

Design and Synthesis of Hybrid Materials with POSS



Ayesha Kausar

Abstract This chapter describes essential aspects related to design and fabrication of organic–inorganic hybrid structure based on polymeric materials and polyhedral oligomeric silsesquioxane (POSS). POSS is a class of organosilicic three-dimensional compounds with cage or non-cage framework. The POSS nanoparticle possesses size of few nm and has monodisperse and rigid structure. The POSS nanoparticle also has unique capability to reinforce numerous polymers (polyamide, epoxy, polyurethane, poly(vinyl chloride), poly(ethylene glycol), etc.). Various strategies have been adopted for the incorporation of POSS into polymer matrices via chemical cross-linking or physical blending. The design and structure of final hybrids have been found to influence by POSS surface functional groups and POSS content. Owing to POSS nanometer size and exceptional features, the hybrid materials own superior structural and functional properties such as mechanical strength, thermal stability, optical properties, low toxicity, and biocompatibility. The state of POSS-containing polymer hybrids with respect to current challenges and future prospects has also been described. The focus of this article is to present an account of fundamental understanding of structure, functional properties, synthesis, and design challenges of POSS-containing polymer hybrids.

Keywords POSS · Polymer · Hybrid · Synthesis · Cross-linking

1 Preface

Polyhedral oligomeric silsesquioxane (POSS) is nanostructure having general formula $(\text{RSiO}_{3/2})_n$ [1]. R in the formula may be a hydrogen atom or an organic functional group (alkyl, acrylate, hydroxyl, or epoxide). POSS is also referred to as silica nanoparticle constituting silica cage core and organic functional groups attached to

A. Kausar (✉)

School of Natural Sciences, National University of Sciences and Technology (NUST), H-12 Islamabad, Pakistan

e-mail: dr.ayeshakausar@yahoo.com

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cage corners. In other words, POSS is a hybrid inorganic/organic structure. POSS consists of both organic and inorganic elements, i.e., an inner core of inorganic silicon and outer core of oxygen and other organic constituents. POSS is also known as one of the smallest nano-sized inorganic particles. The nano-size, structure, and functionalization of POSS lead to essential physical properties such as thermal stability, mechanical properties, dielectric features, and optical properties [2, 3]. POSS nanoparticle imparts functional properties, structural stability, and processability to polymer/POSS hybrids. In addition, inclusion of POSS in polymers as nanofiller may cause superior thermal stability, and electrical, thermomechanical, permeability, and nonflammability properties [4–6]. POSS nanoparticle with outer layer of organic functional group has been found to be compatible with polymers. The unique combination of organic (polymer) and inorganic phases (POSS) may bring about enhanced hybrid performance [7, 8]. The characteristics and performance of polymer/POSS depend on the successful incorporation of POSS particles in polymers. Using suitable technique, POSS has been reinforced in polymers through physical blending as well as chemical cross-linking. Usually POSS is physically mixed with POSS via melt mixing [9]. However, the chemical cross-linking can be induced through in situ method, solution technique with ligand or linker induced interaction between polymer and POSS. Aggregation of POSS nanoparticle may result through physical modes. Surface functionalization of nanoparticle and polymer can be achieved by chemical routes, which may consequently lead to covalently linked polymer/POSS hybrids [10]. In this chapter, initially essential features and structure of POSS have been discussed. Main objective was to highlight the preparation and design strategies used so far for polymer/POSS hybrid. Comprehensive research on these hybrids may lead to a wide range of academic and commercial significance. Future prospects and related challenges have also been stated.

2 Polyhedral Oligomeric Silsesquioxane (POSS)

POSS is an important category of organosilicic three-dimensional compounds having a caged or non-caged framework of silica core and organic functional group attached to the corners. Consequently, POSS consists of both inorganic and organic substituents. Inorganic silicon forms the inner core, while organic constituents form the outer layer. Structure of POSS may range from molecular silica to multifunctional POSS molecules [11]. On the POSS surface, when all the organic groups are non-reactive, it forms molecular silica. POSS is known as monofunctional or MonoPOSS, when one organic group is reactive. If there are more than two functional groups on the surface, POSS is referred to as multifunctional or MultiPOSS. The variation in organic groups attached to the surface and type of cage structure may form different derivatives of silsesquioxane or POSS molecules. POSS can be often classified as caged or non-caged structures [12]. These categories have a range of varied POSS structures (Fig. 1). However, cage-like POSS molecules have gained more research interest [13]. The T8 cubic inorganic core made up of silicon–oxygen ($R_8Si_8O_{12}$) and Q8 structure ($R_8Si_8O_{20}$) have gained

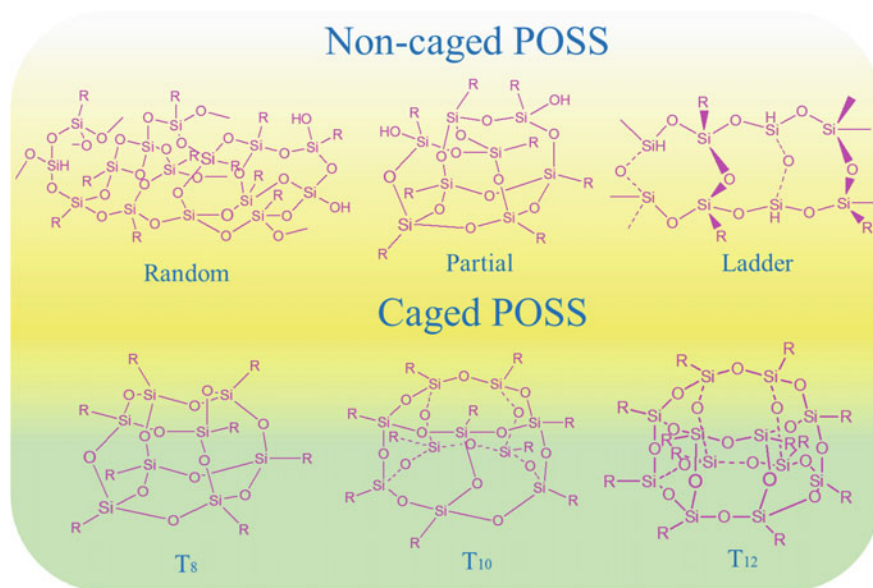


Fig. 1 POSS classified into caged and non-caged silsesquioxane structure

noteworthy importance. The ‘T’ and ‘Q’ are used for silicon atoms bonded to three or four oxygen atoms, respectively [14]. The organic groups attached to the surface are also called vertex groups. POSS is a silsesquioxane molecule, which may yield oligomeric organosilsesquioxane through chemical reaction.

A simple example is the preparation of octakis[(3-glycidoxypropyl)dimethylsiloxy]-octasilsesquioxane [15]. It has been prepared by using tetraethylammonium hydroxide, dimethylchlorosilane methanol, tetraethoxysilane, and allyl glycidyl ether. Initially, octakis(dimethylsiloxy)octasilsesquioxane was synthesized and then octakis(dimethylsiloxy, 3-glycidoxypropyl)octasilsesquioxane was obtained using suitable functional molecules (Fig. 2). POSS is nonvolatile, odorless, and environmentally friendly compound. Apex group functionalization has been used to attain high-performance cage nanoparticle. In polymers, POSS reinforcement may cause improved thermal and mechanical properties [16]. Accordingly, POSS may also improve the flame retardance of the matrix polymers [17]. POSS dispersion in polymers may cause several beneficial effects to the polymers such as enhance mechanical strength, modulus, nonflammability, and rigidity [18]. The main obstruction to the design and synthesis of polymer/POSS materials is the aggregation of POSS nanoparticle. It is an important challenge encountered during the large-scale production of polymer/POSS hybrids. Development and use of suitable technique to prepare and disperse POSS nanoparticle in polymer matrix along with the development of optimum chemical bonding and interface interaction must be the research focus for high-performance polymer/POSS hybrids. POSS nanostructures have shown promise in catalyst supports, scaffolds for drug delivery, and imaging.

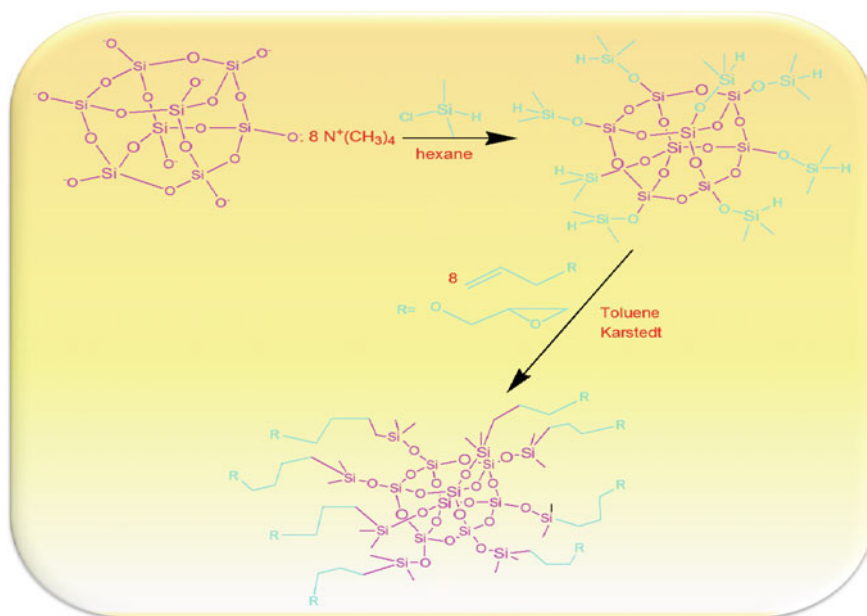


Fig. 2 Synthesis of octakis(dimethylsilyloxy)octasilsesquioxane and octakis(dimethylsilyloxy, 3-glycidoxypropyl) octasilsesquioxane

3 Polymer/POSS Hybrid Nanomaterial

Hybrid material is basically a composite consisting of two or more different constituents. Usually, the constituents in hybrid materials have physical interactions between them. However, according to some definitions, hybrid materials may consist of two or more components linked together by covalent bonds. When one of the constituents in hybrid material is at nanometer level, it is known as hybrid nanomaterial or nanohybrid. Hybrid material usually consists of inorganic and organic components. Mixing of nanolevel phases may lead to a homogeneous mixture with characteristics different than the original phases. In the case of polymer/POSS hybrids, factors such as POSS content, POSS functionalization, polymer/POSS interaction, and mode of cross-linking influence the final hybrid structure [19]. For the functionalization of POSS compounds, three approaches have been generally adopted including (i) corner-capping reactions of POSS compounds; (ii) addition/substitution reactions of edge groups; and (iii) condensation reaction of functional organosilanes [16]. Capping reaction may involve the introduction of monomer, e.g., methylacrylate to POSS molecule using trichlorosilane as a capping agent. Similarly, other functional groups such as styryl monomer may be introduced on POSS surface via corner-capping reactions using coupling agents. The condensation reaction of functional organosilanes and hydrolytic removal of silicon atom from POSS molecule may produce variety of

condensed POSS molecules. The functionalization of POSS compounds promotes their dispersion and compatibility with the polymer matrix. Amalgamation of POSS with polymer causes several enhanced characteristics in hybrid structure depending on nanofiller dispersion, content, and morphological contour. The functionalization of POSS molecules may allow controlled chemical reaction between the functional nanofiller and polymer matrix. The affinity between polymer chains and POSS has been estimated using theoretical calculations, spectral, and morphology analysis. POSS loading has led to improvement in range of functional properties of hybrids compared with the neat polymer. POSS and functional POSS nanofillers have not only been introduced in homopolymers, but also incorporated in block copolymer matrices. The behavior of POSS reinforcement in block copolymers is, however, different than that of homopolymer/POSS hybrids. POSS-containing block copolymer hybrids have been fabricated using living polymerization, bulk polymerization, free radical reaction, and other advanced polymerization approaches. In the case of block copolymers, reinforcement of nanofiller may cause self-assembly phenomenon in the hybrid materials. POSS nanofiller has been used for the self-assembly studies in bulk phases or blocks, where periodically well-organized nanostructures were produced. Development of ordered nanostructure relies on the block copolymer/POSS interaction parameters, volume fraction between the blocks, polydispersity, degree of polymerization of copolymers, etc. Hence, in the presence of POSS nanofiller, block copolymers can develop in situ interactions and may self-assemble to form nanostructures in bulk. Improved physical properties of polymer/POSS materials are desirable characteristics for several technical applications. Moreover, structure–property relationship in polymer/POSS systems has been investigated to define and modify the design and solicitation of these materials. Polymers such as poly(ethylene glycol), polystyrene, poly(vinyl chloride) (PVC), polyamide, epoxy, poly(methyl methacrylate) (PMMA) has been grafted with functional POSS compounds (Fig. 3). Polymer/POSS hybrid has been found with enhanced thermal stability and glass transition compared with neat polymers [20]. Surface functionalization and interfacial interactions have caused superior dielectric and mechanical properties relative to pristine polymers. Inert nature and biocompatibility of POSS have also led to significant biomedical applications [21].

4 Interaction in Polymer/POSS

Polyhedral oligomeric silsesquioxane forms an interesting class of organosilicon compounds with tri-dimensional cage structure. Studies on polymer/POSS materials have shown hybrid inorganic–organic nature, which conglomerates the properties of organic polymers and ceramics [22]. The silicon–oxygen framework possesses high degree of flexibility, and tunable solubility, and reactivity [23]. These properties can be functionalized using organic substituents on POSS. Wide range of functional groups may include alkyl, phenyl, vinyl, alcohol, carboxylic acid, sulfonic acid, epoxide, halide, imide, acrylate, methacrylate, thiols, silane, silanol, etc.

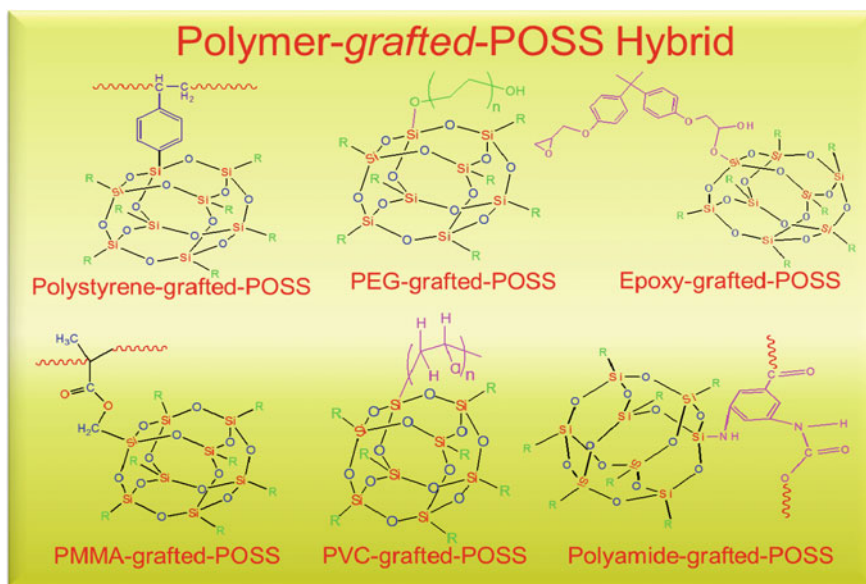


Fig. 3 POSS grafted with different polymers

[24–26]. The chemical nature of matrix can be tailored using desired vertex group. The compatibility of polymer/POSS hybrids strongly relies on the polarity match of polymer and POSS molecules [27]. In this regard, reactive vertex groups can be preferred to attain chemical bonding between polymer chain and POSS [28]. The improved processability, thermal stability, nonflammability, and oxidative resistance of materials are austere correlated with the physical/chemical interaction between the matrix/POSS molecules [29]. The non-covalent interactions such as π - π and hydrogen bonding has been detected. For example, silanol-based POSS molecules may condense with hydroxyl-containing matrix form hydrogen bonding in hybrid [30]. POSS may also form unwavering covalent bonds with the polymer matrix. Furthermore, the structure of inorganic cage and organic vertex group of POSS also affect the reinforcement effects in polymer/POSS hybrids. Type of vertex group and interfacial interaction are also crucial to determine the filler dispersion and morphology of hybrid properties. These hybrids have been prepared using various processing techniques. During melt blending (one of the important method), POSS molecules act as plasticizer and affect the final material characteristics. Here, strong interaction between matrix/nanofiller may illustrate anti-plasticizing effect. The incorporation of POSS may lead to high viscosity values and improved rigidity. The glass transition temperature of hybrids has also been found to influence by POSS type, content, and physical/chemical interaction between matrix/nanofiller. Similarly, these factors also affect the mechanical, thermal, rheological, and other important physical properties of polymer/POSS hybrids.

Self-assembly phenomenon has received considerable interest in the field of block copolymers and hybrids. Self-assembly has been found to develop well-organized nanostructure or nano-pattern. Both the covalent and non-covalent interactions (hydrogen bonding, electrostatic interactions, van der Waals forces, etc.) have found to be involved in the self-assembly of copolymers and hybrids [31]. Wide range of self-assembled nano-organized architectures has been designed with varying morphologies and characteristics. Commonly observed self-assembled morphologies involve cylinders, spheres, rods, lamellae, gyroid, and range of other forms. The periodicities generated during hybrid synthesis depend on processing technique, polymer type, nanofiller, content, temperature, pH, solvent, etc. Initially, self-assembly was supposed to be originated from the phase and morphology differences between the different types of polymer blocks. Later, with the development of nanomaterials, self-assembly was found to be spontaneously initiated using nanoparticles. Self-assembly studies have revealed that the inorganic constituents such as POSS may act as initiator to instigated ordered structures in organic molecules. Consequently, the self-assembly behavior of polymer/POSS hybrids has been investigated in thin films, bulk, and solution form. The self-assembled morphology of POSS-containing polymeric hybrids was outstandingly different than that of conventional amphiphilic polymers. Such type of organic–inorganic architectures may have potential for promising applications such as micro and nanoelectronics, optics, medicine, etc.

5 Design and Fabrication Strategies for Polymer/POSS Hybrid

A variety of POSS nanostructures have been prepared containing reactive functionalities for grafting, surface bonding, and polymerization with other materials [32, 33]. POSS nanoparticle has been incorporated in polymers via simple blending, copolymerization, grafting, or other covalent linking approaches [34]. POSS reinforcement in polymers may lead to affective developments in physical properties. Generally, POSS has been found to enhance the mechanical properties, thermal and oxidation resistance, and nonflammability of polymers. POSS has been reacted with wide range of thermoplastic and a few thermoset systems. Addition of POSS in polymers has not caused dramatic changes in processing parameters; however, conditions need to be optimized for better dispersion of nanoparticle in matrix. For better dispersion, POSS is usually solubilized in monomer and incorporated in polymer or copolymer mixture. In this way, POSS may form better binding with the polymer, and less POSS aggregation and phase separation have been observed [35]. Variety of polymers (polyamide, poly(methyl methacrylate), polyurethane, poly(vinyl chloride), biodegradable polymers, etc.) have been reinforced with POSS. Physical methods, chemical interaction, and chemical copolymerization have been used for polymer/POSS interaction. For chemical interlinking, POSS has been functionalized with various reactive groups. A seg-

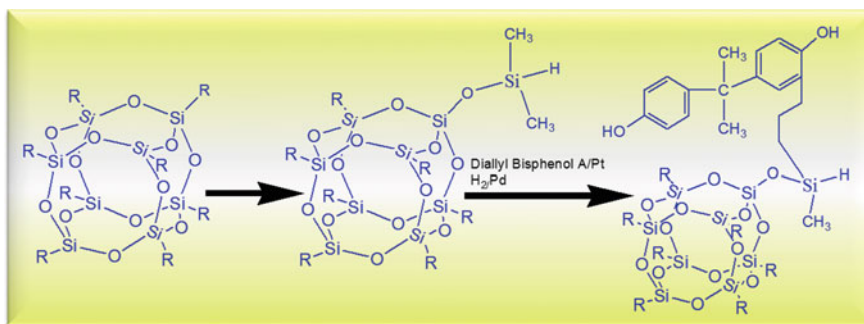


Fig. 4 Route to octacyclohexyl-POSS, with R = cyclohexyl, hydrido-POSS, and BPA-POSS

mented polyurethane has been developed using 4,4'-methylenebis(phenylisocyanate) (MDI) hard segment, polytetramethylene glycol (PTMG) soft segment, and 1,4-butanediol (BD) chain extender [36, 37]. The polyurethane has been reinforced with POSS [38, 39]. The polyurethane system containing POSS cage-like molecules pendent to polymer chain has been reported [40]. The copolymer forms random sequence of PTMG soft segments and MDI hard segment. The polymer was chain-extended by using 1-[3-(propylbisphenolA)propyldimethylsiloxy]-3,5,7,9,11,13,15 heptacyclohexylpenta-cyclo [9.5.1.13,9,15,15.17,13] octa-siloxane (BPA-POSS) (Fig. 4). In this way, POSS was chemically inserted in the hybrid design via molecular reinforcement in hard segment. Incorporation of POSS in epoxy polymer led to enhanced mechanical strength, permeability, high glass transition temperature (T_g), and nonflammability [41, 42]. A series of epoxy/POSS hybrids have been prepared containing 0–15 wt% nanofiller content [43]. Mechanical blending method was used for the purpose. POSS nanoparticle was amine functionalized to form POSS-NH₂ and 4,4'-diaminodiphenyl sulfone (DDS) used as curing agent (Fig. 5). The molten mixture was poured in a mold preheated at 120 °C. The amount of DDS was considered according to the number of epoxy groups. Epoxy/POSS hybrids have also been designed by reaction of octaepoxy-silsesquioxane (OECh) with an epoxy-amine system [44]. The OECh was used to replace diglycidyl ether of bisphenol A (DGEBA) with an aromatic diamine 4,4'-(1,3-phenylenediisopropylidene) bisaniline (BSA).

Environmental-friendly or biodegradable polymers such as polyethylene glycol (PEG) have also been processed with POSS for automotive, packaging, electronics, and textile industry [45, 46]. Aminopropylisobutylpolyhedral oligomeric silsesquioxane was melt compounded with poly(lactic acid) (PLA) and poly(ethylene glycol) (PEG) to form plasticized hybrids [47]. The modified POSS was found to reduce the melt viscosity of the hybrids, so act as lubricating agent. The nanofiller also influenced the thermal properties of hybrids. Correspondingly, poly(lactic acid) and poly(ethyleneglycol)-functionalized polyhedraloligomeric silses-Quioxane (PEG-POSS) hybrids were designed using melt blending [48]. The radiation-induced cross-linking behavior of neat PLA and PLA/PEG-POSS hybrids were explored. The

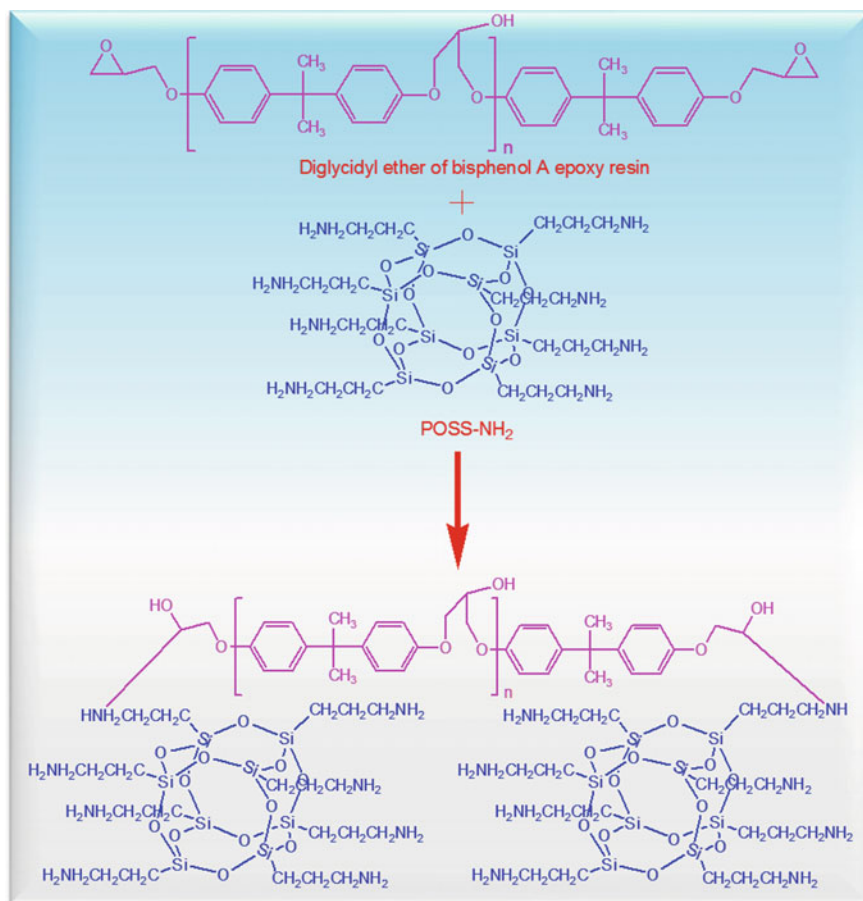


Fig. 5 Chemical reaction of octa(aminopropyl)silsesquioxane (POSS-NH₂) and diglycidyl ether of bisphenol A epoxy resin

cross-linking occurred by electron beam irradiation even at low absorbed dose. The cross-linking degree was increased extraordinarily with an increase in the absorbed dose to 20 kGy. POSS has also been grafted with different types of polyamide. Aliphatic polyamide/POSS hybrids have been reported [49]. Polyamide-6/POSS hybrid has been prepared through the polymerization of ϵ -caprolactam in the presence of ϵ -caprolactam-functionalized POSS [50].

POSS tethered aromatic polyamide hybrids have been prepared using Michael addition between maleimide-containing polyamide and amino-functionalized POSS (Fig. 6) [51]. Polyamide/POSS hybrid membrane has shown high water flux, salt rejection, and membrane properties compared with pure PA membranes [52–54]. The polyvinyl chloride (PVC) was reinforced with methacryl-POSS and dioctyl phthalate (DOP) in matrix through melt blending process [55]. The PVC and POSS hybrid was

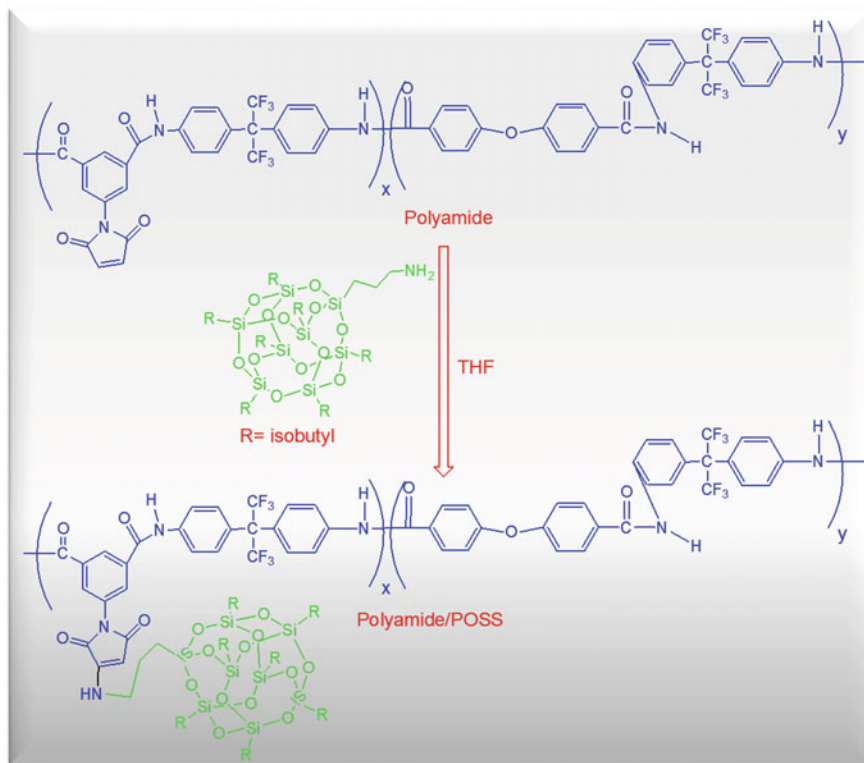


Fig. 6 Preparation of polyamide-tethered POSS hybrid

found transparent with fine dispersion up to 15 wt% loading. However, methacryl-POSS formed submicron-sized aggregates above 15 wt%. Addition of DOP also improved the miscibility of methacryl-POSS in PVC matrix [56]. Polystyrene (PS) and polypropylene (PP) were also used to design PS/POSS and PP/POSS hybrids [57, 58]. Dimeric and oligomeric Al- and Zn-containing isobutyl POSS were reinforced into PP matrix via melt blending [59]. The degradation pathways for POSS derivatives were found to involve evaporation and oxidation. Metal-containing POSS resulted in improved thermal stability of hybrids. Poly(methyl methacrylate) (PMMA)/POSS hybrids have been prepared by bulk polymerization [60]. The thermal and flame stabilities of hybrids were evaluated using thermogravimetric analysis (TGA) and cone calorimetry. The number of attempts to design various combinations of polymers and POSS or functional POSS compounds involves melt blending, mechanical mixing, as well as chemical interaction routes. The nanoparticle dispersion, mechanical, thermal, flammability, rheological, cross-linking, and other physical characteristics have been measured and compared to approach an ultimate high-performance polymer/POSS motif.

Few important and conventional types of polymerization techniques need to be mentioned here for the fabrication of polymer/POSS hybrids such as atom transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP), reversible addition–fragmentation chain transfer polymerization (RAFT), and click chemistry. These techniques have shown their significance, particularly in the formation of self-assembled polymers and block copolymers hybrids with functional POSS molecules. As mentioned in the preceding section that the incorporation of nanoparticles may initiate periodicity in copolymers, therefore, the design of self-assembled polymer/POSS hybrids is essential to deliberate. ATRP has been used to develop an important class of self-organized star-shaped POSS-containing hybrids [61]. Polymerization of methylmethacrylate (MMA) monomer using octabromide POSS as initiator may yield the star-shaped hybrids. Monomer as well as initiator concentrations were kept low for ideal conversion of monomers to a ordered poly(methyl methacrylate) (PMMA)/POSS hybrid. Moreover, the star-shaped POSS-containing PMMA had narrow molecular weight distribution. ROMP has also been used as an effective technique to form self-assembled hybrids. Using ROMP, POSS-containing hybrid diblock copolymer of 2-endo-3-exo-5-norbornene-2,3-dicarboxylic acid trimethyl ester has been produced. The norbornene monomer has also been converted to a well-defined self-assembled polymer with POSS via ROMP [62]. In this technique, the norbornene ethyl POSS monomer was processed using Ru-based catalyst. RAFT polymerization has also yielded self-assembled star-shaped hybrids [63]. Here, azido-terminated PMMA was produced and attached to octa-alkyne-POSS core to form a well-organized structure. In this method, octa-alkyne-POSS acted as RAFT agent. It was important to control the molar ratio of MMA/RAFT agent to control the polymerization degree and morphology of final hybrid. Another successful approach to form self-assembled polymer/POSS hybrids is click chemistry. It is a rather simple way to conjugate polymer blocks and POSS together [64]. Copper-catalyzed Huis-gen 1,3-dipolar cycloaddition catalyst has been commonly used in this technique. Click chemistry has also been combined with the RAFT, ATRP, or ROMP polymerization techniques to form new self-assembled polymeric architectures using advanced method [65]. Click reaction between polymer chain and POSS molecules may form hemi-telechelic POSS-containing hybrids [66].

6 Structure–Property Relationship in Polymer/POSS Hybrid System

To acquire full knowledge of this field, it is essential to investigate and understand the structure–property relationship in the designed polymer/POSS hybrid systems. Effect of structural parameters on final properties of polymer/POSS hybrids with functional nanoparticles has been studied using different techniques [27]. Hoy's method, solubility parameters, and morphology analysis have been used to explore

the affinity between polymer and POSS sample. Investigations revealed that the POSS nanoparticles acted as plasticizer for the polymer chains. Thus, POSS functionality, dispersion, and content have been found responsible for better compatibility between the matrix and nanofiller. Slight differences in the morphology and solubility parameter of POSS and matrix may cause aggregation of nanofiller in matrix. Furthermore, type of processing technique may significantly influence the interaction between the matrix and POSS functional groups. Incorporation of inorganic appropriate amount of POSS framework and suitable polymerization technique may also form self-assembled network in hybrids. Incorporation of different POSS content, POSS functionality, polymer type, processing technique and parameters, may lead to pronounced effects on the properties of resulting hybrids. Very high POSS loadings may increase the system rigidity by enhancing the glass transition temperature, crystallinity, and damping factor of the nanocomposite system. Structure–property relationship of such polymer/POSS systems can be investigated using rheological measurements and solubility parameters. High nanofiller loading beyond optimum concentration may deteriorate the mechanical and tribological properties of the hybrids, while the thermal stability of the system may increase. On the other hand, fine dispersion of POSS molecules in matrix may decrease friction between organic macromolecules and POSS, reduce entanglement density of polymer chains, and so increase the free volume. Thus, glass transition temperature and crystallinity of the system may decrease. Consequently, POSS molecules act as plasticizers for organic matrices. However, the plasticization efficiency depends on the type of interaction between polymer and hybrids, and nature and length of pendent organic group attached with POSS [67]. POSS with closed-cage structure and short organic pendent groups are more prone to aggregation, while long pendent functionalities and open-cage structure may offer increased free volume in the hybrid. Besides, multifunctional POSS may also possess good miscibility with the organic matrix and disperse well. Influence of the structure of organic substituent of POSS on hybrid properties has been investigated using range of techniques such as scanning electron microscopy, transmission electron microscopy, atomic force microscopy, wide-angle X-ray diffraction, etc. [68].

7 Challenges and Future Scenarios

Polymer/POSS hybrid materials have gained noteworthy curiosity owing to nanoscopic structure and advance functional properties compared with conventional hybrid materials. POSS compounds own true hybrid inorganic–organic architecture having inner inorganic framework of silicone and oxygen. The inner inorganic core is covered by organic substituents and polar functional groups. The surface groups can be nonreactive or reactive depending upon the desired design of polymer/POSS. POSS is actually smallest possible particles of silica. Incorporation of POSS nanoparticle in thermoplastic/thermoset polymeric matrices by physical or chemical cross-linking has provided an excellent route to high-performance hybrids.

POSS reinforcement has impacted the mechanical, thermal, glass transition, as well as biomedical properties of final materials. POSS surface functionalization has also performed crucial role in governing hybrid characteristics. Modification of POSS has also considerably improved its dispersion in polymer matrix. Constant dispersal of POSS nanoparticle in matrices caused improvement in physical properties. Alternatively, non-functional POSS have not been found compatible with matrix, so cannot be dispersed uniformly. Moreover, meager dispersion may result in microphase separated systems, which may not offer appropriate reinforcement [69, 70]. Usually, POSS units chemically bound with polymer do not cause phase separation. Consequently, functional POSS possesses significant recompenses over other current filler technologies. The POSS content also plays imperative role in determining thermal, mechanical, and other structural properties of POSS-containing hybrids. The materials may exhibit superior physical properties depending on the amount of POSS present in the matrix. Optimum nanofiller loading level needs to be identified to attain better results. Though polymer/POSS hybrids possess outstanding physical properties, large-scale production of these materials for potential commercial applications is limited due to high cost [71]. Despite significant upgrading in design and functional characteristics of polymer/POSS hybrids, still there are number of challenges that need to be addressed. However, substantial advancement has been made in controlling POSS interaction and distribution with polymers, well-defined structure–property relationships need to be defined. Interaction in polymer/POSS and modified polymer/POSS hybrids require more research and knowledge for the contribution of both the components.

Research on polymer/POSS hybrids is getting huge attention. These hybrids are still under research and require more attention to explore on large industrial scale. Fabrication and preparation of polymer/POSS hybrids are versatile and economical technology, though there are certain problems in processing of these materials. Solution processing of these hybrids requires the use of less hazardous organic solvents. In this regard, several studies have employed melt mixing method; however, POSS aggregation and agglomeration are major problems in this case. In situ polymerization have been adopted using suitable surfactants and initiators to better compatibilize polymer with POSS. The properties of polymer/POSS also depend on the POSS content. Nevertheless, above optimum POSS concentration, self-interaction between POSS cages cause aggregation. The appropriate design and processing conditions are definitely needed to attain fine dispersion of POSS in matrix, even at higher concentration. The design of modified POSS with desired functionalities may develop strong optimum interaction with matrix to enhance the overall miscibility. In this way, new high-performance functional material can be developed for industrial applications such as aerospace and automotive materials, electronics, energy devices, coatings, desalination membranes, adsorbents, packaging materials, etc. The polymer/POSS hybrids have developed several superior features such as mechanical strength, thermal stability, optical properties, low toxicity, and biocompatibility. The research so far has mentioned few significant applications of polymer/POSS hybrids in textiles, fire-retarding materials, gas transport membranes, and biomedical. Though, improvement in rheological, mechanical, and thermal properties must be focused for

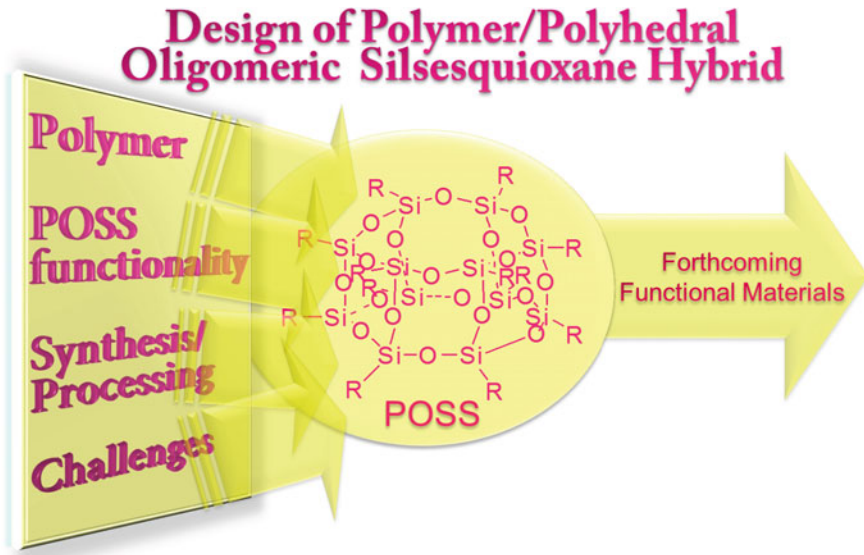


Fig. 7 Prospects of polymer/POSS hybrids

extensive future use in these and new areas. In the future, a suitable redirection is needed to study the processing of various polymers with modified POSS compounds for tailoring the desired high-performance characteristics (Fig. 7).

8 Summary

This chapter summarizes significant and versatile research on polymer/POSS hybrid materials. POSS nanoparticle has been amalgamated in thermoplastic as well as thermoset polymer matrices using solution method, in situ procedure, melt mixing, physical blending method, and other techniques. Final design of polymer/POSS hybrid depends on the mode of reinforcement using physical integration, chemical cross-linking, and covalent bonding. The miscibility and intermolecular interaction of organic–inorganic interpenetrating network of polymer/POSS have played essential role in determining the material characteristics. Surface functionalization of POSS has been employed to improve its compatibility with polymer matrices. Successful dispersion of POSS in polymer matrices depends on surface interaction such as polar interaction, van der Waals forces, hydrogen bonding, etc. in matrix nanofiller. These interactions may control POSS dispersion in polymeric matrices. Though, sometimes inter-particle interactions may result in the aggregation of particles. However, performance of hybrid materials has been enhanced by using different functional vertex groups, still there are several desired features need to be achieved.

Research on specific functionalization of POSS and its mode of integration in matrix is, consequently, indispensable to design high-performance hybrids. Nevertheless, standard models are definitely essential to attain unique designs of polymer/POSS hybrids, i.e., needed for research and industrial community. Established knowledge of structure–property relationship in these hybrids needs to be developed. Functional properties and interaction of polymer/POSS necessitate profound studies related to optimum design and processing conditions. One can imagine future nanostructured polymer/POSS materials of great variety and designs being industrialized. Coupling of functional polymers with POSS chemistry may be utilized to build regular three-dimensional repeating structures and networks of polymer/POSS having nanophases. These hybrid materials have found relevance in miscellaneous areas such as aerospace, textile, devices, and biomedical appliances. Although, noteworthy developments have been reported for these hybrids, yet there are several design challenges needed to be addressed in these technical fields.

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