Rubbers Reinforced by POSS

Anna Kosmalska and Marian Zaborski

Abstract In this chapter, a brief account of the recent researches on the properties of POSS-containing polymeric materials, i.e., polyurethanes, resins, and thermoplastics, has been done. On this background, rubbers, generally known as elastomers, have been presented as an important class of polymers and a very essential material in industry due to their unique properties. The general characteristics of elastomers and the common classification of different types, including general-purpose, special-purpose, and specialty elastomers, together with the relevant examples, have been described. To extend service life, reduce cost and therefore improve service efficiency of elastomeric materials, various fillers have always been extensively used in the rubber industry and are addressed in the chapter. Particular attention has been given to POSS. The influence of POSS moieties in rubber matrix on the functional properties of the composites fabricated is discussed. Attempt has been made to explain the role of POSS surface functional groups in controlling the properties of POSS-containing materials, and the reinforcement mechanism is presented.

Keywords Rubber · Elastomer · Reinforcement · Filler · Silsesquioxanes · POSS

1 Introduction

Polyhedral oligomeric silsesquioxane (POSS) nanoparticles have attracted much attention recently due to their nanometer size, the ease of which these particles can be incorporated into polymeric materials and the unique capability to reinforce polymers. Summing up briefly the literature review, it follows that research on the use of silsesquioxanes to obtain polymeric materials with interesting and valuable properties is largely related to polyurethanes (PUs), as well as resins and thermoplastics, mainly polyethylene (PE), polypropylene (PP), polystyrene (PS), polyamide-6

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[1–6]. In such systems, silsesquioxanes usually play the role of nanofillers, cross-linking coagents or compatibilizers, and the materials obtained with their use show improved mechanical and thermal properties.

Silsesquioxanes, depending on the structure and functional groups, change the surface properties of these materials. Due to small amounts of POSS in polyurethanes (3%), a significant increase in surface hydrophobicity and reduction of surface energy was observed [7]. Such behavior may contribute to corrosion protection of POSS-modified polymers or influence the adhesion forces with other materials [8]. In the case of polyurethanes (PUs), modification with POSS, both through chemical reactions and physical mixing of the components, leads to polymer strengthening at the molecular level. As a result, the obtained composite materials are characterized by better hardness than the base polymer and resistance to scratches, tensile strength, heat resistance, gloss, and quality (in the case of coatings) [9]. The reduction in the emission of volatile degradation products clearly demonstrates the increased thermal stability of polyurethanes, as well as other hybrid polymeric materials containing POSS [10].

Another group of materials showing significant improvement of properties, due to the POSS addition, are resins. A clear increase in the thermal stability of epoxy resins can be considered as the result of two main elements coupling: achievement of the degree of POSS dispersion at the nanometric scale and interactions between the matrix and POSS cages to form the aromatic structure [11]. The structures of the obtained hybrid polymers were characterized with Fourier-transformed infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM). According to Liu and coworkers [12, 13], the FT-IR spectra suggested successful bonding between POSS molecules and methyl silicone resin, followed by TEM microscopic analysis which showed the very good solubility of silsesquioxanes in the resin, at the molecular level. Furthermore, the increase of decomposition temperature and oxidation resistance in these materials is related to the formation of an inorganic layer of SiO_2 (also called in the literature as the “ceramic layer”) preventing further degradation of the resin.

Polymeric materials based on thermoplastics are also characterized by new or improved physicochemical parameters. In such systems, the modification of the matrix is usually carried out using conventional processing techniques, such as mechanical melt blending or by in situ polymerization [14, 15]. In thermoplastics, especially polystyrene (PS), poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA), silsesquioxanes are often used as effective and efficient plasticizers [15]. Though, the effect depends, among others, on the type of POSS functionalization, the amount in which it is incorporated into the polymer matrix, as well as the nature of the host chains. Hence, POSS has been also proved to be effective nucleating agents of isotactic polypropylene (iPP) and high-density polyethylene (HDPE). A number of studies have been published revealing, that the inclusion of octamethyl-POSS at different loadings, depending on the host, can significantly promote nucleation rate of iPP or HDPE to increase (or retard) the crystallization processes, that were tested under various conditions, such as isothermal or non-isothermal cooling, quiescent or shear states [16–19].

Typically, mixing POSS into a thermoplastic polymer affects the increase in hardness and the mechanical properties are generally improved as well. An increase in the glass transition temperature may be also observed, probably resulting from segmental mobility reduction due to relatively large POSS molecules. Furthermore, decomposition temperature and resistance to oxidation, as well as the network density, are also increased [20]. Studies describing the effect of POSS on flame retardancy of PP [21] and reduction of viscosity of HDPE under processing conditions have been published as well [22].

Also, research on the effect of silsesquioxanes in the field of modeling the surface character of thermoplastic nanocomposites obtained with their participation was described. As a rule, POSS molecules, especially POSS functionalised with fluorine or containing nonpolar groups, increase hydrophobicity. However, nanocomposites based on polyamide-6 (PA6) were also obtained, in which silsesquioxanes used in higher concentrations, act as surfactants, and, on the contrary, increase the hydrophilicity of the surface of the hybrid materials obtained [23].

The scope of research involving the use of POSS in order to modify and improve the properties of elastomers is somewhat less diverse and extensive than in the case of the polymers mentioned above. The patented results largely concern the use of silsesquioxanes in elastomers for needs of the tire industry and to a lesser extent the use of POSS to modify the properties of common synthetic elastomers. Among the available literature of the subject, there are a significant number of papers describing a positive influence of POSS on the polysiloxane characteristics, which due to their unique properties have found broad application in many branches of industry. In most cases, however, available data concern silicone rubbers cross-linked at room temperature (RTV type) [24, 25], showing the features and range of applications different to a large extent than high-temperature cross-linked silicone elastomers.

Different example may be, for example, new hybrid materials based on thermoplastic elastomers (TPEs), which are also readily described recently. Combining nanometer POSS molecules with such copolymers, of multifunctional properties and showing advantages typical of both rubbery and plastic materials, may result in the novel inorganic–organic materials with a unique combination of properties and thus being useful in a variety of demanding technological fields. These hybrid materials may gain many unique advantages by bridging the space between inorganic materials (rigidity, high thermal stability, and unique optical, electronic or magnetic properties) and organic matrix (flexibility, strength, and processibility) [26–28]. More detailed description of POSS-containing thermoplastic elastomers (TPE/POSS) is given in the further section of the chapter.

Nonetheless, the research area regarding developing of POSS-containing elastomeric materials and their properties remains therefore interesting, both from a scientific and application point of view, and still encourages the intensification of research in this area.

2 Elastomers and Rubber—General Characteristics

Elastomers are a group of polymers that, over a wide range of temperatures, usually from about −70 °C up to 60 °C, exhibit the ability to large deformations of a reversible nature, reaching up to 1000%, i.e., they are in the so-called state of high flexibility. According to the standards, "*elastomer*" is defined as a macromolecular substance, which undergoes significant deformation under considerable stress and, after its removal, returns quickly to the initial dimensions and shape [29]. The proposed definition is not strict, especially that elastomers commonly include rubbers, cross-linked rubbers, and rubber mixtures (rubber compounds), as well as cross-linked rubber compounds, commonly referred to as "*rubber*" (in the common sense as "*gum*"). And so, the terms rubber and elastomer may be used interchangeably. As in the case of the terms, rubber composition (or mixture), compounded rubber, and rubber compound, that are used interchangeably as well, to refer to rubber which has been blended or mixed with various ingredients and materials.

Non-cross-linked block copolymers, containing rigid domains of one of the components, show the state of high elasticity, fixed in elastomers as a result of the spatial network formation. From the aforementioned materials, primarily the following reveal the technical significance: "*rubber*" and thermoplastic rubbers (TPE), while the cross-linked rubbers and latexes—to a lesser extent.

There are plenty of different rubber types available but still the largest single type used is natural rubber (NR) produced of latex from the tree *Hevea Brasiliensis*. The synthetic types of polymers, mainly manufactures from oil, have been developed either to replace or to be used together with NR or to make polymers with properties superior of NR in special areas, typically with better high-temperature resistance, better outdoor resistance and/or resistance to fuels and oils. A common classification of different types of rubber includes general-purpose elastomers, special-purpose elastomers, specialty elastomers. Each type comprises the rubbers presented in Table 1.

General-Purpose Rubbers mean polymers which, in their processability and mechanical properties, meet the requirements of the main application areas and which are also sufficiently cheap. Therefore, they have good physical properties, good processability, and compatibility, are generally economical, and are typical polymers used in tires and mechanical rubber goods with demand for good abrasion resistance and tensile properties. They constitute the largest volume of polymer used [30]. Today inexpensive hydrocarbon rubbers belong to the group of general-purpose rubbers, including both polymers and copolymers of butadiene, isoprene and styrene (SBR, NR, BR, IR). The hydrocarbon rubbers EPDM and IIR are classified among rubbers for special purposes.

Special-Purpose Rubbers have all unique properties which cannot be matched by the general-purpose types and are very important for manufacturing of industrial and automotive rubber products. Table 2 shows the classification of rubbers according to their distinct properties through which they surpass the general-purpose rubbers.

Table 1 Common classification of different types of rubber

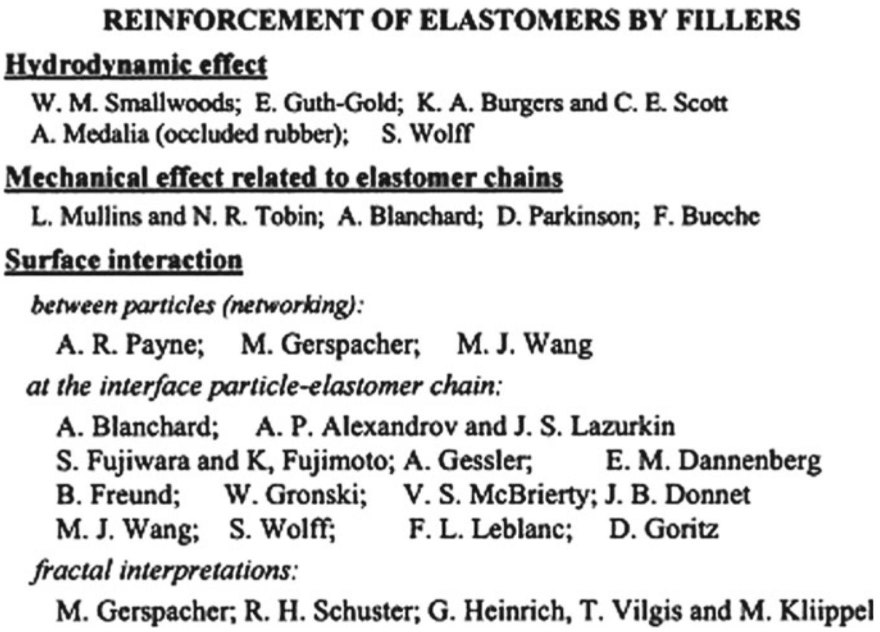
General-purpose rubbers	Natural rubber (NR) Polyisoprene rubber (IR) Styrene-butadiene rubber (SBR) Butadiene rubber (BR)
Special-purpose rubbers	Ethylene propylene rubber (EPM and EPDM) Butyl rubber (IIR) Chloroprene rubber (CR) Acrylonitrile-butadiene rubber or nitrile rubber (NBR) Polysulphide rubber (T)
Specialty rubbers	Chlorosulfonated polyethylene (CSM) Acrylic rubber (ACM) Silicone rubber (MPQ/MPVQ/MQ/MVQ) Fluorosilicone rubber (MFQ) Fluorocarbon elastomers (FPM/FFKM/FEPM, CFM) Polyurethane rubber (AU/EU/PUR) Epichlorohydrine rubber (CO/ECO/GECO)

Table 2 Classification of rubbers according to their specific feature

Description/special-purpose	Rubber
Oils and hydrocarbon liquid-resistant	NBR, CO, ECO CR, CSM ACM, T FKM, CFM
Chemical-resistant	CR, CSM IIR, EPDM, EPM FKM, CFM
Heat-resistant	CSM, NBR (up to 120 °C) IIR(vulcanized with resins), EPDM, EPM (140-150 °C) ACM (150–170 °C) MQ, FKM, CFM (above 200 °C)
Low temperature-resistant	EPDM, BR MPQ
Ozone-resistant	IIR, EPDM, EPM CR, NBR/PVC CSM, CO, ECO, ACM MQ, FKM, CFM

The *Speciality Rubbers* are a great number of polymers with very special properties, in many cases of great importance for the automotive-, aircraft-, space-, and offshore industries, as well as for medicine.

Thus, rubbers, generally known as elastomers, have been an extremely useful and essential class of materials since time immemorial. Typical properties of pre-cross-linked elastomers are low glass transition temperatures and low secondary forces.



REINFORCEMENT OF ELASTOMERS BY FILLERS

Hydrodynamic effect

W. M. Smallwoods; E. Guth-Gold; K. A. Burgers and C. E. Scott
A. Medalia (occluded rubber); S. Wolff

Mechanical effect related to elastomer chains

L. Mullins and N. R. Tobin; A. Blanchard; D. Parkinson; F. Bucche

Surface interaction

between particles (networking):

A. R. Payne; M. Gerspacher; M. J. Wang

at the interface particle-elastomer chain:

A. Blanchard; A. P. Alexandrov and J. S. Lazurkin
S. Fujiwara and K, Fujimoto; A. Gessler; E. M. Dannenberg
B. Freund; W. Gronski; V. S. McBrierty; J. B. Donnet
M. J. Wang; S. Wolff; F. L. Leblanc; D. Goritz

fractal interpretations:

M. Gerspacher; R. H. Schuster; G. Heinrich, T. Vilgis and M. Kliippel

Fig. 1 Reinforcement of elastomers by fillers. Reprinted from [57], © 2003 with permission from Elsevier

These polymers, to behave as “*rubber,*” require macromolecular chains to be partially interconnected by chemical bonds and to the most extent conformationally entangled.

They are then chemically cross-linked, most frequently by sulfur or peroxides. Cross-linking gives elastomers their strong mechanical and elastic properties. However, a cross-linked elastomer in its own does not qualify to the accurate performance requirements for many applications. To meet these requirements and reveal its valuable and unique functional properties, particularly viscoelasticity, it must be homogeneously blended with comparatively rigid components offering high surface to volume ratio, known as “reinforcing fillers” [29, 31, 32]. The phenomenon of “*reinforcement,*” which is related to very important properties in the practice, may thus be defined by the improvement of mechanical properties of the compounds, notably the strength properties, hardness and stiffness, abrasion and tear resistance and hence improvement of their service life. Although the theories of the reinforcement have been diverging and Fig. 1 recalls the main proposals considered in this matter, it is usual to accept the Payne proposals illustrated in Fig. 2.

Fillers are therefore used to make the elastomers applicable in various fields and to result in the manufacture of varieties of composites. They impart high elastic moduli and durability for the elastomers, which were always limiting their practical usage. Fillers, generally, improve the poor mechanical condition of neat elastomers. The exception is natural and chloroprene rubber, which even when not filled are characterized by good strength.

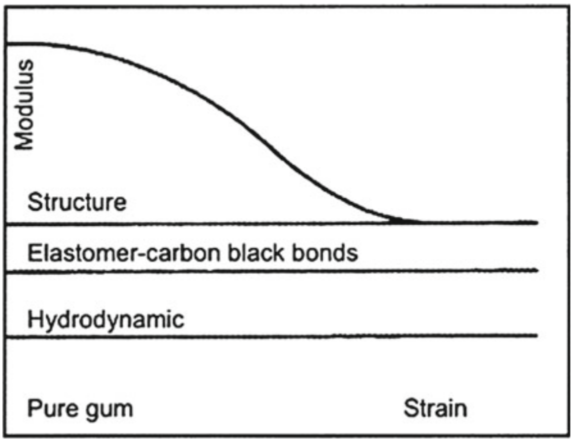


Fig. 2 Contributions to the stiffening effect. Reprinted from [57], © 2003 with permission from Elsevier

A whole range of substances, organic or inorganic, characterized by an appropriate degree of disintegration, has been used for this purpose. They exhibit different reinforcing capacity in relation to the rubber, depending on the size of rubber–filler interactions, measured by the size of the solid-phase surface and interactions at the interface.

A brief overview of the fillers used for elastomers is presented in the following section.

3 Fillers for Elastomers—General Characteristics

As it was mentioned above, a large number of diverse substances, both organic and inorganic, are added to the elastomers as the fillers. Particulate of them is added for mechanical reinforcement, the others for electrical or thermal conductivity modification, and ease of processing. Mineral fillers are known to improve the strength and stiffness of rubbers. However, the extent of property enhancement depends on various factors, such as the size and shape of the particles, filler aspect ratio, degree of dispersion and orientation of particles in the matrix and the interfacial adhesion between filler and polymer chains [33]. In general, it is said that the filler–filler [34–36] and the filler–rubber interactions [37] cause better reinforcement.

The most important group of fillers for elastomers consists of various types of carbon black (CB), followed by synthetic silicas and silicates. However, CB remains the predominant reinforcing filler, especially for high-performance elastomers (which means a type of elastomers, which are characteristic of high tensile strength, high tear strength, and low abrasion). Therefore, CB finds the leading application in the production of rubber goods, accounting for more than 90% of total carbon black consumption. In 2010, use in tires accounted for 73% of world consumption, with other rubber goods (hoses, belts, etc.) accounting for an additional 19% [38].

Other substances that have been used in the rubber technology are also such as kaolin, calcium carbonate, talc, magnesium carbonate, barium sulfate, diatomaceous earth, ebonite dust and some polymers, such as novolak phenolic resins, styrene-butadiene resins, polystyrene, polyethylene, isotactic polypropylene or emulsion polyvinyl chloride. The attempts have been made to synthesize hybrid carbon–silica fillers that combine the advantages of carbon black and silica [39].

Since the most conventional filler used for elastomer reinforcement, which is carbon black, is entirely dependent on the non-renewable petroleum resource, there is a growing interest and demand for research in the field of using substances derived from renewable sources as fillers for elastomers. Thus, a separate group is such fillers, which include starch, vegetable fibers, and wood flour, as well as recycled products (reclaimed rubber, or rubber powder, granulate and scrap) and products of elastomers pyrolysis (mainly carbon black).

Starch is of great potential due to its limitless source and friendly environmental processing. But the basic problem is its destructuring, and unfortunately, the previous research indicates an unsatisfied reinforcement by starch [40–45]. Buchanan et al. prepared styrene-butadiene rubber (SBR) composites by a co-precipitation procedure, but the mechanical property improvement was not as good as expected (the tensile strength was only improved from 2.6 to 6.3 MPa with 10 phr of zinc starch). Nevertheless, some patents in this area have been used in the technology of tread compound production [46, 47] and recent research shows different approaches to overcome this problem [48–51]. According to Qi et al. [52], starch will become an effective filler if modified properly. They described a novel starch modification for filler-reinforced elastomer, using two types of modifiers, i.e., resorcinol–formaldehyde (RF) and a silane surfactant (S). Originally used as a curing agent for rubber vulcanization, the RF was applied to interact with starch and rubber and thus improved the interface.

Recently, some interest was also aroused by the natural hybrid, containing in its composition also fullerenes and carbon nanotubes, called *shungite*. Shungite is a mineral consisting of silicate particles (60%) and amorphous shungite carbon (30%) with the addition of inorganic substances; it is low in cost and high in ecological safety. Usually, microdispersed (5 μm) shungite is used as a non-reinforcing filler for elastomeric materials (up to 60%) or as an additive (3–15%) to standard compositions. However, from the research published it follows, it is also of interest to investigate the possibility of using shungite, of a greater degree of dispersion, as the main filler for elastomeric materials [53–56].

Meanwhile, the most commonly and conventionally used fillers for the reinforcement of rubbers still remain particulate fillers, such as carbon black and silica [57]. Their primary particles are in the nanometer range, but they also reveal a strong tendency to form aggregates and agglomerates having size in the micrometer range. This provides a problem to overcome and often becomes a challenge when preparing rubber (and generally polymer) composites since one of the crucial factors in controlling the reinforcing effect on rubbers is the filler dispersion degree. For this reason, nanofillers, due to the small size and increased surface area, have emerged as promising fillers for improving polymer properties with only low filler loadings.

With average particle size in the range of 1–100 nm, the nanomaterials are extremely useful polymeric reinforcing agents [58].

Several types of nanofillers with different geometry, such as nanosilica, carbon nanotubes, layered silicates, graphene, metallic nanoparticles, metal oxides, and polyhedral oligomeric silsesquioxane (POSS) are used extensively in rubber composites.

Among the 1D (one dimensional, i.e., plates or layered type) fillers, the predominant role is played by montmorillonite and other natural aluminosilicates with a layered structure and products of their chemical modification (i.e., organophilization). In the case of montmorillonite, the thickness of a single plate is about 1 nm, and the remaining dimensions are in the range of 200–1000 nm. Since the clays are highly hydrophilic, as resulted from the surface charges, they show poor compatibility with a wide range of nonpolar elastomers, which subsequently causes inferior filler–polymer interaction. As a consequence, clay-filled composites reveal impaired mechanical properties when compared to the carbon black fillers. In many examples, however, the presence of nanoplatelets has a very beneficial effect on reducing the flammability of the filled material. They impede heat transfer into the composite much more efficiently than conventional fillers, increasing the initial temperature of the composite decomposition. Furthermore, clay composites exhibit improved gas barrier properties and therefore are used in many applications where they are helpful in reducing the air permeability, e.g., in tire inner liners. It is believed that the basic mechanism limiting the permeability is the increase in the so-called *path tortuosity* of fluids through the structure of the polymer nanocomposite, in relation to the corresponding microcomposite. Then, the penetrating molecules must bypass physical obstacles in the form of impermeable filler particles or polymer crystallites, which both the orientation and morphology are determined by specific interaction with the surface of the modifier. That way, the permeability of small molecules (O_2, H_2O, He, CO_2) in the polymer nanocomposite may be reduced several times with relatively low filler content, resulting in the permeability coefficient lower by approximately 60–90%. There are numerous studies on the incorporation of nanoclays into natural rubber, styrene-butadiene rubber, ethylene-propylene-diene rubber, epoxidized natural rubber, and blends thereof [58, 59].

The best-known 2D (two dimensional, i.e., nanotubes and nanofibres) fillers are carbon nanotubes and nanofibers. Carbon nanotubes (CNT) made of cylindrical graphitic sheets with fullerene end cups, depending on the structure may be single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes, having diameter ranging from 1 to 100 nm and the length up to several mm. The basic problems occurring in the synthesis of rubber nanocomposites with CNT are the tendency of nanotubes to agglomerate and create entangled, multi-fiber strands, as well as weak interactions at the interphase between CNT and the matrix. For this reason, systems containing unmodified CNTs are relatively rare. Nevertheless, the CNTs are also considered as an attractive nanofillers which add the valuable properties to elastomers. The published results indicate that the homogeneous dispersion of MWCNT throughout styrene-butadiene rubber (SBR) matrix and strong interfacial adhesion between oxidized MWCNT and the matrix are responsible for the considerable enhancement

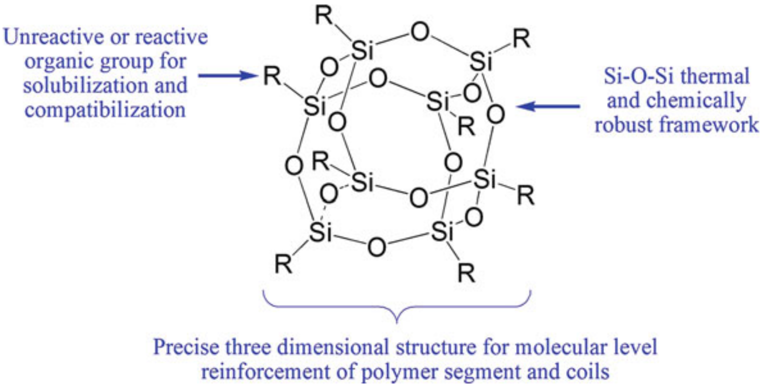


Fig. 3 POSS features. Reprinted from [65], © 2016 with permission from Elsevier

of mechanical properties of the composites. A comparison with carbon black filled SBR showed the significant improvement in Young's modulus and tensile strength by incorporating scarcely 0.66 wt% of the filler without forfeiture of SBR elastomer high elongation at break [60]. Additionally, CNTs improve the thermal as well as electrical conductivity of elastomers, that is very important in the tire industry, for example, regarding the static charge dissipation. Moreover, they provide better skid resistance and reduced tire abrasion.

Recently, graphite and its derivatives are also distinguished for their valuable properties like transparency superior barrier properties and excellent conductivity (both thermal and electrical) that make these materials a great substrate, e.g., for the production of touch screens, new generation batteries that are able to recharge within of seconds, or photovoltaic cells. High conductivity of these fillers makes them applicable in electronics for instance in sensor skins, flexible display, and in dielectric actuators.

On the background of the mentioned fillers, polyhedral oligomeric silsesquioxanes (POSS), being an example of 3D (three dimensional, i.e., nanogranules, nanocrystals, and spherical type) fillers, are excellent, high-performance materials used to modify many polymer properties, including rubbers [58, 59, 61]. They reveal combined organic–inorganic properties and are included in the group of reactive fillers, i.e., those that can be compounded with a polymer matrix by covalent or ionic bonds. This type of nanocomposites is called nanohybrid materials (Fig. 3).

Unlike most nanofillers (carbon nanotube or nanoclay), POSS molecules contain organic constituents on their external surface, which create their peculiar tailormade peripheral organic functionality that enables the preferential interactions with a variety of matrices and makes POSS nanofillers compatible with many polymers. As a result, having 1–3 nm diameter, POSS generally can enhance the service temperatures providing improved thermal stability and modifying the polymer glass transition temperature as well as decomposition temperatures. Moreover, incorporation of POSS molecules influences the rate of combustion in the event of fire, flame retardancy, heat evolution, and oxidation resistance. It is also responsible for improved dielectrical properties, surface hardening, mechanical properties, etc., to a great extent. More detailed description of diverse rubbers composites with POSS will be presented in the following sections of the chapter.

The preparation methods of polymer/POSS materials are mainly dependent on the chemical structures of POSS and polymer. Two approaches have been adopted to incorporate POSS particles into polymer matrices: chemical reactions in the molten state (melt reactive blending) and physical interactions (simple melt blending). In the chemical reaction approach, POSS nanoparticles are bonded covalently with the polymer backbone, which obviously requires a chemical reaction to occur. Then, radical grafting reaction may be applied, which is widely used especially for compatibilization of immiscible polymer blends as well as functional polymers or polymerization [6, 61–64]. Chemical reactions between POSS and polymer chains are considered to be very appealing method of new materials synthesis with controlled structure and properties, being fast, inexpensive, and environmentally friendly. There are some examples of POSS grafted with polymer chains by atom transfer radical polymerization, reversible addition fragmentation chain transfer polymerization, ring-opening polymerization, anionic polymerization, and click chemistry technique [84–90]. However, it is thought that due to the complicated synthesis and purification procedures POSS grafted with polymer chains is not expected for massive production. Farther, POSS grafted α-olefins, for example, may be good filler choice for natural rubber composites on account of molecular polarity; however, POSS grafted α-olefins are very difficult to obtain [91].

In the physical blending approach, POSS nanoparticles are physically blended with the polymer by melt mixing or solvent casting methods. The physical blending, which is more typical for preparation of rubber composites, presents several advantages as well, being the same inexpensive, fast, and versatile technology. Indeed, standard equipment used for polymer and rubber compounding, such as twin screw extruders or internal mixers, is generally suitable for the processing of nanostructured thermoplastic polymers, for example, and/or rubber composites [14, 65]. Compared to the chemical reaction approach, however, aggregation of POSS during the extrusion process is difficult to control that influences the final dispersion of POSS nanoparticles [66]. It requires the strict control of the balance between polymer and POSS interactions, as well as POSS–POSS self-interactions. Thus, to provide effective interactions, the organic groups which are chemically similar to the polymer and long enough are needed.

Although POSS nanoparticles could be incorporated into almost all the polymers by chemical reaction or physical blending, the difficulties in obtaining molecular dispersion of POSS still remain open challenge. A major role seems to be played by the balance between interactions (van der Waals forces, hydrogen bonding, etc.) between POSS and the polymer, as well as the POSS–POSS self-interactions. By the same token, the control of nanostructure and location of nanoparticles, responsible, and crucial for reinforcing effect in polymer—and/or rubber-POSS nanocomposites—is not an obvious achievement and results to be challenging issue.

4 General-Purpose Rubbers/POSS

As it was briefly mentioned in the Introduction, often the patented results concern the use of silsesquioxanes (POSS) in elastomers for needs of the tire industry [67–70].

Silsesquioxanes containing alkoxysilane groups, that can interact with silica, behave then as silica dispersing agents in the rubber. Additionally, these compounds are useful in compounding, processing, cure, and storage of silica-reinforced rubbers, especially for a pneumatic tire production, because they contain low levels of volatile organic compounds (VOC) [69]. The patent describes a modification with this type of POSS [70]. The alkoxy-modified silsesquioxane (AMS) compounds contain the alkoxysilane group that participates in alkoxysilane–silica reaction, with the release of zero to about 0.1% by weight of the rubber of VOC during compounding and further processing. Particularly, suitable rubbers for use in the vulcanized elastomeric compound of the invention, mainly include of natural rubber (NR), butadiene rubber (BR), styrene-butadiene rubber (SBR), and combinations thereof.

As a result, the vulcanized rubber compounds containing the alkoxy-modified POSS revealed enhanced rubber reinforcement, increased polymer–filler interaction and lower compound viscosity. Such alkoxy-modified silsesquioxane compounds may be successfully applied in the production of tires having improved wet and snow traction, lower rolling resistance, increased rebound, and decreased hysteresis [70].

The usefulness of using similar POSS compounds, namely amino alkoxy-modified silsesquioxanes as adhesion promoters in rubber, has been also demonstrated and patented. Amino alkoxy-modified silsesquioxanes (amino AMS) and/or amino co-AMS compounds, that also comprise a mercaptosilane or a blocked mercaptosilane, have proven to be an excellent adhesives for coating the conductive and non-conductive wires for adherence to a rubber stock. These adhesives can be used with all types of rubbers. Additionally, what is valued and important, and there is no requirement for the use of special adhesive additives to the rubber vulcanizate.

In particular, the use of amino AMS and amino/mercaptan (co-AMS) compounds as adhesives for bonding wire to the rubber also improves the adherence performance of the reinforcement. It is possible then to obtain sufficient bonding that is resistant to degradation, especially to the thermal and thermo-oxidizing aging, in particular corrosion in the presence of water [71].

The use of POSS to modify the properties of common synthetic elastomers for ordinary applications is patented to a lesser extent. An example is an invention that contains the results of research on the use of one or more polyhedral oligomeric silsesquioxanes in butadiene (BR) and styrene-butadiene rubber (SBR) [72]. The POSS compounds under study may be included in the rubber composition during mixing, as a part of the rubber compound masterbatch, or alternatively after production of the rubber compound masterbatch, as an additive. The amount of POSS, preferably included in or added, was 1–10 parts per hundred rubber (phr), more preferably 1–6 parts phr, and most preferably 2–4 parts phr.

The addition of POSS, in particular trisilanol isobutyl polyhedral oligomeric silsesquioxane, affected the cure characteristics of the rubber compositions and caused rise to a decrease in optimum cure time (T_{90}). In other words, the rubber compounds may reach 90% of cure in a shorter time and by the same token spend a shorter time in the mold before they can be removed. The obtained rubber compositions revealed improved hysteresis and physical properties after vulcanisation. The point at which the polyhedral oligomeric silsesquioxane additive is added in the mixing cycle was also important to the hardness of the compound obtained. Furthermore, the results showed also that POSS, in particular the same trisilanol isobutyl polyhedral oligomeric silsesquioxane, has the ability to modify the viscoelastic properties [72].

Nevertheless, the number and scope of patents dealing with the use of silsesquioxanes in elastomeric composites further encourage the intensification of research in this field.

Another example dealing with the application of POSS compounds to the general-purpose rubbers, concern studies on natural rubber (NR). The NR-based nanocomposites were prepared using POSS-intercalated rectorite (POSS-REC), as the nanofiller [73]. Such elastomer composites have not been studied before. Rectorite (REC) is a type of regularly interstratified clay mineral which reveals larger interlayer distance, higher aspect ratio, and better separable layer thickness compared with montmorillonite, especially organomodified rectorite (OREC). The unique structure of the filler translates into better properties of the composites produced with its use, i.e., higher thermostability, barrier property, and better dispersion in polymer matrix [74–76, 79–82]. Nevertheless, as layered silicates, in general, which are hydrophilic, likewise REC needs to be modified to improve its affinity with organic polymers. Since POSS compounds have been considered as a type of promising surfactant, they have been employed readily and widely to modify layered silicates [77, 78].

Thus, POSS with amino group was intercalated into REC to obtain POSS-REC nanofiller, which was then dispersed into NR matrix [73]. The obtained material was investigated via X-ray diffraction (XRD) and transmission electron microscopy (TEM) which revealed that the composites were obtained successfully, with a relatively even dispersion and no serious agglomeration was observed. However, due to the difference in the polarities as well as the limited shear forces, the POSS-REC nanofiller was present both in intercalated and in exfoliated state. Measurements of thermal properties indicated that the presence of POSS-REC improved thermostability of the composites. SEM observations of fracture surfaces showed that POSS-REC nanofiller could prevent primary crazes from developing into macroscopic cracking, as well as absorb energy through inducing new smaller crazing in the composites. Mechanical tests proved that the presence of POSS-REC brought about remarkable increase in the tensile strength and elongation at break. Maximum mechanical properties were at 4% content of POSS-REC nanofiller and then reduced. To conclude, according to the authors a new type of the nanocomposites obtained may have excellent prospects in the fields demanding high performances, including high-speed train and aircraft [73]. However, the amino-POSS-REC nanofiller showed relatively weak influence on the thermostability of NR composites.

Better results in this field were noted by Zhao et al. [83] and presented very recently. In this case, octavinyl-polyhedral oligomeric silsesquioxane (OV-POSS) was applied and incorporated into NR matrix. It is thought so far that OV-POSS is the most representative member of POSS family containing multiple vinyl groups. Further, it has been produced industrially for many years providing its price very attractive for engineering applications.

It was expected that as a result of POSS incorporation into NR, the co-cross-linking reaction could be triggered between NR and OV-POSS, after vulcanization, and hence, macroscopic phase separation via POSS agglomeration would be hindered [83]. Thereby, both the mechanical properties and thermostability of the vulcanizates should be improved. The co-cross-linking between OV-POSS and NR matrix may reduce the stress of the molecular chains around OV-POSS particles and increase the entropy elasticity of the macromolecular chains [92].

Morphologies of the resulted OV-POSS/NR vulcanizates, investigated with the use of scanning electron microscopy (SEM), revealed that with a relatively low loading of OV-POSS (i.e., less than 10 wt%), no distinguishable OV-POSS aggregates were detected in the NR matrix, indicating that the macroscopic phase separation can be strangled owing to the co-cross-linking reaction (Fig. 4). With OV-POSS content more than 10 wt%, some agglomerated domains with the size of 340–620 nm, attributable to POSS crystals, appeared (Fig. 4c) or even some large and vesicle-like features with the size of 4–6 μm, indicating poor miscibility, when the OV-POSS content was higher than 15 wt% (Fig. 4d, e).

The morphology and structure of the obtained vulcanizates influenced their mechanical properties, such as tensile strength, tearing strength, hardness and elongation at break. Generally, compared to the unmodified (i.e., neat) NR, the mechanical properties of the OV-POSS/NR vulcanizates were improved. Both, tensile and tearing strength were slightly enhanced with the addition of OV-POSS. The highest elongation at break was obtained at 5 wt% loading of OV-POSS, which increased by about 25% compared to that of pristine NR, however apparently decreasing with higher OV-POSS loading. Accordingly, the agglomeration of OV-POSS tends to reduce tensile and tearing strength acting as strong stress concentrators [83] (Fig. 5).

Similar relationships were observed in the case of hardness which is, in general, proportional to the cross-linking density of natural rubber vulcanizates. Thus, due to the rigid character of OV-POSS, as well as co-cross-linking reaction between OV-POSS and NR matrix, the increase of OV-POSS loading almost resulted in increase of hardness of the vulcanizates. Nevertheless, cavities of the vesicle-like aggregates could decrease hardness and at the relatively high OV-POSS loading (i.e., more than 15 wt%) hardness of the vulcanizates decreased slightly [83].

Lastly, advantageous results were achieved in the range of thermal stability of NR composites. Thermogravimetric analysis (TGA) revealed significant increase, of about 27 °C, in the onset degradation temperature (T_{onset}) for the vulcanizates modified with OV-POSS compared to the plain NR sample. With the loading of 5–20 wt% OV-POSS, the observed increase in T_{onset} was from 317 to 344 °C (Table 3). In summary, based on the properties presented in the work, the OV-POSS/NR vulcanizates could be adopted as a heat-resistant elastomeric material.

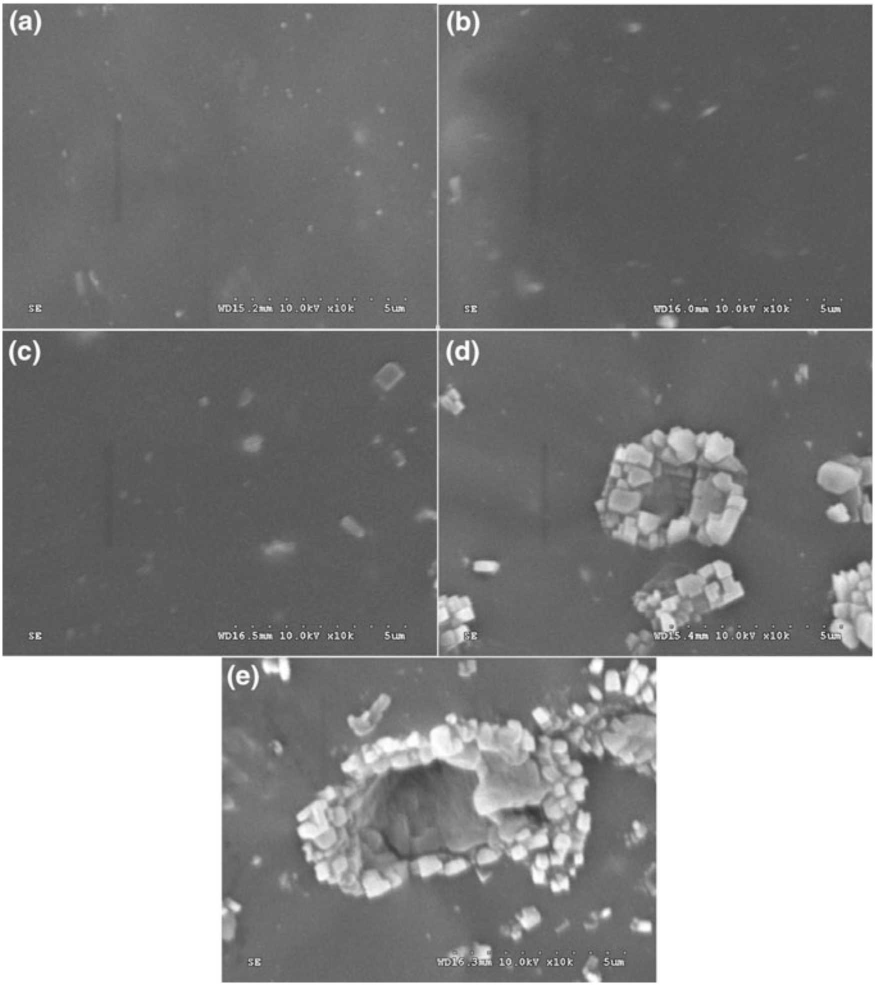


Fig. 4 SEM images of the natural rubber (NR) vulcanizates with different octavinyl-polyhedral oligomeric silsesquioxane (OV-POSS) loading (**a**) 0 wt%; (**b**) 5 wt%; (**c**) 10 wt%; (**d**) 15 wt%; (**e**) 20 wt%. Reprinted from [83], © 2017 with permission from Elsevier

5 Special-Purpose Rubbers/POSS

As mentioned at the beginning, rubbers for special purposes reveal one or more definite properties that exceed the general-purpose rubbers. The particularly relevant examples may be heat-resistant rubbers and rubbers resistant to swelling in oils and other liquids that comprise the most important subgroups of specialty rubbers (Table 2). In addition to C and H atoms in their chain, most special-purpose rubbers contain, then, other atoms, such as N, O, S, Si, Cl, Br, and F. The hydrocarbon

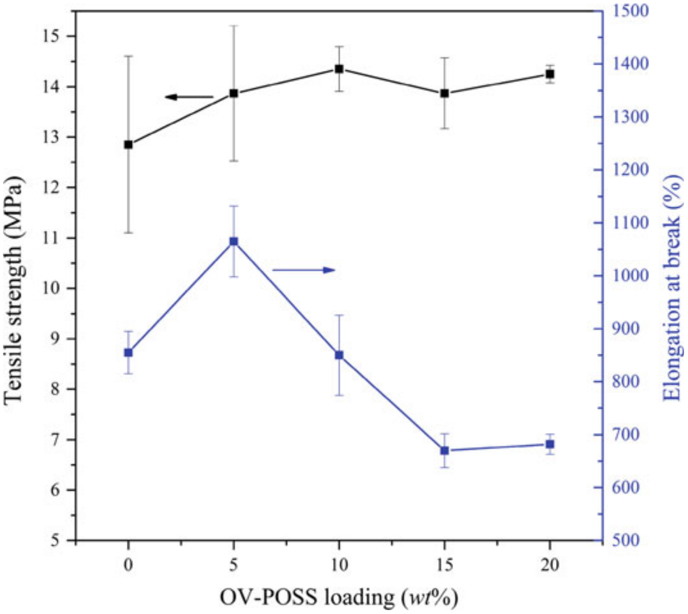


Fig. 5 Effect of OV-POSS loading on the tensile properties of OV-POSS/NR vulcanizate. Reprinted from [83], © 2017 with permission from Elsevier

Table 3 Thermal properties of the OV-POSS/NR vulcanizates. Reprinted from [83], © 2017 with permission from Elsevier

Sample	T_g (°C)	T_{onset} (°C)	Char yield at 800 °C (wt%)
Plain NR	−60.4	317	8
5% OV-POSS/NR	−59.9	343	12
10% OV-POSS/NR	−59.8	340	18
15% OV-POSS/NR	−59.6	343	20
20% OV-POSS/NR	−58.3	343	23

polymers are the cheapest, while on introduction of O, N, S, and Cl atoms the price increases. Ultimately, the two polymers containing Si (silicone, MQ rubbers) and F (fluorocarbon, FKM rubber) are the most expensive [30]. Special-purpose rubbers have been developing with progress of automotive technology and their consumption rises with the expansion of the world automotive market. However, they have many other applications, in addition to tires, which we may not even notice, as they for example are hidden in various devices.

In the past few years, POSS has been incorporated into some polymeric elastomeric materials including polydimethylsiloxane (PDMS), polystyrene-block-polybutadiene-block-polystyrene (SBS), polyurethane (PU), and ethylene-propylene-diene-monomer (EPDM) rubber to improve the comprehensive performance of the materials. The effect of POSS particles on many properties of silicone rubber, for example, primarily thermal and oxidative stabilities and mechanical behavior, has been investigated by number of researchers in the literature [93–99]. As it was mentioned in the Introduction, a large number of scientific papers often concern silicone rubbers cross-linked at room temperature (RTV type), showing the features and range of applications quite different than high-temperature cross-linked silicone elastomers.

Recently, however, the number of publications regarding composites with POSS molecules dispersed in high-temperature vulcanized (HTV) silicone rubber also has been increasing (Table 4). When compared to most organic elastomers, silicone rubbers owe its popularity to better and longlasting functional properties at elevated temperatures. At room temperature, they are almost equal with good electro-insulating materials, while at elevated temperatures these properties are much better than in most materials. Due to high hydrophobicity of silicone rubber, moisture and water do not significantly affect these properties. A further advantageous feature, among the many other properties, is the puncture resistance during a fire, as a result of the outer silica layer on the surface of silicone rubber that provides good electrical insulation. In addition, silicone rubbers are characterized by an extremely high gas permeability, which is due to the large free volume as a result of free space presence between macromolecules. Unfortunately, this feature, as well as weak intermolecular interactions caused by, for example, the Si–O bond length, results in poor mechanical behavior. This is why, in general, the scientific research focuses mostly on the topic of improving mechanical properties of silicone rubber. More examples on this subject, showing the influence of POSS as modifying agents in the composites filled with silica as a reinforcing filler, will be given later in the chapter.

Apart from typical studies, on thermal and mechanical properties influenced by POSS, equally important and interesting is the impact of POSS molecules on added and specific properties, e.g., the adhesive properties of POSS-incorporated rubber to any reinforcing fibers. According to a recent paper quoted here, for the first time in the literature octamaleamic acid-POSS (OM-POSS), having reactive polar groups, was used to improve the adhesive properties of silicone rubber compounds [100]. Earlier some studies on adhesion, as well as flocculation and dispersibility in different elastomers, were reported with the use of new classes of nanosized substances other than POSS, namely organophilic clay or carbon nanotubes in combination with carbon black or silica [101]. According to Sirin et al. [100], the advantage of this POSS type (i.e., OM-POSS) is the presence of double bonds on the side chains (Fig. 6). It provides grafting of POSS onto silicone rubber molecules during cross-linking, which can be carried out in high temperature (HTV) with dicumyl peroxide (DCP). Additionally, the -COOH groups, present in this POSS-type nanoparticle, are supposed to play the role of an adhesion promoter in potential industrial applications, such as fiber-reinforced hoses.

In the studies, the silicone composites containing POSS were compared with the reference, which was a 5-phr silica-filled silicone rubber compound. The added value of elastomeric composites with POSS has been demonstrated based on H-adhesion test, measuring the interfacial properties of the rubber. It was shown that

Table 4 Some examples of POSS beneficial influence on rubber properties

Rubber/POSS	Characteristic	Additional benefit/Ref.
HTV silicone rubber/OM-POSS (octamaleamic acid-POSS)	– Adhesion force vs. reference sample: 1,5 fold greater (at 3 phr OM-POSS) – Thermal stability vs. reference sample: T_{d5} = 442 °C vs. 400 °C; T_{d10} = 494 °C vs. 434 °C (at 3 phr OM-POSS)	– Possible to decrease dicumyl peroxide (DCP) amount and to avoid the adverse effects of DCP decomposition products – Possible to eliminate the usage of toxic adhesives, e.g., resorcinol formaldehyde latex (RFL)Ref. [100]
HTV silicone rubber/amine-functionalized-POSS (OAPS—octa(aminophenyl)silsesquioxane; NPAMS—N-phenylaminomethylsilsesquioxane)	– Enhanced mechanical properties, especially tear strength: TS = 9,8 MPa; T_R = 42,3 kN/m (OAPS) TS = 9,9 MPa; T_R = 48,1 kN/m (NPAMS) – Markedly better thermal stability, resistant to oxidation up to 400 °C	Ref. [102]
HTV silicone rubber/vinyl-,carboxyl-, amine-functionalized-POSS	– Enhanced mechanical properties vs. reference sample: TS = 11,7 MPa vs. 6,8 MPa (at 5 phr POSS)	– Better damping properties – Higher relaxation rates Ref. [112] – Possible to obtain materials with increased surface hydrophobicity and barrier properties, as well as self-healing after damage Ref. [113]
HNBR/MV-POSS (monovinylisobutyl-POSS); OV-POSS (octavinyl-POSS); MM-POSS (methacryloisobutyl-POSS); OM-POSS (octamethacryl-POSS)	– Higher modulus (SE300) and tensile strength (TS) vs. reference sample: TS = 26,7 MPa (OV-POSS); TS = 32,7 MPa (OM-POSS) vs. 19,6 MPa	– stabilizing effect and improved aging resistance Ref. [123]

T_{d5}, T_{d10}—decomposition temperatures at 5 and 10% weight loss, respectively; TS—tensile strength; T_R—tear resistance

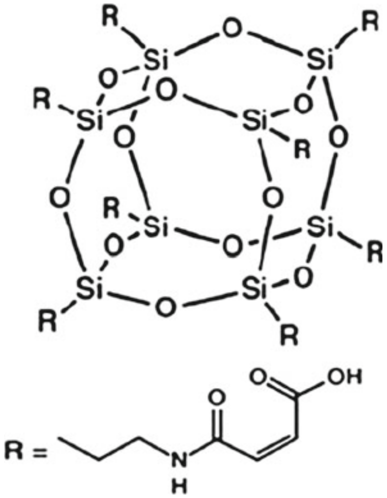


Fig. 6 Chemical structure of octamaleamic acid-POSS (OM-POSS). Reprinted from [100], © 2016 with permission from Elsevier

the application of OM-POSS in the silicone rubber composites improved the adhesion of the matrix to the reinforcing fiber, which was regenerated cellulose fiber (Rayon fiber), used to reinforce rubbers mostly in continuous woven or braid form. The typical application is the technical hoses. As a result of OM-POSS application as the adhesion enhancer, the OH groups of the Rayon interact with the –COOH groups of OM-POSS during the cross-linking process. The interaction may be either a condensation reaction yielding an ester bonding or hydrogen bonding. In this way, by the usage of OM-POSS as the adhesion enhancer, it is possible to eliminate the application of toxic adhesives such as resorcinol formaldehyde latex (RFL).

Sirin et al. [100] revealed also the different mechanism of silicone rubber cross-linking in the presence of OM-POSS and demonstrated some interesting findings of the chemical interaction between OM-POSS and the peroxide radicals. Based on DSC analysis, they showed that in the presence of OM-POSS and depending on its concentration, the cross-linking reaction in silicone rubber matrix started at lower temperatures. In the presence of OM-POSS, the radicals from DCP decomposition react preferentially with the C=C groups of OM-POSS, than taking hydrogen from the main chain of silicone rubber, what may have an obvious effect on the cross-linking density decrease. The cross-linking peak temperature of silicone rubber without OM-POSS showed an exothermic peak at 189 °C, whereas in the presence of POSS the cross-linking exotherm was obtained around 150 °C. This lowering in cross-linking onset temperatures can be associated with the dominating reaction between OM-POSS and DCP, as mentioned above.

On the basis of conducted studies, Sirin et al. [100] draw attention to the additional application of practical importance. By the introduction of OM-POSS as the main cross-linker, it is possible to decrease the amount of dicumyl peroxide (DCP) and therefore to avoid the adverse effects of DCP decomposition products in the composites. The obtained results are also valuable in order to evaluate the cross-linking temperature to be applied in compression molding and rheology. It was revealed from the curves that the curing temperature in compression molding and in rheological analysis can be taken as 160 °C for all the compounds. At this temperature, cross-linking starts for all of the compounds, regardless the OM-POSS loadings.

Other measurements, commonly carried out for POSS-filled composites and obtained from TGA analysis, also revealed apparently improved thermal stability of the silicone composites, induced by the presence of OM-POSS. For instance, decomposition temperature at 5% weight loss increased from 400 to 441 °C with only 1 phr OM-POSS loading, whereas the maximum thermal stability was obtained at 3 phr OM-POSS [100].

Another example of the very recent studies on POSS-incorporated special-purpose rubbers concern application of amine-functionalized POSS with polysiloxane containing γ-chloropropyl groups [102]. Polysiloxane containing γ-chloropropyl groups (CPPS) is an important group of functional polysiloxanes containing halogen groups, recently used as key chemical intermediates or additives to prepare advanced functional materials [103, 104]. In order to produce a heat-curable silicone rubber based on CPPS, namely methyl chloropropyl silicone rubber (MCSR), an innovative curing system has been developed [105–107] that offers many advantages over the conventional one (e.g., peroxide curing system). Among others, the resulting vulcanizates obtained by the application of novel curing system exhibits excellent mechanical properties and thermal stability; moreover, the by-product can be easily eliminated. Many compounds containing amino groups can be chosen as cross-linkers in this curing system, as well, e.g., functionalized POSS nanoparticles with highly reactive amine groups at the corners of their cage structures [108–110]. Thus, it can be considered as a promising technique for the preparation of a heat-curable silicone rubber with improved performance as a result of chemical reaction between amino and γ-chloropropyl groups. The most recent paper, mentioned above [102], deals with these compounds, i.e., octa(aminophenyl)silsesquioxane (OAPS), an aromatic amine-functionalized POSS exhibiting a T_8 cage structure, and N-phenylaminomethylsilsesquioxane (NPAMS), another aromatic amine-functionalized POSS, which is a mixture of T_{10} and T_{12} cage structures (Fig. 7).

Typical procedure and technology for rubber (elastomer) compounds were used, i.e., the materials and other ingredients were mixed on a two-roll mill. The mixtures were then cured, typically for HTV rubbers, in a mold under pressure and high temperature of 160 °C. In order to obtain final samples for testing, the post-curing procedure was carried out in oven with air circulation, at 180 °C for 4 h.

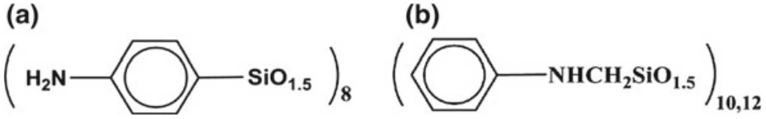


Fig. 7 Structures of amine-functionalized POSS: A) octa(aminophenyl)silsesquioxane (OAPS); B) *N*-phenylaminomethylsilsesquioxane (NPAMS). Reprinted from [102], © 2018 with permission from Elsevier

As a result, the vulcanizates cross-linked with the amine-functionalized POSS (OAPS or NPAMS) exhibited enhanced mechanical properties, especially tear strength (Fig. 8 and Table 5). The obtained effect was compared with other possible cross-linkers for silicone rubber, i.e., amine-functionalized silicone oils. Compared to them, when amine-functionalized POSS particles were used as cross-linkers of CPPS, more efficient concentrative cross-linking network could be formed and distribute stress to many adjacent and more cross-linked chemical bonds. The results indicate that the amine-functionalized POSS used as cross-linkers in the novel curing system can lead to more effective concentrative cross-linking compared with other cross-linkers. Thus, higher mechanical properties of the vulcanizates were obtained.

In addition, the results of thermal analysis showed that the cross-linked networks built by OAPS and NPAMS revealed markedly better thermal stabilities. It can be attributed to the presence of functional corner groups of aromatic structures, present in OAPS and NPAMS, which, thus, delay the decomposition of MCSR/POSS. Hence, according to the paper, the MCSR/POSS composites remained resistant to oxidation at temperatures up to 400 °C [102].

Different examples of using POSS molecules to reinforce silicone rubber matrix, which due to very weak intermolecular interactions results in a poor network structure and the composites showing much worse mechanical properties than other synthetic rubbers, deal with POSS functionalized with vinyl-, carboxyl, or amine- groups [111, 112]. They were applied as modifying agents toward methyl vinyl silicone

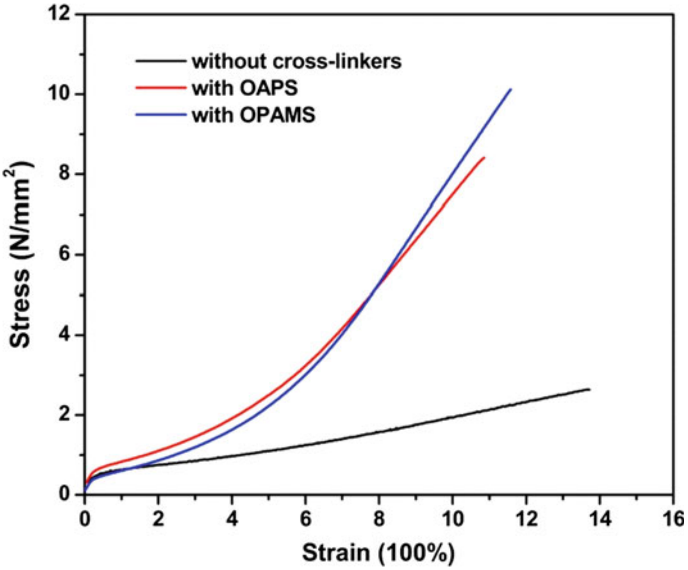


Fig. 8 Stress–strain relations of model specimens of heat-curable silicone rubber (MCSR—methyl chloropropyl silicone rubber) filled and unfilled with cross-linkers. Reprinted from [102], © 2018 with permission from Elsevier

Table 5 Mechanical properties of MCSR (methyl chloropropyl silicone rubber) cured with linear silicone oil or amine-functionalized POSS concentrative cross-linkers

Mechanical properties	Linear silicone oil		Amine-functionalized POSS	
	APPS	AEAPPS	OAPS	NPAMS
Tensile strength (MPa)	9.8	9.3	9.8	9.9
Tear strength (kN/m)	41.1	38.6	42.3	48.1

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APPS—(poly(dimethyl-*co-3*-aminopropylmethyl) silicone oil; AEAPPS—poly(dimethyl-*co*-3-(2-aminoethylamino)propyl) silicone oil; OAPS—octa(aminophenyl)silsesquioxane; NPAMS—N-phenylaminomethylsilsesquioxane

rubber (MVQ). Additionally, oxazoline derivative and itaconic acid were used as the coupling agents. As a result, the most significant effect was observed for the composite obtained with vinyl-isobutyl-POSS, which resulted in twice the tensile strength, compared to the reference sample, and good rubber damping properties [111].

From the point of view of silicone rubber special applications, some interesting results were also obtained in reduced temperature, e.g., the temperature of silicone rubber crystallization. The studied silicone rubber composites with monovinyl(isobutyl)-POSS exhibited then very good mechanical properties; at temperature of −50 °C, tensile strength was over 17 MPa. The studies also revealed that suitably functionalized POSS could reduce the aging effect and increase the surface hydrophobicity, while at the same time influencing oxygen barrier properties. Moreover, the addition of POSS, containing acidic or basic groups, to the silicone rubber resulted in the material with self-healing properties after damage [112].

The literature review shows also the examples of rubber nanocomposites preparation using non-reactive POSS particles [113]. In such a case, lack of polymer–filler bonding available through chemical cross-linking can be overcome by using a coupling agent that could increase the polymer–filler interaction. Thus, in the case of non-reactive particles, the hydrodynamic reinforcement that results from the incorporation of rigid particles can be obtained.

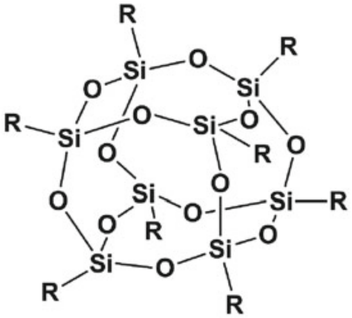
According to a paper, fumed silica was functionalized by aliphatic and aromatic groups by silane coupling agents and then used in combination with non-reactive POSS particles, namely octamethyl-POSS and octaphenyl-POSS, to obtain heat-curable silicone elastomer nanocomposites.

TEM analysis showed a good dispersion in the matrix, however, only in the composites having silica and POSS fillers with similar modifications. Moreover, aliphatic POSS owing to the small size and good compatibility, acted as a lubricant, reducing the polymer–silica filler interaction and also the filler–filler interaction within fumed silica. According to the authors of the published studies, there will be a competition between the POSS and fumed silica fillers in interacting with the silicone rubber matrix and this destroys the existing filler–filler interaction within silica, which was actually responsible for the strength of the material and forming new POSS–silica interactions as well as resulting in the aggregates [113].

As it was emphasized, interfacial adhesion between polymer and nanoparticles is one of the key factors to prepare polymer nanocomposites with excellent performances [114–117]. It can be realized then by introducing strong interactions facilitating an easy and homogeneous dispersion of nanoparticles in the polymer matrix, leading eventually to a great improvement in mechanical properties [116]. Based on these concepts, there are many studies on POSS application in carboxylated nitrile rubber (XNBR) by means of the interactions between organofunctional groups of POSS, such as epoxycyclohexyl [118, 119], glycidyl [120] or hydroxyl groups [121], and carboxyl groups of XNBR.

Studies on acrylonitrile-butadiene rubber (NBR), which is a kind of polar rubber and one of the most extensive synthetic rubbers, have been reported less often, mainly due to the absence of carboxyl groups in NBR molecular chain, thereby because of the lack of intermolecular interactions. However, some recent studies [122] reveal the application of a novel kind of POSS derivate, octa-(polyethylene glycol)-POSS (PEG-POSS—Fig. 9) to prepare NBR/POSS nanocomposites based on the nature coordination ability of electron-rich groups (–CN and –C–O–C- groups) with metal (Li^+) cations. Considering the results, the possible microstructure has been proposed to express the experimental observation and relationship between mechanical properties obtained (Fig. 10).

According to the authors, a novel network structure consists of several kinds of effective cross-links, which facilitates strong interface cohesion between POSS and NBR matrix and effective dispersion of POSS. The addition of POSS not only increased the cross-linking density of NBR/$LiClO_4$/PEG-POSS nanocomposites, but also improved the 300% modulus and tensile strength greatly. It was observed, that at 20 wt% of POSS loading, the 300% modulus and tensile strength are about 4 and 13 times in comparison with the pristine NBR, respectively, with almost the same elongation at break (Table 6).



R=$-CH_2CH_2(OCH_2CH_2)_mOCH_3$, m=~13.3

Fig. 9 Chemical structure of octa-(polyethylene glycol)-POSS (PEG-POSS). Reprinted from [122], © 2016 with permission from Elsevier

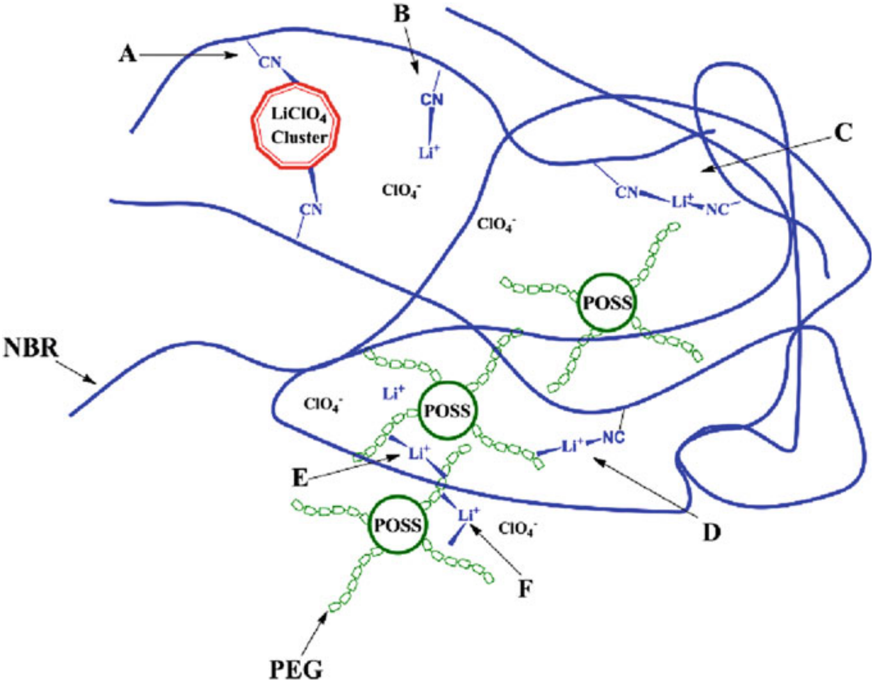


Fig. 10 Fig. 10. Possible microstructure in NBR/$LiClO_4$/POSS nanocomposites. Reprinted from [122], © 2016 with permission from Elsevier

Since the most important properties of rubbers are closely in association with the network structure, the stress–strain behavior is not only controlled by chemical cross-

Table 6 Mechanical parameters of NBR and NBR/$LiClO_4$/PEG-POSS nanocomposites.

Sample	300% modulus (MPa)	Tension strength (MPa)	Elongation at break (%)	G_c	G_e
NBR	0.40	0.57	910	0	0.53
NBR-Li-10 wt% POSS	0.97	2.68	921	0.096	0.67
NBR-Li-20 wt% POSS	1.85	7.17	865	0.15	1.43
NBR-Li-30 wt% POSS	0.98	4.29	681	0.14	0.55

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where G_c represents the cross-link contribution and G_e represents the constraint contribution

linkages, but also by the contributions of confinement, where G_c represents the cross-link contribution and G_e—the constraint contribution. According to the published paper, only the topological confinement (G_e), particularly the chain entanglement, contributes to the stress–strain behavior of neat NBR, whereas the G_c value is zero. Higher values of G_c and G_e indicate that the addition of $LiClO_4$/POSS can bring cross-links to NBR matrix, implying PEG-POSS is a potential cross-linking candidate for NBR/$LiClO_4$/POSS nanocomposites. The network structure could relax then to a more perfect regime by applied stress distribution with the aid of the effective NBR-POSS cross-linking network (G_c and G_e), which was good for the mechanical properties of the rubber nanocomposites (Table 6).

The possibility of using POSS as nanofillers or modifying additives to elastomers was also reported for Hydrogenated Acrylonitrile Butadiene Rubber (HNBR) [123]. The POSS used in the study were vinylisobutyl-POSS (MV-POSS), octavinyl-POSS (OV-POSS), methacryloisobutyl-POSS (MM-POSS), and octamethacryl-POSS (OM-POSS). According to the paper, it follows that they were successfully incorporated into silica-filled HNBR matrix as modifying agents, since they enhanced cross-link density and improved properties of the resulting network. Especially, larger POSS molecules, with eight reactive groups at the vertices (e.g., OV-POSS or OM-POSS), considerably increased interfacial interactions in studied HNBR matrix thus leading to a rigid and robust elastomeric composites, as evidenced by much higher modulus (SE300) and tensile strength (TS) in comparison with vulcanizates filled with silica, without the presence of POSS molecules.

Therefore, it was concluded that octafunctional POSS molecules could be successfully used as cross-linking species, what could allow to reduce loading levels of traditional chemical cross-linkers. It is also worth noting that the incorporation of POSS molecules into silica-filled HNBR matrix resulted in stabilizing effect against adverse changes induced by both the climatic and UV radiation aging [123].

6 Thermoplastic Elastomers/POSS

Where conventional elastomers cannot provide the range of physical properties needed in the product then thermoplastic elastomers (TPEs) are used. These materials find large application in the automotive sector and in household appliances sector. About 40% of all TPE products are used in the manufacturing of vehicles. They are sometimes referred to as thermoplastic rubbers, being a class of copolymers or a physical mix of polymers, which consist of materials with both thermoplastic and elastomeric properties. Thus, they show advantages typical of both rubbery and plastic materials. The principal difference between thermoset elastomers and thermoplastic elastomers is the type of cross-linking bonds in their structures. In fact, cross-linking is a critical structural factor which imparts high elastic properties. Nowadays, many types of injection-moldable thermoplastic elastomers (TPEs) are replacing traditional rubbers.

TPEs are characterized, hence, by intermediate properties between cross-linked rubber and a thermoplastic material, and they reveal the ability of large reversible deformations in a certain temperature range, although they are not chemically cross-linked. TPEs are the only class of elastomers that do not require chemical cross-links, as they gain their strength from physical interactions between polymer components [124, 125].

Following the various nanosized fillers, mainly layered silicates, polyhedral oligomeric silsesquioxanes were also incorporated in these types of block copolymers. Some examples of POSS chemically incorporated into TPEs may be studies dealing with a novel hybrid organic–inorganic triblock copolymer of polystyrene-butadiene-polystyrene (SBS) containing POSS molecules grafted onto 1,2-butadienes in the polybutadiene soft block by hydrosilylation method [126–128]. Unlike typical free radical copolymerizations (generally one-pot copolymerization methods) commonly used for POSS incorporations, the applied method of synthesis allowed POSS molecules to be selectively grafted to the copolymer segments without introducing other effects that might arise from changes to the molecular structure of the main SBS backbone. As a result, X-ray diffraction analysis revealed that the grafted POSS molecules were very well dispersed in the matrix of the hybrid polymer. The presence of POSS in the soft segments of SBS enhanced the value of T_g for the polybutadiene block, and according to the authors, an interesting effect has been observed, mainly an improved load carrying capability for the POSS-modified SBS triblock copolymer at temperatures where the styrene block begins to soften [127].

Another example of interest in thermoplastic elastomers that contain POSS are the studies referring to the POSS molecules chemically incorporated into ethylene–propylene copolymers [129, 130]. These novel thermoplastic elastomers, ethylene–propylene-POSS (EP-POSS) terpolymers, were synthesized as a result of polymerization using a hafnium-based metallocene catalyst [130]. This method was applied in contrast to the traditional one, which uses vanadium-based Ziegler–Natta catalysts. According to the authors of the paper, the applied metallocene polymerization offers advantages over the traditional one, giving unimodal polymer distributions with sufficiently high molecular weights, good propylene and diene incorporation, relatively low polydispersities, and easier removal of cocatalysts.

An important feature of POSS is the ability to aggregate in copolymers, thereby creating physical interactions between polymer chains, where POSS can act as a physical cross-link. The published studies revealed that POSS particles aggregation is strongly dependent on the nature of the POSS peripheral group off each silicon atom. It was thus shown, based on X-Ray studies, that aggregation of POSS in the EP-POSS elastomer did not occur with isobutyl and ethyl peripheries, as they disperse well within the polymer matrix. The obtained results suggest that such POSS particles can act as a plasticizer. In contrast, nanoparticles of POSS with the phenyl periphery showed a tendency to aggregation and the formation of POSS nanocrystals increased the mechanical properties of these thermoplastic elastomers, leading as a result to mechanically robust material [130]. Therefore, the storage modulus of the terpolymer increased significantly with increasing POSS loading in the rubbery plateau region, as compared to the ethylene–propylene parent polymer. Tensile studies revealed also an increase in the elastic modulus with increasing POSS with the phenyl periphery (EP-PhPOSS) loading, as well as elongations at break as high as 720% for EP-PhPOSS sample, with the others between 400 and 500%.

Other examples of research may concern tetrafluoroethylene–propylene copolymer (TFE/P) which is a type of elastomer with a unique combination of high-temperature, electrical, and chemical resistance properties [131, 132]. In general, TFE/P elastomers emerged also in chemical, agrichemical, automotive, and aerospace industries [133–135]. Because of the superior advantages of chemical stability and better mechanical properties, TFE/P elastomers have found wide industrial applications in corrosive oilfield environments, such as the fabrication material for O-rings, seals, and gaskets.

TFE/P copolymer cannot be cured by most cross-linking agents, it is only slightly susceptible to peroxide at high temperatures. It has been demonstrated that POSS compounds, functionalized with appropriate groups, may function as auxiliary cross-linking agents in the peroxide vulcanization of the copolymer [131]. Octavinyl-polyhedral oligomeric silsesquioxane was therefore used in the studies, as a type of POSS providing eight vinyl double bonds at every corner that can react with the TFE/P molecular chain to form a cross-link structure with the help of dicumyl peroxide (DCP).

The obtained results showed that the incorporation of octavinyl-POSS significantly enhanced the mechanical property and elevated the glass temperature of the composites. However, the thermal endurance properties were only improved slightly [131].

Accordingly, another paper of the same authors presents the results of the same TFE/P and octavinyl-POSS composites on account of improving the working performance of the composites under special working conditions, i.e., under conditions that cause the material aging [132]. The composites were aged in a 10 wt% hydrochloric acid solution for 2, 4, and 6 days at 140 °C. Combining the results of the XRD and SEM with ^{29}Si NMR and XPS analyses, it was determined that there are two types of changes that occur during the aging process of the examined composites. During the initial degradation period, the crystalline structure of the octavinyl-POSS aggregates was partly damaged (but still existed). Later in the degradation process, the POSS aggregates converted into certain Si–OH compounds and gradually disappeared. Meanwhile, the cross-links between the POSS and TFE/P chains were also damaged. Consequently, the cross-link density decreased, leading to deterioration in the mechanical and thermal properties.

Next examples of the novel hybrid materials obtained with use of different thermoplastic elastomers refer to poly(styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) triblock copolymer which is a kind of useful commercial thermoplastic elastomer [136–140]. It is characterized by excellent resistance to thermal degradation and ultraviolet irradiation, owing to the rubbery nature of the inner blocks, and mechanical strength, offered by polystyrene hard block domains that act in similar way to physical cross-linkings [141–143]. Thus, SEBS has been widely used as biomimetic gels, shock absorbing materials, adhesives, sensors, sealants, coatings and wire insulation, etc. [144, 145]. Besides, the hard segments (S blocks) in SEBS may be functionalized to improve the performance of thermoplastic elastomer.

Various studies have been reported on the SEBS chloromethylation of styrene units in polystyrene segments [137, 138]. Based on the advantages of hybrid inorganic–organic materials, increasing number of functional nanomaterials were grafted onto the side phenyl group in SEBS; worth mentioning here, multi-walled carbon nanotubes or graphene oxide sheets, for example [139, 140].

The click coupled bonding of nanoadditives with SEBS can be considered as an efficient and facile method for controlling the resulting properties and achieving high-performance materials. Such materials are believed to offer possibilities to fully combine the extraordinary performances of the applied nanoadditives with multifunctional properties of block copolymers and thus be useful in a variety of technological fields.

The click coupling chemistry was employed in order to introduce alkyne-functionalized POSS molecules into the hard polystyrene segments in SEBS thermoplastic elastomer to improve its mechanical and thermal properties [136]. As a result, based on FT-IR, ^{1}H NMR, and GPC measurements, it was proved that POSS was quantitatively bonded onto the polystyrene hard segments in SEBS via clicking chemical reaction. TEM images showed clearly that self-aggregates inorganic phase (of around 30 nm in size, originating from POSS) was formed and homogeneously dispersed in organic SEBS matrix, resulting in the SEBS-g-POSS hybrid material. No separated phase could be observed in the SEBS without staining of phenyl groups in hard segments (Fig. 11).

The resulting SEBS-g-POSS copolymer revealed interesting surface characteristic, which was a great increase of hydrophobicity due to low surface energy of cage-like nanostructure of POSS [146, 147]. POSS would like to migrate to the surface in POSS-containing hybrid polymers, leading to a remarkable hydrophobic change on the polymer surface performance. As a result, the contact angle of SEBS-g-POSS increased to 94,8°, which is larger than that of SEBS (86,7°)—see Fig. 12.

Moreover, valuable properties in the range of thermal stability have been obtained. The final decomposition temperature was increased by c.a. 20 °C in comparison with that of SEBS, and it was attributed to heatproof of Si–O–Si framework of POSS.

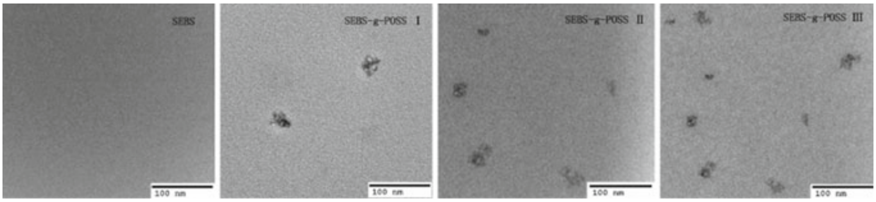

Fig. 11 TEM images of thermoplastic elastomer of SEBS poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) and SEBS-*g*-POSS hybrid copolymers without any staining (I, II, and III). Reprinted from [133], © 2013 with permission from Elsevier

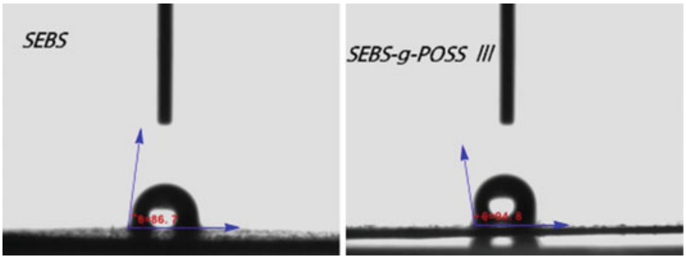

Fig. 12 Water contact angles images of neat SEBS and SEBS-*g*-POSS. Reprinted from [133], © 2013 with permission from Elsevier

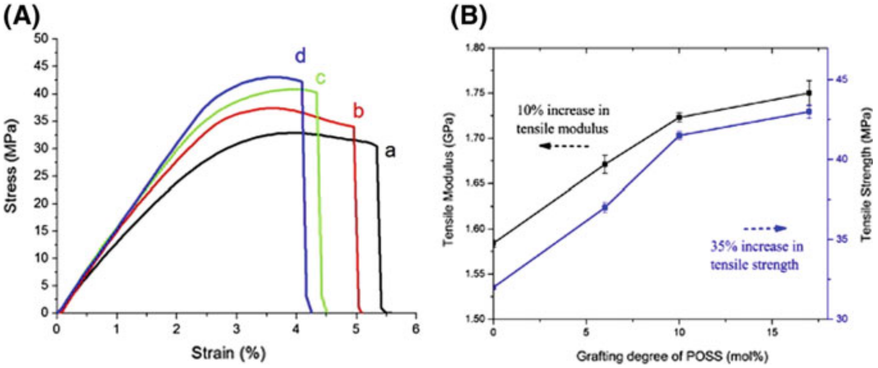

Fig. 13 (A) Stress–strain curves and (B) mechanical properties of PS/SEBS (a) and PS/SEBS-*g*-POSS composites (b: SEBE-*g*-POSS I; c: SEBE-*g*-POSS II; d: SEBE-*g*-POSS III). Reprinted from [133], © 2013 with permission from Elsevier

In addition, SEBS-g-POSS makes a contribution to tensile stress and modulus improvements of PS/SEBS-g-POSS composites due to the hard core with Si–O–Si inorganic structure of POSS and its nanoscaled aggregates. Compared to parallel PS/SEBS composite without any inorganic phase, tensile strength and modulus of PS/SEBS-g-POSS (90/10) blend could be increased by 35% and by 10%, respectively (Fig. 13).

Lastly, there are also researches on POSS application in block copolymers in order to obtain novel elastomer dye-functionalised nanocomposites [148]. It has been shown that preparing dye-functionalised POSS nanoparticles, with the purpose of further dispersing them throughout a polymer, provides many advantages over conventionally colored polymers that can fade, lose color or undergo unexpected color changes. The reported studies concern a popular choice of block copolymer which is polystyrene-butadiene-polystyrene elastomer, i.e., SBS, already mentioned at the beginning of the chapter [127]. The applied POSS molecules were functionalised with two dichlorotriazine reactive dyes, and next SBS-POSS nanocomposites were prepared using a solvent dispersion technique. The obtained results showed that hybrid-pigment encouraged dispersion, allowing a degree of control over the functionality and producing a more uniform, stable, and visually pleasing material. Additionally, functionalised POSS improved thermal stability by imparting restrictions on SBS chain motions. Tensile stress–strain analysis revealed an increase in modulus with filler concentration. Storage modulus, loss modulus, and glass transition temperature increased with filler content due to effective SBS-POSS interaction [148].

7 Summary and Perspectives

Since the first *Polyhedral Oligomeric Silsesquioxanes* (POSS) application to polymer modifications, there has been a huge increase in interest in this type of compounds. Despite the lapse of years, research on materials containing POSS derivatives continues to develop dynamically.

Application possibilities of POSS compounds are very broad, including resistors used to obtain new materials in lithography, high-temperature lubricants or low-dielectric constant materials or pigments and dyes carriers. POSS can be used in biomaterials (drug delivery systems, antibacterial coatings, dental nanocomposites), optics and electronics (materials exhibiting properties of quantum dots, OLED diodes, electrolytes, fuel cells, lasers) and in space industry (fire-resistant materials and resistant to conditions prevailing in outer space). Polyhedral silsesquioxanes can also be used in cosmetics, printing inks or to modify the surface of materials in order to obtain hydrophobic, self-cleaning properties and increased abrasion resistance. POSS compounds, however, find the greatest application in the production of new polymer hybrid materials that combine both the properties of inorganic materials and organic polymers, Unlike most fillers, POSS molecules contain organic constituents on their external surface, which can make them compatible with many polymers.

The focus of this chapter was to discuss the influence of POSS incorporation into rubber matrix on functional properties of their composites. The POSS surface functional groups play a crucial role in controlling properties of POSS-containing materials and their reinforcement. Generally, the properties of hybrid polymeric materials mainly depend on the methods of their synthesis, the amount of POSS introduced and physical properties, and chemical substituents attached to the polyhedral cage of silsesquioxane. POSS compounds can be dispersed at the molecular level, and they can form aggregates, amorphous, or crystalline phase. POSS having surface functional groups that have favorable surface interactions can disperse uniformly in the matrix and uniform dispersion helps to improve physical properties of the nanocomposites. On the other hand, POSS having surface functional groups not compatible with the polymer matrix leads to phase-separated systems with POSS-rich domain and polymer-rich domains. Such microphase separated systems cannot provide proper reinforcement and may even lead to a decrease in desired properties.

The reinforcement mechanisms in the rubber nanocomposites are complicated and still remain an open question. The complications of a heterogeneous system very often present in rubber composites and cross-linking structure of the rubber cause that the observed effective enhancement of the properties cannot be explained by one simple theory.

The main challenge restricting the commercial POSS applications in polymer nanocomposites is the cost. However, POSS has obtained practical application in the military field, aviation and aerospace fields, and some other high-performance materials where the cost is not relevant. On the other hand, cost of POSS is not the right issue when developing the novel materials having an excellent physical properties or niche applications where POSS can deliver what no other additive is able to. Some promising areas for POSS, that would potentially increase the market for POSS particles, are therefore probably related to biomedical applications and may include bone growth or tissue healing, for example.

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