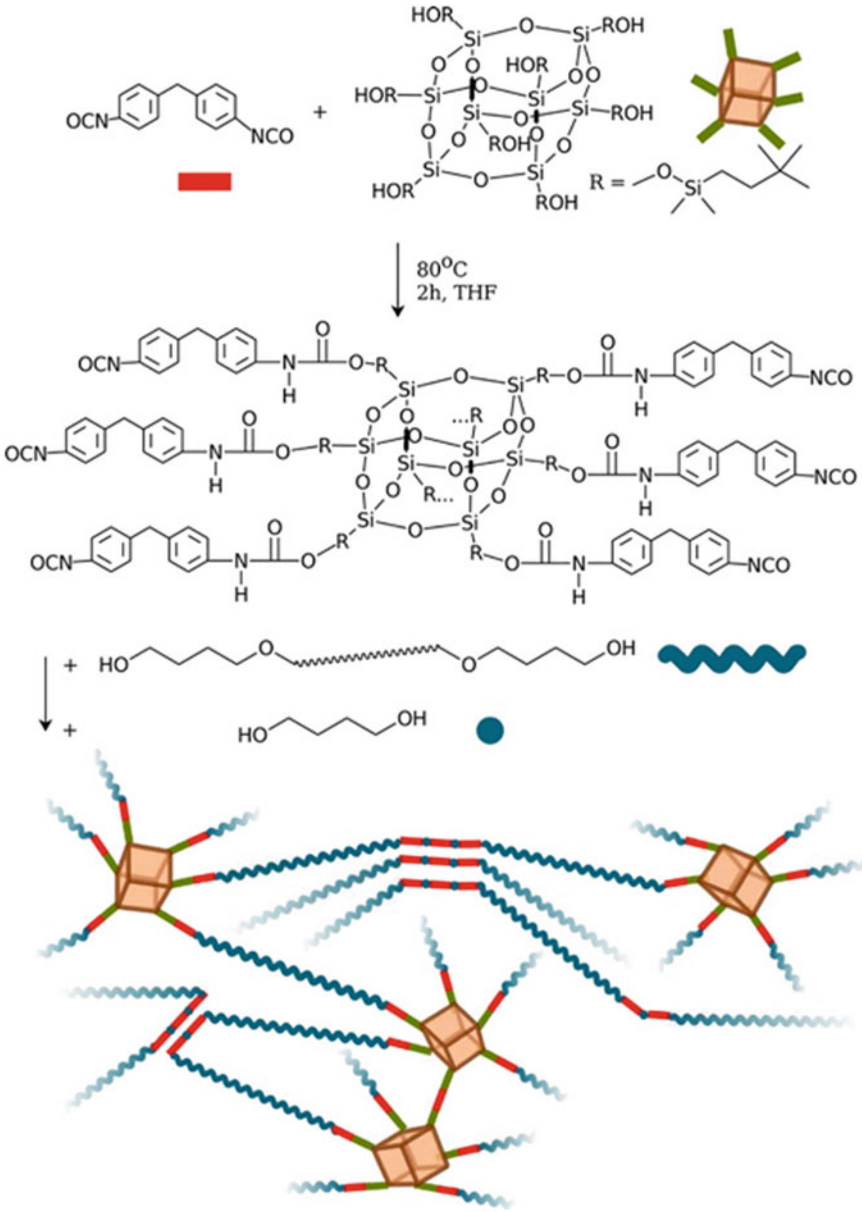


Fig. 5.16 Reaction route and sketch of the anticipated complex network. Some links have been omitted for clarity [110]

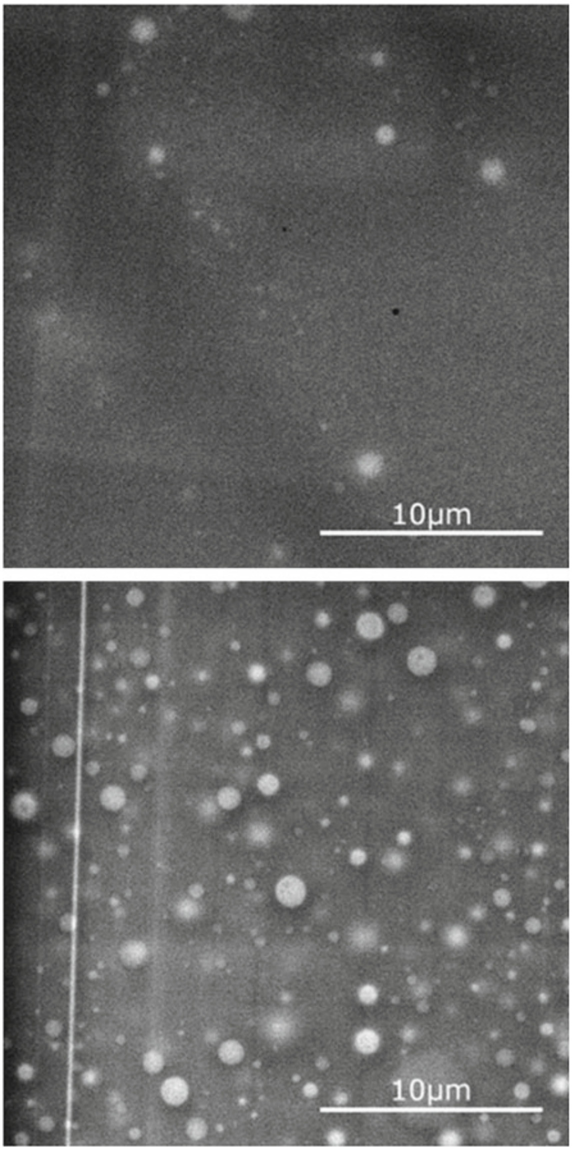


Fig. 5.17 SEM images of NIPU hybrid materials; SEM samples were obtained from NIPU specimens for tensile testing using the cryomicrotome technique [112]

NIPU coatings via the reactions of gallic acid-based cyclic carbonate with diamines which were then modified with epoxy-functionalized POSS to form NIPU/POSS coatings with chemically linked POSS groups [114]. The results revealed that the gallic acid-based NIPU coatings show excellent impact strength, adhesion, flexibility, pencil hardness, and thermal stability, but are suffering from low water resistance. Incorporation of POSS into the NIPU networks enhanced the pencil hardness, water

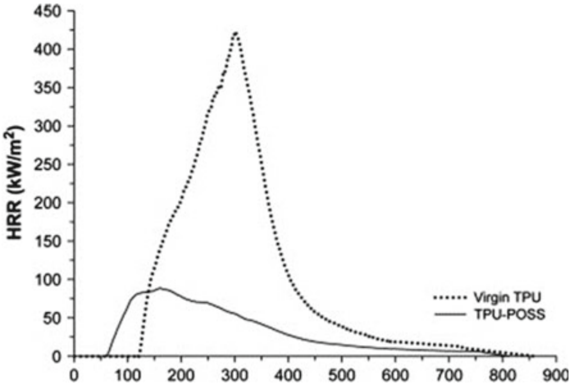


Fig. 5.18 Heat release rate (HRR) as a function of time of virgin TPU compared to TPU-POSS composite (external heat flux = 35 kW/m^2) [116]

resistance, and thermal stability of the NIPU/POSS coatings; however, the adhesion of the coatings was slightly decreased.

3 Physical Blending

Incorporation of POSS through physical blending offers several advantages, such as ease of processing, versatility, being fast, and cost-effective. The successful dispersion of POSS into polymeric matrices depends on the surface interactions of POSS, such as van der Waals and hydrogen bonding, with polymers [115–117]. However, interparticle interactions often result in the aggregation of POSS particles which may be a serious technological problem [118]. Polyurethane and POSS can be blended by using a solution or melt method [85].

Bourbigot et al. [119] reported on the preparation of POSS-containing composites based on PU by melt blending. Thermoplastic polyurethane was mixed with 10 wt% of poly(vinylsilsesquioxane) using a Brabender mixer running in nitrogen flow at 50 rpm for 10 min and at 180 °C. In the TEM image obtained at smaller magnification (17,000x), POSS particles were visible evenly dispersed in a thermoplastic polyurethane. At high magnification (30,000x), it turned out that POSS tended to create aggregates with micron size probably formed in the melt during processing. The silsesquioxane particle size was in the range of 200–400 nm, and the particles had an ellipsoidal shape.

Figure 5.18 shows a large reduction of the maximum peak of heat release rate (PHRR) in thermoplastic composites from 430 to 80 kW/m^2 as compared to pure TPU. The intumescent material has been found to be composed of ceramified char made of silicon network in a polyaromatic structure. This intumescent PU nanocomposite acts as a thermal barrier at the surface of the substrate limiting thus the heat and mass transfer as evidenced by lowered HRR [85, 120].

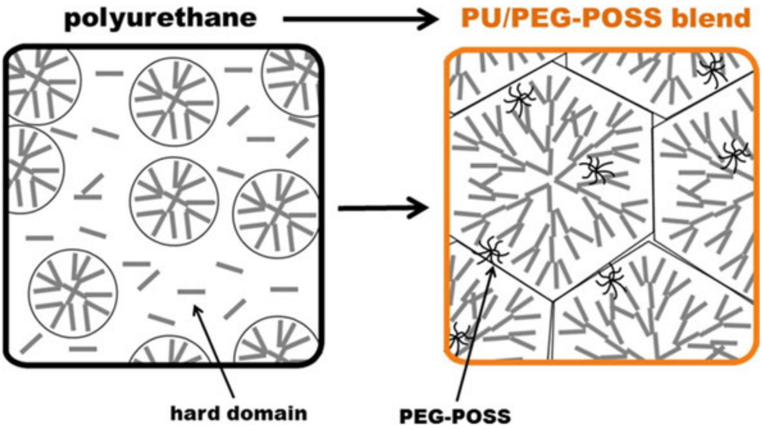


Fig. 5.19 Sketch of the mesostructure and organization of the microstructure of the reference polyurethane (left) and the PU/PEG-POSS blend (right) [120]

Reactive blending was applied by Montecelli et al. too [121]. to prepare polyurethane/POSS hybrids As a result of controlled scission of the thermoplastic polyurethane, isocyanate functional groups are formed during melt mixing, which react with OH groups in the functionalized POSS molecules: octaisobutyl POSS or *trans*-cyclohexanediolisobutyl POSS. These systems were prepared for mixing at 220 °C under the inert atmosphere for 10 min. The morphology studies using TEM microscopy revealed that there is no segregation or aggregation of POSS particles in TPU/POSS-OH (5 wt%), thus indicating that POSS-OH has chemically reacted with the polymer. DSC data showed an increase in glass transition temperature with increasing POSS content in TPU matrix from −48 °C for pristine TPU to −37 °C for TPU/POSS-OH (10 wt%).

Gu et al. [122] introduced octa(3-hydroxypropyl) polyhedral oligomeric silsesquioxane (POSS-$(OH)_8$) into ester-based thermoplastic polyurethane matrix by solution blending. The obtained composites displayed glass transition temperature around −25 °C, which can be used as trigger temperature of the shape-memory recovery. Moreover, they showed high shape fixity and shape recovery ratios with low trigger temperature.

Blended hybrid systems of PU with POSS having eight poly(ethylene glycol) (PEG) vertex groups (PEG-POSS) were prepared and characterized by Pielichowski's group [123]. The main change induced by the PEG-POSS is a plasticization effect which is observed by lowering the glass transition temperature. AFM and SEM analyses showed that hard segments form spherulites, and their size increases with the increase of POSS content. No POSS aggregates are observed while the storage modulus (DMA) in the rubbery phase decreases in the blends. This change in morphology, combined with the softening of the material on addition of POSS, suggests decreased microphase separation in polyurethane. Based on the results obtained, microstructure morphology development has been postulated—Fig. 5.19.

4 Application of PU-POSS Hybrid Materials

Hybrid materials by combining the features of organic and inorganic matter offer advantageous properties for different materials science applications. One of the application areas is polyurethane/POSS materials with controlled gas transport properties, as well as multilayer membranes [94, 124]. Specifically, by using amino-POSS to modify PU matrix, a reduction in permeability was achieved. The O_2/N_2 permeability and CO_2/N_2 permeability could be controlled by the POSS load and the PU structure [75]. It was postulated that bulky POSS moieties located on the polymer surface hinder transport of gas molecules. Moreover, POSS substituents influence formation of ordered crystalline structures [95, 124].

Hybrid thermally stable materials [38, 119, 125, 126], as well as materials with high dielectric constant, resistant to creeping currents [127], are considered as potential candidates for future applications. For instance, incorporation of PHI-POSS into polyurethane matrix composed of MDI and polytetramethylene glycol caused an increase in temperatures at which the degradation rate was the highest and a decrease in the intensity of emission of volatile decomposition products. This is most likely related to the reduced mobility of polymer chains in the presence of chemically linked POSS molecules [38]. Octaminophenyl-POSS (OapPOSS), added to epoxy-imine-polyurethane resins, caused an improvement in the heat resistance and in the Young’s modulus values [125].

POSS nanoadditives were tested toward flame retardancy behavior of various polymers, and the best synergistic effects were found for a combination of conventional flame retardants with silsesquioxanes [126]. POSS mode of action includes preventing the fire by creation of ceramic, fire-resistant char layer on the surface of the burning material [116].

Special attention is focused on protective polymeric materials with POSS—due to good adhesion and improved durability, an effective protection against corrosion [128] and weathering effects has been reported [129]. Incorporation of POSS moieties into the polymer chain resulted in increased compressive strength [130], stretching [26], and improved thermoplasticity [128]. By using octaphenyl and glycidoxypropyl-POSS in the polyurethane matrix, glues with improved adhesion and shear strength could be obtained [131, 132]. Moreover, POSS nanofillers have been successfully used to obtain novel aerogels [130, 133] and shape-memory composites [134].

POSS modified polyurethane materials can also be used as high-strength coatings. The electrochemical and salt spray test evaluation of the PU films demonstrated the barrier and corrosion resistance properties improved by the POSS. The low current density over a wide potential indicated that the PU/POSS film provided an effective barrier to water. Additionally, the POSS components retain their partial cage structure, which give the product a high glass transition and enhanced thermal stability as compared to conventional polyurethanes, which is essential in their application as weatherable coatings [135, 136]. PU/POSS show also potential as flame retardants in textile coatings applications [137]. The unique POSS cage structure, non-toxicity, and ease of properties control decided on the use of silsesquioxanes in the biomedical field. The main features that determine the medical applicability of POSS-containing materials are biocompatibility, biodegradability, cytological compatibility, and dimensional stability, as well as the already-mentioned no toxicity. Vast attention was paid to polycarbonate urethane-based (PCU) materials with POSS embedded in the main chain [138–140]. An increased mechanical strength and thermal stability [138], as well as better resistance to enzymatic and oxidative biodegradation, compared to pristine polymer, were reported [142]. Importantly, it was also found that PCU/POSS composites undergo calcination to a much lesser extent than non-modified polycarbonate urethane [69]. Through the incorporation of POSS, a continuous, porous matrix is formed, with a pore size of 150–250 μm [143], which turns out to be an excellent substrate for propagation and cell differentiation [141]. Materials of this type do not degrade inside mammalian organisms; therefore, they can be considered as a replacement for silicones [54, 144].

In general, research works on PCU/POSS hybrids are focused on three groups of biomaterials—blood vessel implants, lacrimal canal implants, and scaffolds that help regenerate tissues in the nervous system [142, 145]. As the fabrication route foaming extrusion proved to be a useful technique, enabling control of the porous structure formed [58].

Promising path is covering of shape-memory stents, made of nickel and titanium alloy (Nitinol), by electrohydrodynamic sputtering of PCU/POSS hybrids [70]. The layer formed shows antithrombogenic properties and facilitates endothelialization process [57, 71]. Noteworthy, Nitinol coating with POSS-containing polymer layer extends the usefulness of stents by about 10 years [74].

Another use of PCU/POSS materials in medicine is as scaffolds. These are mostly cell scaffolds capable of trapping cells and facilitating the creation of new tissues, such as RGD peptide (arginine-glycine-aspartic acid)-grafted PCU [146, 147]. The obtained materials are currently in the phase of clinical trials, and it is possible that they will initiate a new generation of scaffolds capable of regenerating nerves to a larger than 30 mm barrier. Using cell scaffolds, it is also possible to treat liver [148] and brain damages [149].

Materials containing POSS and nanotubes that can be used in the treatment of serious diseases are also of great interest. In this case, the nanotubes are coated with the PCL/POSS composite to ensure a biocompatible surface. Such materials exhibit strong near infrared absorption, emitting large amounts of thermal energy, and can be used for destruction of cancer cells [150].

5 Conclusions

In this work, diverse and significant research on polyurethane/POSS–hybrid materials has been presented. Two major routes of silsesquioxanes incorporation into polyurethane matrix—via chemical or physical path, leading to various organic–inorganic architectures, have been described. The crucial role of POSS functionalization in the synthesis and during processing of polymers was highlighted. POSS moieties in nanohybrid polyurethanes influence the crystallization process of polymer matrix, leading to formation of stable morphological forms. The aggregation or crystallization behavior of POSS in nanocomposites plays an important role in manipulating the physical properties of materials, such as viscosity and melt elasticity. It is also important to limit the segment vibrations by large POSS substituents, which increases the glass transition temperature. There is also the possibility of occurrence favorable second-order interactions between macrochains containing POSS in their structure. The described polyurethane-POSS systems, due to their special properties, can find numerous applications, such as membranes, high-strength coatings and adhesives, aerogels, flame retardant materials, and shape-memory materials. The unique POSS cage structure, its non-toxicity, and broad functionalization possibilities make them useful modifiers for polyurethanes devoted to biomedical applications.

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