POSS-Containing Polyamide-Based Nanocomposites

Biswajit Sarkar

Abstract Polyamide (PA) family of polymer is known as engineering plastics which are used in diverse industries such as synthetic fibers, automobiles, membranes. PA6 and PA66 are two major synthetic PAs that are widely used. Even though PAs possess several essential qualities, still some functional properties such as mechanical strength, rheological behavior, membrane permeability/permselectivity, flame retardancy need further improvement. Incorporation of POSS in PAs can improve those properties. In this chapter, we discussed POSS-containing PA nanocomposites. The influence of POSS on the structure and functional properties of PAs is discussed in particular.

Keywords Polyhedral oligomeric silsesquioxane (POSS) · Polyamides
Nanocomposites · POSS-polyamide nanocomposites · Morphology
Functional properties · Processing of nanocomposites

1 Introduction

Polymers possess several properties such as lightweight, ductile (easy to process), which make them highly valuable in various industrial applications as well as in our day-to-day life [1–4]. Compared to metals and ceramics, polymers lack sufficient mechanical properties such as Young's modulus and strengths which restrict their applications in many heavy-duty uses. The mechanical properties can be improved effectively by embedding a proper reinforcing material (filler) in polymer body. Various fillers are incorporated in polymer matrices such as fibers, platelets, nanoparticles. Based on the size, fillers can be broadly classified into two major categories,

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B. Sarkar (✉)
Department of Chemical and Biological Engineering, University at Buffalo, Buffalo,
NY 14260, USA
e-mail: bsarkar@buffalo.edu

B. Sarkar
Intel Corporation, Hillsboro, OR 97124, USA

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e.g., macrofillers and nanofillers. The improvement of mechanical properties by incorporating macroparticles often involves trade-offs of desirable properties, like stiffness can be improved at the cost of toughness. On the other hand, the incorporation of nanosized fillers (typical size 1–100 nm) into polymer matrices can improve desirable properties without harming other desired properties [5–8].

Nanofiller-containing polymers are known as polymer nanocomposite materials which are relatively new family of material. Nanofillers (nanoparticles) provide functional properties, and polymer provides processability. As a result, a family of processable functional hybrid materials with improved mechanical and functional properties can be produced. Polymer nanocomposite (clay/polyamide-6) was first commercially introduced by Toyota Motor Corp in the early 1990s [6]. Since then, substantial amount of work has been performed on polymer nanocomposites materials to improve various functional properties such as mechanical, electrical, thermal, membrane. Nanoparticles help in improving the properties of composites mainly in two ways: (i) by improving physical properties of polymer that depends on polymer–particle surface interactions and (ii) by embedding novel functional properties of nanoparticles.

1.1 POSS

Polyhedral oligomeric silsesquioxanes (POSS), also known as molecular silica, are nanoparticles (diameter in the range of 1–3 nm) with very well-defined organic–inorganic hybrid structure (see Fig. 1) [9–11]. POSS consists of inorganic silica (Si and O) core surrounded with organic ligands with empirical formula $(RSiO_{1.5})_n$ where R could be hydrogen or some organic ligands and $n = 4$ (T4), 6 (T6), 8 (T8, most common), 10 (T10), 12 (T12) (see Fig. 1). Surface properties of POSS particles depend on the properties of R which can vary from polar to nonpolar, reactive to nonreactive, and/or positively charged to negatively charge. A series of R ligands are presented in Table 1. Moreover, a range of POSS particles of various surface properties is commercially available. Depending on the nature of R, POSS can be classified into three types: (i) molecular silica (All R ligands are nonreactive), (ii) monofunctional POSS (one of the surface ligands is reactive), and (iii) multifunctional POSS (more than one surface ligands are reactive).

POSS can be incorporated into polymer matrices to improve various properties [12, 13]. For example, the incorporation of POSS into resin improved mechanical properties and surface finish. Depending on the nature of surface ligands, POSS particles can be incorporated into different polymer matrices [12]. The incorporation of POSS into polymer matrices can enhance various mechanical properties such as strength of modulus and rigidity, thermal stability without increasing weight of the materials (POSS-polymer composites remain lightweight). As a result, POSS-polymer nanocomposites are rapidly gaining interests in numerous commercial applications in the area of thermoplastics, thermosetting plastics, drug delivery, solid polymer electrolytes [14–17]. POSS are also used as additives to help other

Table 1 Various types of POSS surface ligands (R)

	R-type	Example of R
1	Acrylates	Acrylo
		Acryloisobutyl
2	Alcohols	Diol-isobutyl
		Cyclohexanediol
		Propanediol-isobutyl
3	Amines	Aminopropylisobutyl
		Aminopropylisooctyl
		Methyl-aminopropyl-isobutyl
4	Carboxylic acid	Maleamic acid isobutyl
		Octa maleamic acid
5	Epoxides	Epoxycyclohexyl
		Glycydyl
		Glycidyl isobutyl
6	Fluroalkyls	Trifluropropyl
		Trifluropropyl-isobutyl
7	Halides	Chlorobenzyl isobutyl
		Chlorobenzyl ethyl isobutyl
		Chloropropyl isobutyl
8	Methacrylates	Methacrylo isobutyl
		Methacrylate isobutyl
		Methacrylate ethyl
9	Alkane	Isooctyle
		Dodecaphenyl
		Phenylisobutyl
10	Olefins	Allylisobutyl
		Vinylisobutyl
11	PEG	PEG
12	Silanes	Octasilane
13	Silanol	Disilanol-isobutyl
		Trisilanolthyl
		Trisilanolisobutyl
14	Thyols	Mercaptopropylisobutyl
		Mercaptopropylisooctyl

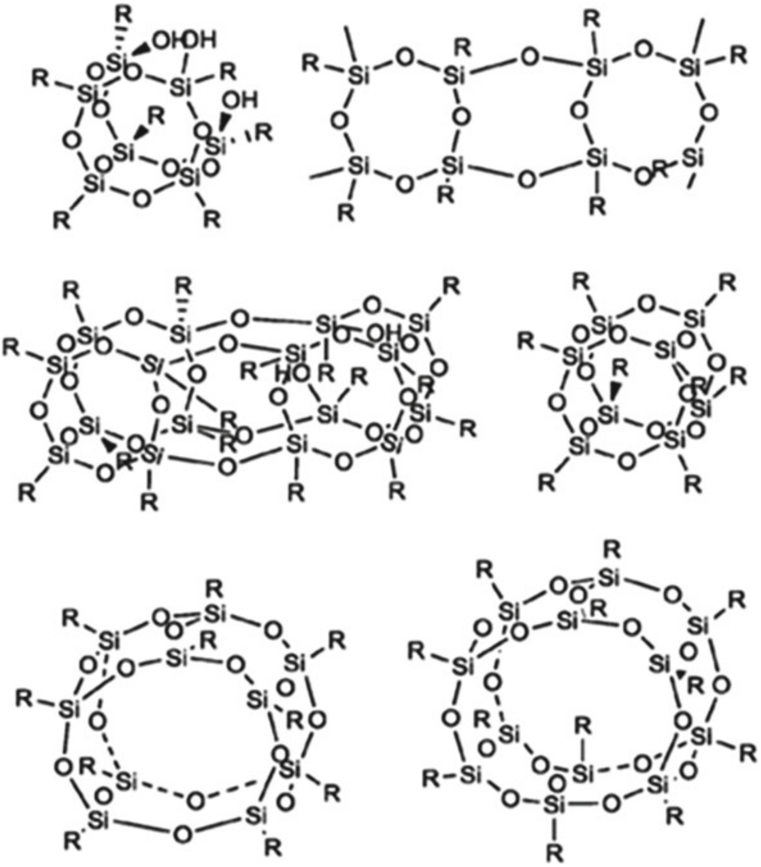

Fig. 1 Various chemical structure of polyhedral silsesquioxanes. Top left: partial cage structure; top right: ladder structure; middle left: random structure; middle right: T8; bottom left: T10; and bottom right: T12

nanoparticle dispersions in polymer matrices [18–20]. Moreover, POSS particles are environment-friendly, nonvolatile, and odorless, which are some additional benefits for using POSS.

The improvement of POSS-polymer composite properties lies in successful embodiment of POSS particles in polymer matrices without any macrophase separation. POSS can be incorporated in polymeric matrices in three different ways: (i) chemically cross-linking of POSS with polymer chains, (ii) in situ synthesis of POSS in side polymer matrices, and (iii) physical blending of POSS (synthesized ex situ) and polymer [12, 21]. Chemical cross-linking involves selective reaction between polymer chain and POSS active ligands and depends on active pair of polymer chain and POSS ligands. Therefore, the application of POSS is limited. On the other hand, in situ synthesis of POSS in polymeric matrices depends on the supply of chemical which restricts amount of POSS particles in polymer matrices. For physical blending of POSS with polymer such restrictions do not exist. Physical blending depends on surface compatibility between POSS and polymers.

1.2 Polyamides

Polyamide (PA) is a family of polymers (also known as engineering plastics) which contain amide (–CONH) linkages along their molecular backbone. PA can broadly be classified into two types: (i) natural (various proteins) and (ii) artificial (nylon, aramide, etc.). Artificial PAs can be synthesized by condensation chemical reaction between and carboxylic acid group and amine group. Polyamide 6 (PA6) and polyamide 66 (PA 66) are two major types of commercial PAs (also known as nylon). PA6 is produced commercially by the polymerization of caprolactam. PA 66 is synthesized through polycondensation reaction of hexamethylene diamine and adipic acid. Several other commercial PAs are (i) PA 4,6 (poly(tetramethyleneadipamide)), (ii) PA 6.9 (poly(hexamethyleneazelamide)), (iii) PA 6.10 (poly(hexamethylenesebacamide)), (iv) PA 6.12 (poly(hexamethylenedodecanedioamide)), etc.

PA polymers possess various essential properties such as: (i) better chemical stability, (ii) good wear resistance, (iii) high strength. As a result, PAs are widely used in transport, automotive, textile, carpet, sportswear, etc., industries [22]. However, use of PAs without any modification is associated with many disadvantages such as (i) higher moisture absorption, (ii) poor notch toughness, (iii) bad dimensional stability. Therefore, the improvement of physical properties by incorporating nanosized filler POSS in PA matrices would be beneficial and attract significant attention of academics as well as industries. In this chapter, we discussed PA-POSS composite materials [23–26].

2 Polyamides-POSS Nanocomposites

2.1 Incorporation of POSS in Polyamides

Understanding the full potential of POSS-containing PA nanocomposites, the successful incorporation of POSS in PA matrices is needed without macrophase separation. POSS can be incorporated in PA matrices either by chemical cross-linking or by physical blending (melt blending or solvent blending). Incorporation by chemical cross-linking can be achieved via various complex polymer chemistries (such as coordination polymerization, ring-opening metathesis polymerization, free radical polymerization), and therefore, commercialization of such process is challenging. POSS particles are available with various surface properties, and the incorporation of

POSS in PA by physical blending is advantageous over chemical methods. However, the successful incorporation of POSS in PA matrices by physical blending without macrophase separation requires favorable POSS-PA surface interaction which is discussed in this section.

2.2 POSS-Polymer Interaction

For developing a suitable process for incorporation of POSS in PA or any other polymer matrices by physical blending (melt blending or solvent blending) without causing macrophase separation, it is critical to understand POSS-polymer surface interactions. In POSS-polymer systems, POSS-POSS, POSS-polymer, and polymer–polymer interactions are the three main surface interactions, which are present. The interplay of these three surface interactions determines the final POSS-polymer composites. Dominant POSS-POSS and polymer–polymer interactions would lead to aggregation of POSS particles and segregation of aggregated POSS particles toward the composite surface resulting macrophase separation. Favorable POSS-POSS interaction can lead to the formation of a network morphology [27, 28]. However, POSS-POSS interactions depend on their surface ligands. For example, triol-POSS forms dimer in solution through hydrogen-bonding interactions, whereas diol/monool-POSS did not form any dimer in solution [29].

Dominant POSS-polymer surface interactions result in successful incorporation of POSS in polymer matrices. The strength of POSS-polymer interactions determines the extent of reinforcement by POSS. For example, 10 wt% incorporation of more compatible trisilanolphenyl POSS in PA6 increased storage modulus from 1.3 GPa (neat polymer) to 1.96, while 10 wt% incorporation of less compatible octaisobutyl POSS in PA6 increased the storage modulus to 1.81 GPa [30]. Hydrogen-bonding interaction can increase the miscibility of POSS and results in successful incorporation of POSS in PA matrices. For example, octa-ammonimum POSS (OA-POSS) can form hydrogen bonds with N–H groups of PA6, and as a result, 5 wt% OA-POSS can be homogeneously dispersed in PA6 matrices [31].

POSS-PA surface interactions can be described by solubility parameters which are related to the enthalpy of mixing. A closer value of solubility parameters of POSS and PA indicates a favorable enthalpy of mixing. For example, a lower solubility parameter difference of 1.2 $(\mathrm{cal/cm}^3)^{1/2}$ between PA6 and trisilanolphenyl POSS (Tsp-POSS) than that of PA6 and octaisobutyl POSS (Oib-POSS) (3.2 $(\mathrm{cal/cm}^3)^{1/2}$) indicates that Tsp-POSS has better surface compatibility with PA6 than that of Oib-POSS. As a result, Tsp-POSS exhibited better dispersion in PA6 [30]. Therefore, solubility parameters can be used to determine the miscibility of POSS in PA and other polymers. Solubility parameters of PA6, aminopropylisobutyl POSS (apib-POSS), aminoisopropyl-isooctyl POSS (apio-POSS), and aminopropyl-phenyl POSS (app-POSS), and various other polymeric ligands and functional groups are presented in Table 2. Method for estimating solubility parameters was discussed elsewhere [32, 33]. POSS-polymer Flory–Huggins interactions parameter can also be used to

Table 2 Solubility parameters of PA and various POSS and POSS ligands

	δ_d (J$^{1/2}$ cm$^{-3/2}$)	δ_p (J$^{1/2}$ cm$^{-3/2}$)	δ_h (J$^{1/2}$ cm$^{-3/2}$)	δ (J$^{1/2}$ cm$^{-3/2}$)
PA6	15.9	34.6	13.4	18.0
Apib-POSS	17.5	0	0	17.5
Apio-POSS	18.6	0	0	18.6
App-POSS	19.2	1.5	0	19.3
-CH$_3$	19.49	0	0	19.49
-C(CH$_3$)$_3$	17.45	0	0	17.45
-C(CH$_3$)$_7$	18.59	0	0	18.59
-Phenyl	19.19	1.48	0	19.25
-CH$_{2-}$)	17.36	0	0	17.36
-COO-	16.46	20.68	17.19	17.91
-CONH-	15.90	34.63	13.42	18.01

explain the surface compatibility and can help to determine whether a specific POSS will disperse in a particular polymer matrices or not. For example, aminopropyl-isobutyl POSS (AB-POSS) possess a more favorable surface interaction with PA6 (Flory–Huggins parameter = −0.42 cal/cm^3) and can be dispersed in PA6 uniformly up to 0.5 wt%. On the other hand, aminopropyl-isooctyl POSS (AO-POSS) and aminopropyl-phenyl POSS (AP-POSS) possess less attractive surface interactions with PA6 (Flory–Huggins parameters for PA6/AO-POSS and PA6/AP-POSS are −0.35 and −0.23 cal/cm^{-3}, respectively) and form POSS aggregates during melt mixing with PA6. Smaller Flory–Huggins interaction parameter suggests a more favorable thermodynamic favorable interaction.

3 PA-POSS Structure and Morphology

Physical properties of PAs and their composites are directly influenced by their microstructure and morphology. Therefore, it is important to understand how incorporation of POSS in PA can influence the structure and morphology of nanocomposites. Polyamide PA6 is a semi-crystalline polymer with two polymorphs: α and γ. α is thermodynamically stable phase and γ is kinetically trapped phase. The nature of hydrogen bonds between N–H and C=O is different for α and γ phases. Hydrogen bonds are formed between anti-parallel polymer chains in α phases, whereas in γ hydrogen bonds are formed between parallel chains. Also, lattice parameters are different for α and γ phases. For α phase, $a = 0.96$ nm, $b = 1.72$ nm, $c = 0.80$ nm, and $\beta = 67.5°$. For γ phase, $a = 0.93$ nm, $b = 1.69$ nm, $c = 0.48$ nm, and $\beta = 121.0°$. The incorporation of aminoisopropyle isobutyl POSS (APOSS) (0–5 wt%) by melt blending did not alter the crystal structure of α phase [31]. Similarly, the incorporation of glycidil-isobutyl POSS (G-POSS) in PA6 by melt blending did not show

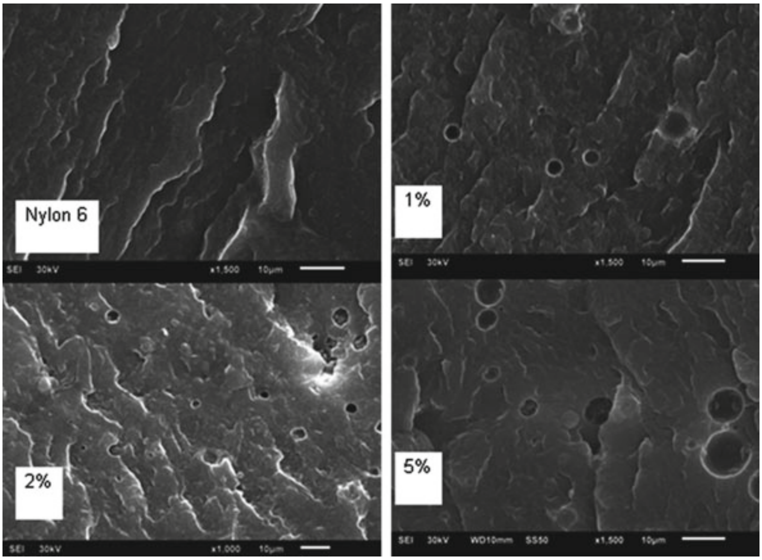

Fig. 2 SEM images of cross section of neat PA6 (top left), PA6 + 1% APOS (top right), PA6 + 2% APOSS (bottom left), and PA6 + 5% APOSS (bottom right). Images are adopted with permission from [37]. Copyright 2014 Elsevier

any significant influence on crystalline structure and degree of crystallinity [34]. On the other hand, the incorporation of POSS by chemical cross-linking in PA6 leads to crystalline phase transition from α to γ and degree of crystallinity decreased [35]. The incorporation of 5 wt% octaisobutyl POSS and trisilanolphenyl POSS in PA66 did not alter the polymer crystallinity [36]. The incorporation of OA-POSS in PA6 by solution blending also did not alter the crystalline structure (α phase) as well [31].

Morphology of melt blended PA6-aminopropylisobutyl POSS (AB-POSS) was studied using cross-sectional SEM [37]. AB-POSS phase separated and formed spherical aggregates in PA6 matrices (see Fig. 2). Number and size of phase-separated spherical aggregates increased with the increasing amount POSS in PA6. This phase separation suggests that AB-POSS is not very compatible with PA6, and at higher loading concentration, POSS formed spherical aggregates and phase separated. Different POSS with reactive and nonreactive side groups have been incorporated in PA6 matrices via synthetic methods where PA6 was synthesized in situ from ε-caprolactam in the presence of POSS [38]. In the presence of nonreactive apolar POSS, poor dispersion was obtained due to their poor interactions with polar PA6. In the case of POSS with reactive side groups, better dispersion of POSS in PA6 matrices was obtained where POSS was covalently bonded to PA6. POSS-containing PA6 composites were semi-crystalline, and degree of crystallinity decreases with increasing POSS content.

Uniform dispersion of POSS in PA or any other polymer matrices requires favorable surface compatibility. However, the surface compatibility is not sufficient which can ensure the uniform dispersion of POSS in polymer matrices particularly when POSS is incorporated by melt blending due to higher viscosity of polymer melts. Depending on the processing type, POSS may disperse uniformly and form desired morphology which can provide better reinforcement or not. For example, the incorporation of AB-POSS in PA6 by injection molding could not provide better POSS dispersion in PA6 matrices; rather, it resulted in macrophase separation of spherical POSS aggregates (see SEM cross-sectional images Fig. 3, right) [39]. On the other hand, the incorporation of AB-POSS in PA6 by melt-spun technique provided better inclusion of POSS in PA6 matrix (see SME cross-sectional images Fig. 3, left). Composites fiber made by melt spun exhibited elongated POSS morphology in PA6 below 5 wt% POSS loading. However, above 5 wt% POSS loading, melt-spun technique could not provide better POSS dispersion. POSS particles formed spherical aggregates and macrophase separated above 5 wt% POSS loading. In melt-spun technique, a combination of shear and favorable PA6-POSS surface interactions helps forming elongated POSS structures inside amorphous POSS domain.

Polyamides are widely used as membranes materials, and therefore, it is important to investigate the thin-film surface and bulk structure. THF solvent cast PA6 film exhibited porous surface structure with microvoids (see Fig. 4) [40]. Film prepared under 55% relative humidity contains pores of diameter in the range of 5–7 μm. As RH increased, the pore size also increased. In the presence of moisture, water vapor condenses on PA6 film, coalesces, and forms a disordered array of droplets which resulted in the formation of disordered arrays of pores in PA6 film. At higher RH, water droplet size increased leading to larger pore size. When AB-POSS was incorporated in PA6 film, film surface becomes rougher (see Fig. 4 Bottom row). The presence of AB-POSS disrupts the water distribution resulting in an hetereogeneous smaller-sized pores. Introduction of AB-POSS also makes film more porous [40]. Similar impact of AB-POSS on pore film structure was visualized at cross-sectional SEM (see Fig. 5).

3.1 Morphology of POSS-Containing PA-Polymer Blends

To achieve desired polymer properties, PA often blends with another polymer. For example, PA is blended with methyl methacrylate-butadiene-styrene copolymer to achieve desired toughness [41]. Therefore, POSS-containing nanocomposites of PA6-polymer blend merit a discussion. The incorporation of epoxycyclohexyl-POSS in poly(2,6-dimethyl-1,4-phenylene-oxide)/PA6 (PdMPO/PA6) blends via melt mixing leads to morphological transformation from a droplet/matrix to co-continuous morphology [42] (see SEM images in Fig. 6). PdMPO phase (darker domains in SEM images) tends to coalesce during melt mixing due to their higher viscosity than PA6. As a result, equal mixture of PdMPO/PA6 blend exhibits a droplet–matrix morphology where PA6 formed the matrix and PdMPO formed the droplets (diameter ~0.67 μm) (see Fig. 6a). PdMPO droplet size decreases to 0.2 μm due to the incorporation of 2 wt% of POSS (see Fig. 6b). POSS particles localize at PdMPO-PA6

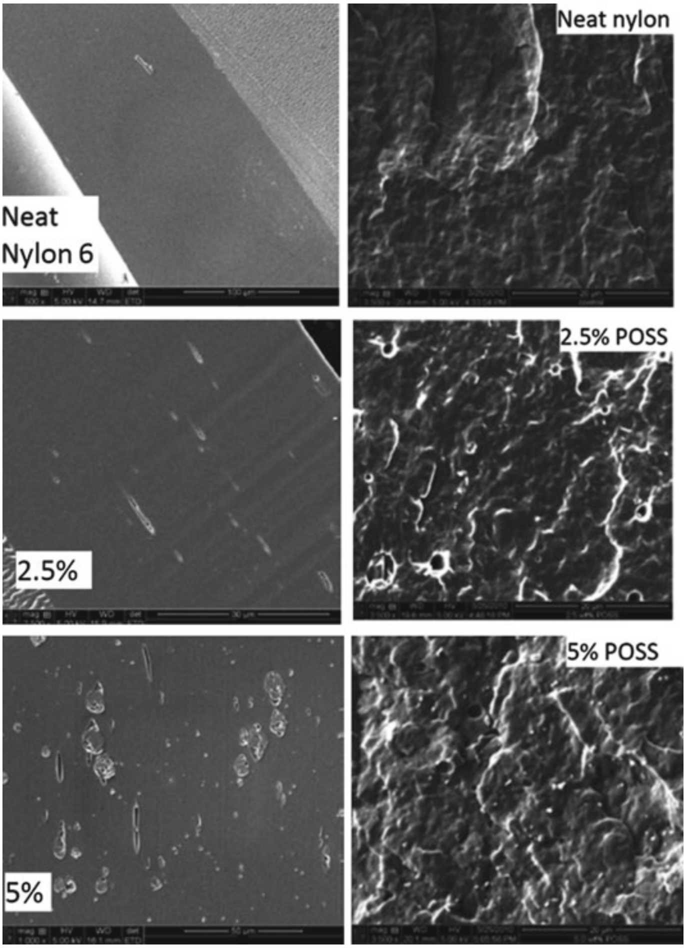

Fig. 3 Effect of processing and POSS loading on POSS dispersion. Aminopropylisobutyl-POSS was incorporated in PA6 by melt spin (left side) and by injection molding (right). SEM images are adopted with permission from [39]. Copyright 2012 American Chemical Society

interfacial regions, and as a result, PA6-PdMPO interfacial tension decreases leading to decrease in PdMPO droplet size.

As amount on POSS increased in PA6-PdMPO blend, more POSS particles localize in PA6-PdMPO interfacial region which further decreased the interfacial tension, break the complex cross-linked morphology, and generated new co-continuous morphology. 4 wt% POSS-containing PdMPO-PA6 blend composite exhibited a co-continuous morphology (see Fig. 6c) [42]. Further increase of POSS to 6 wt% in PA6-PdMPO blend, co-continuous morphology becomes coarse and rough (see Fig. 6d). On further increase of POSS content above 6 wt%, PA6 starts cross-linking to POSS, and melt viscosity of PA6 increased and becomes more viscous than PdMPO.

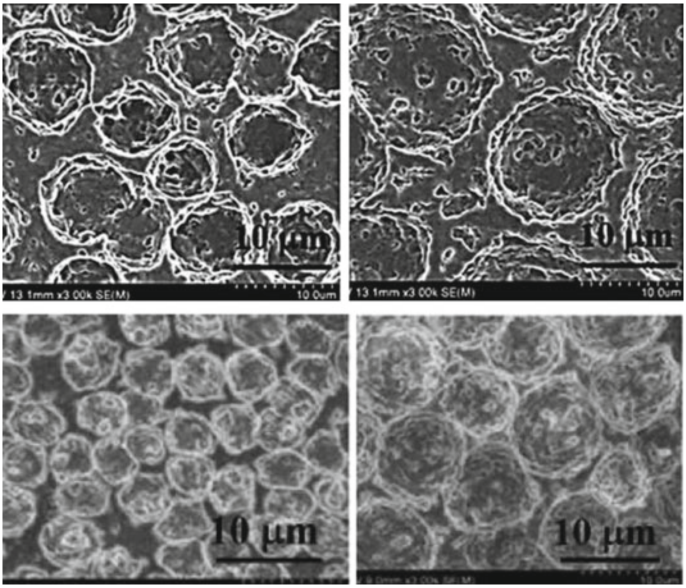

Fig. 4 Effect on AB-POSS incorporation of surface morphology of PA6 film under different relative humidity. Top left: PA6 film, 55% humidity; top right: PA6 film, 85% humidity, bottom, left: PA6 + AB-POSS film, 55% humidity, bottom, right: PA6 + AB-POSS film, 85% humidity. Images are adopted from [40]. Copyright 2016 Royal Society of Chemistry

As a result, PA6 starts coalescing during melt mixing at 8 wt% POSS loading to an inverse droplet–matrix morphology where PA6 formed dispersed droplets and PdMPO formed the matrix (see Fig. 6e). Note that POSS-containing PA6-PdMPO co-continuous morphology exhibits superior mechanical properties compared to droplet morphologies which is further discussed in next section.

4 PA-POSS Functional Properties

In the previous section, we discussed the structure and morphology of PA-POSS composites. In this section, we discuss different functional properties of PA-POSS composite materials.

4.1 Mechanical Properties

Mechanical properties (Young's modulus, tensile strength, elongation break, etc.) of PAs can be improved by incorporating POSS which can reinforce the polymers [41].

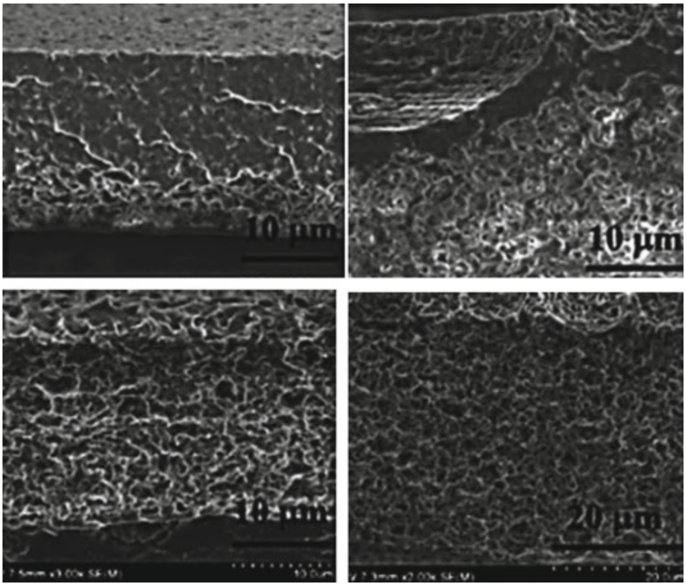

Fig. 5 Influence of AB-POSS incorporation on PA6 film cross-sectional morphology under different relative humidity. Top left: PA6 film, 55% humidity; top right: PA6 film, 85% humidity, bottom, left: PA6 + AB-POSS film, 55% humidity, bottom, right: PA6 + AB-POSS film, 85% humidity. Images are adopted from [40]. Copyright 2016 Royal Society of Chemistry

The mechanical property improvement of POSS-containing PA composites depends on several parameters such as (i) POSS surface property (that determine state of the POSS dispersion), (ii) POSS loading, (iii) morphology, (iii) shape and size of the aggregates, and (iv) processing type.

The POSS-PA surface interactions play a crucial role in improving mechanical properties. Favorable surface interaction can help successfully disperse POSS in PA matrices and reinforce mechanical properties of PA-POSS composites. On the other hand, unfavorable PA-POSS surface interactions can lead to POSS aggregation and phase separation.

Young's modulus of POSS-containing PA6 composites can increase up to 2 wt% POSS loading as shown in Fig. 7, left, and above 2.5 wt% POSS loading, Young's modulus starts decreasing. The mechanical property improvement below 2.5 wt% POSS loading is related to the longitudinal organization of POSS in PA6 fibers. Beyond 2.5% loading, POSS starts forming spherical aggregates. Elongated POSS aggregates reinforce polymer matrices and can change the flexibility of the polymer chains located along the particle assembly. As a result, Young's modulus of PA6-POSS composites starts to increase. However, the increase in Young's modulus is not equivalent to the arithmetic average of Young's modulus of PA6 and POSS. Similar increase in stress yield is also reported for aminoisopropyle-POSS-containing PA6 composites produced by melt-spinning process [39]. Incorporation of octaisobutyl

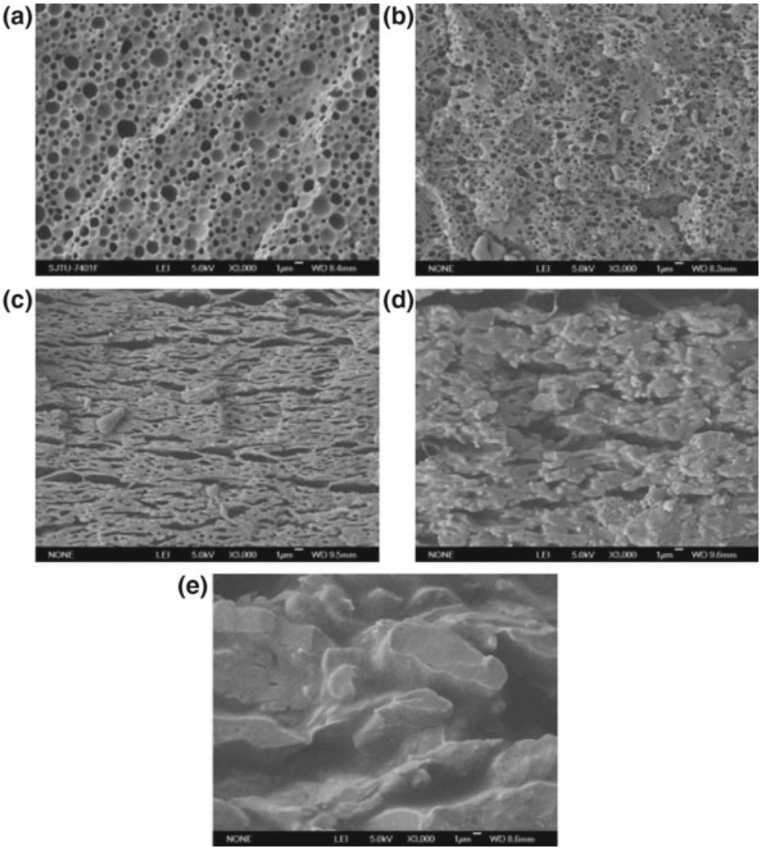

Fig. 6 Influence of POSS incorporation on 50:50 PA6-PdMPO blend (PA6 = polyamide 6 and PdMPO = poly(2,6-dimethyl-1-4-phenyl oxide). **a** 0 phr POSS, **b** 2 phr POSS, **c** 4 phr POSS, **d** 6 phr POSS, **e** 8 phr POSS. Reproduced with permission from [42]. Copyright 2009, Elsevier

POSS and trisilanol-phenyl POSS in PA66 enhances mechanical properties such as elongation at break and stiffness [36].

The processing condition can impact the degree POSS dispersion which influences the mechanical properties of nanocomposites. For example, the incorporation of aminoisopropyl-POSS in PA6 (nylon 6) by injection molding decreases mechanical properties (see Fig. 7), and thermal properties remained unchanged. The decrease in mechanical properties is attributed to spherical aggregates formation by POSS. On the other hand, incorporation of aminoisopropyl-POSS (up to 2.5% loading) in PA6 by melt-spinning process lead to an increase in mechanical properties (see Fig. 7) [39]. Chemical cross-linking of POSS to PA6 results to a decreases in the stiffness of PA6 due to decrease in degree of polymer crystallinity [35]. The increase in stiffness by POSS reinforce is overwhelmed by the loss of stiffness due to the decrease in degree of crystallinity.

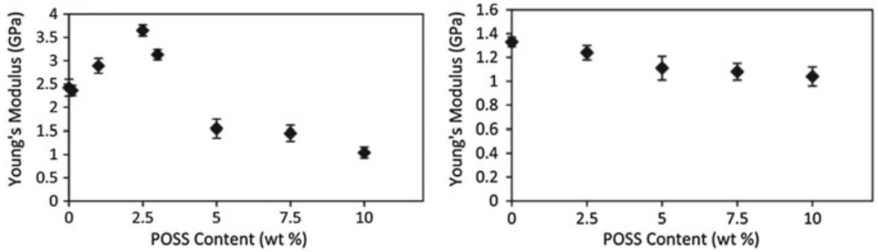

Fig. 7 Effect of processing and POSS loading on mechanical properties of PA6-POSS composites. Aminoisopropyl-POSS was incorporated in PA6 by melt spin (left side) and by injection molding (right). (Figures were reproduced from [39]. Copyright: American Chemical Society 2012.)

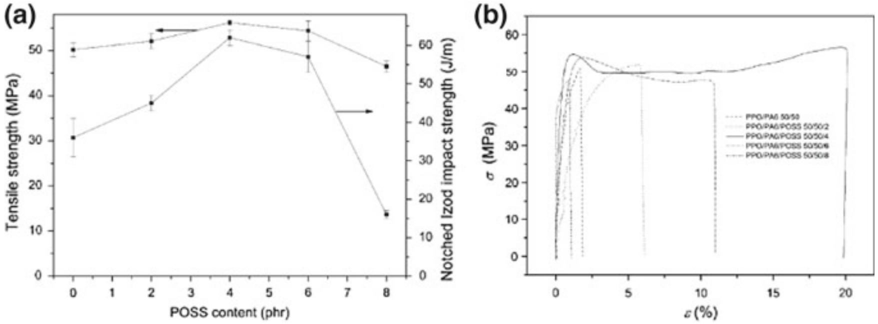

Fig. 8 Influence of POSS incorporation in PdMPO-PA6 polymer blends on mechanical properties: **a** tensile strength and notched izod impact strength; **b** stress–strain curve. Reproduced with permission from [42]. Copyright 2009, Elsevier

POSS-containing PA6-PdMPO composites possess superior tensile strength and notched izod impact strength (see Fig. 8a) [42]. Tensile strength and izod notched impact strength increase with increasing POSS concentration, and reach to maximum (55.2 MPa and 61 J/m, respectively) at around 4 wt% POSS loading, and above 4% POSS loading start decreasing. These variations in mechanical properties are related to the morphology of POSS-containing PA6-PdMPO campsites. At lower POSS loading, PA6-PdMPO form a droplet morphology (PdMPO droplets are dispersed in PA6 matrix). As POSS concentration increases, the drop morphology transforms to a co-continuous morphology which exhibits very high tensile strength and notch izod impact strength. On further increase in POSS concentration, co-continuous morphology transforms to inverse droplet morphology (POSS-containing PA6 formed droplets in PdMPO matrix). As a result, both tensile strength and notch izod impact strength decrease. The incorporation of POSS in PA6-PdMPO blends also help to increase elongation at break as suggested by stress–strain curve (see Fig. 8b) [42]. PA6-PdMPO blends show brittle break when no POSS is incorporated and more than 8 wt% POSS is incorporated.

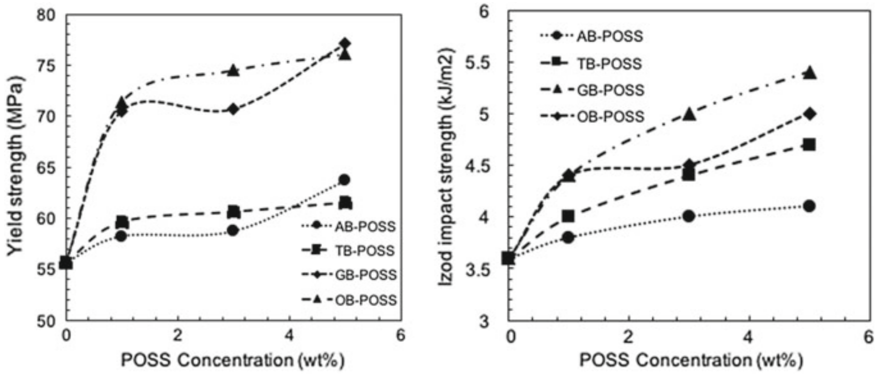

Fig. 9 Influence of amount and types of POSS on mechanical properties of PP-PA6 blends. Left: yield strength; right: izod impact strength. Data adopted from [43] and plotted

Incorporation of four different types of POSS (aminopropyl-isobuty POSS (AB-POSS), trisilanol-isobuty POSS (TB-POSS), glycidyl-isobuty POSS (GB-POSS), and octaisobuty POSS (OB-POSS)) in polypropylene (PP)-PA6 blend helps to improve the yield strength and izod impact strength irrespective of POSS types (see Fig. 9) [43]. General improvement in yield strength and izod impact strength due to the incorporation of POSS in PP-PA6 blends originates from the improvement of interfacial adhesion by POSS localization. PP-PA6 blends formed droplet-type morphology where larger PA6 droplets disperse in PP matrix. POSS particles localize at PP-PA6 interface and improvise interfacial adhesion, and PA6 droplet size decreases resulting in improved yield strength and izod impact strength. Yield strength and izod impact strength improvement depends on the POSS type and GB-POSS and OB-POSS exhibited higher improvement over AB-POSS and TB-POSS at a given POSS loading. This finding suggests that GB-POSS and OB-POSS are better candidates in providing PP-PA6 interfacial reinforcement over AB-POSS and TB-POSS.

4.2 Thermal Degradation

Poor thermal stability of polymeric materials often limits their applications to high-temperature applications due to their poor thermal stability. The incorporation of POSS nanofillers into polymeric matrices can enhance the thermal stability of polymeric materials due to the rigid POSS case. POSS-polymer interfacial interactions, cross-linking, and amount of POSS control the thermal stability of POSS-polymer thermal stability. For example, the incorporation of 0.5 wt% AB-POSS in nylon 6 increased the thermal decomposition temperature by about 10 °C (see Fig. 10) [44]. On further increase in AB-POSS, the thermal degradation temperature starts decreasing. When AB-POSS was replaced with less compatible AO-POSS or AP-POSS,

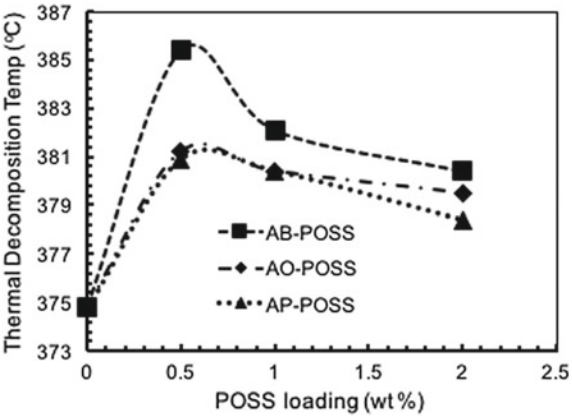

Fig. 10 Effect of various POSS on thermal degradation temperature of PA6-POSS composites. Data adopted from [44] and plotted

thermal degradation temperature increased by about 6 °C at 0.5 wt% POSS loading (see Fig. 10). On further increase in AO-POSS or AP-POSS, thermal degradation temperature starts decreasing similar to AB-POSS. The incorporation of octaphenyl POSS and octaamminophenyl POSS in PA66 also increases the decomposition temperature of PA66 [45].

4.3 Glass Transition Temperature

Glass transition temperature (T_g) is a characteristic of amorphous polymer or polymeric material above which hard glassy polymer turns into viscous or rubbery polymer. T_g is related to the rigidity of polymer chains and an important polymer property. PA is semi-crystalline polymer, and T_g is the property of disorder amorphous part of PA. The presence of nanoparticles in polymer matrices can influence the mobility of adjacent polymer chain and thus can influence the T_g. The incorporation of POSS that is attractive to the polymer surface can increase the glass transition (T_g) temperature as well as storage modulus [44]. T_g indicates the mobility of polymer chains, and an increase in T_g suggests that polymer becomes less mobile and more rigid. The incorporation of POSS particles, which are attractive to polymer, can interact favorably with polymer surface and arrest the mobility of polymer, and as a result, T_g increases. For example, incorporation of AB-POSS and AP-POSS in nylon 6 matrix increases the T_g as well as the storage modulus [44]. Also, the incorporation of AB-POSS and AP-POSS in nylon 6 increases the cross-linking density which also contributes partially to the storage modulus. T_g of a POSS-containing nanocomposites depends on several factors such as particle–polymer, particle–particle interactions, and amount of POSS. The incorporation of POSS in dimer fatty acid polyamide membrane prepared by solvent cast method exhibits an increase in T_g for 57 to 62 °C at about 20 wt% POSS loading [46].

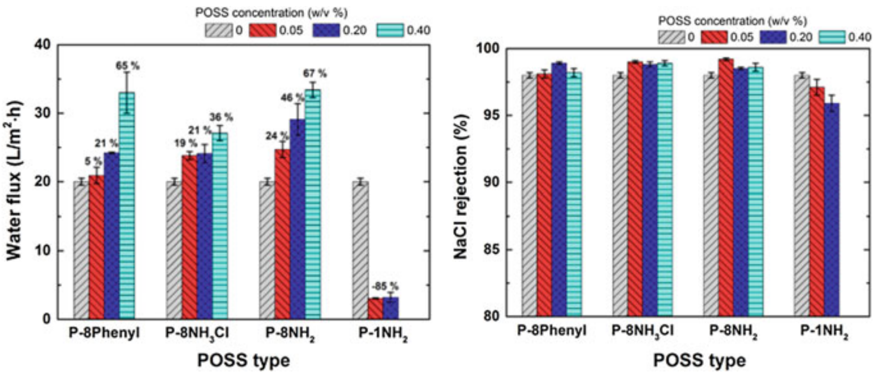

Fig. 11 Influence of 8Ph, $8NH_3Cl$, $8NH_2$, and $1NH_2$-POSS on water flux (left) and **b** NaCl rejection (right) of PA6 membranes. Figure adopted with permission from [53]. Copyright: Elsevier 2015

4.4 Membrane Properties

Polyamides and their composites are widely used in membrane technology which find many commercial applications in desalination [47–51], gas separation [52], biological applications [46], etc. Commercial reverse osmosis membranes consist of two major components: (i) active polyamide layer that is selective and (ii) pours support. The incorporation of POSS in PA layers could improve desired membrane properties and increased membrane performance (faster transport of desired material through the membrane and rejection of unwanted material). The incorporation of nanosized filler-like POSS into polyamide membranes can improve the water filtration performance of PA6 membranes. The incorporation of hydrophobic POSS (octaphenyl POSS (8Ph-POSS), octaammonium POSS ($8NH_3Cl$-POSS), octaaminophenyl-POSS ($8NH_2$-POSS), and aminopropylisobutyl POSS ($1NH_2$-POSS)) into PA6 thin-film membrane increased water flux and salt rejection (see Fig. 11) [53]. The incorporation of different hydropobic POSS in PA6 thin-film membranes increased free volume. Improved gas diffusivities were reported due to POSS incorporation in apliphatic polyamide membranes [52].

Fatty acid polyamides can be used in membrane applications. The incorporation of POSS in such biomembranes can improve bionanocomposite properties. A series (19) of bionanocomposite membranes which consist of dimer fatty acid polyamide in the presence of various POSS loading were investigated for structure, surface morphology (see Fig. 12), and membrane property (permeability) [46]. A series of characterization suggests that incorporation of POSS in PA nanobiocomposite membranes increased surface roughness, membrane density and decreased surface free energy and free volume. The incorporation of POSS in fatty acid polyamide membrane decreased permeability of various gases: N_2, O_2, and CO_2. In addition, the incorporation of POSS in PA membrane increased the permselectivity. This would

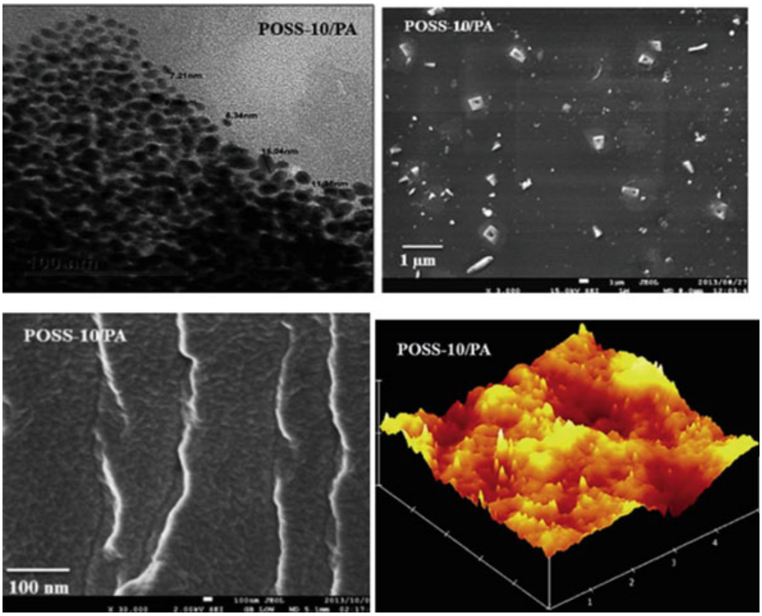

Fig. 12 10 wt% POSS-containing fatty acid polyamide bionanocomposite. Top left: TEM; top right: surface SEM; bottom left: cross-sectional SEM; bottom right: 3D AFM image. Images are adopted from [46]. Copyright 2015 Royal Society of Chemistry

enable POSS-containing nanocomposite membranes in various industrial applications such as food packaging.

4.5 Fire Retardancy

Successful application of POSS-containing PA composites requires superior fire retardant. This is particularly important for polyamide materials used for automobile parts such as tank, fuel line. Halogen is used as flame retardant, but due to environment regions, halogens are not useful as fire retardant. Si–O in POSS can provide flame retardancy, and therefore, POSS is a suitable candidate which can impart fire retardancy in POSS-containing PA composites [54–58]. The incorporation of 3.3 wt% in PA12 by melt compounding improved fire retardancy. Peak heat release rate decreases from 1635 to1521 kW/m^2 [56]. However, a combination of carbon nanotube and POSS incorporation in PA12 exhibited dramatic improvement in fire retardancy; peak heat release rate decreased from 1653 to 425 kW/m^2 [56]. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-0-oxide POSS (DOPO-POSS) was incorporated in diglycide ether of bisphenol A (DGEBA) cured by PA650 or aromatic 4,4-diaminodiphenylsulphone (DDS) [57]. The heat release rate curve for

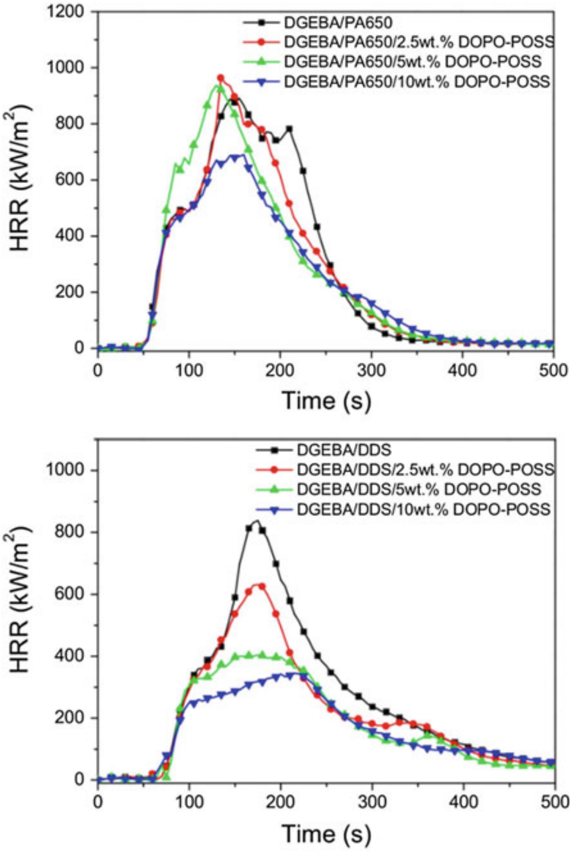

Fig. 13 Influence of DOPO-POSS on heat release rate of polyamide (top: PA650, bottom: DDS) cured DGEBA-DOPO-POSS nanocomposites. Reproduced with permission from [57]. Copyright 2012 Elsevier

these polyamide-cured nanocomposites (see Fig. 13) exhibits that peak heat release rate decreased with increasing amount of DOPO-POSS. The influence of PA650 cured composites is subtle. Also, incorporation of DOPO-POSS in polyamide-cured composites showed blowing out effect.

A combination of trisilanophenyl-POSS (T-POSS) and nanoclay inclusion in PA6 exhibits improved fire retardancy. In the presence of POSS, at higher temperature, POSS might transform to glassy material and can improve flame retardancy. Clay silicate can add further improvement on fire retardancy by adding an additional layer on silica glass. The incorporation of 15 wt% T-POSS in PA6-clay composites provides substantial fire retardancy improvement over PA6-clay composites. POSS provides a uniformly distributed composite (see the TEM image in Fig. 14) which helps improve fire retardancy [59]. POSS and clay seem to synergize their fire retardant properties. This idea was further taken a step forward where clay and POSS were combined and cross-linked to make clay-POSS surfactant line molecule. Further, the incorporation of POSS–montmorillonite clay surfactant in PA6 exhibits improved thermal and fire safety properties.

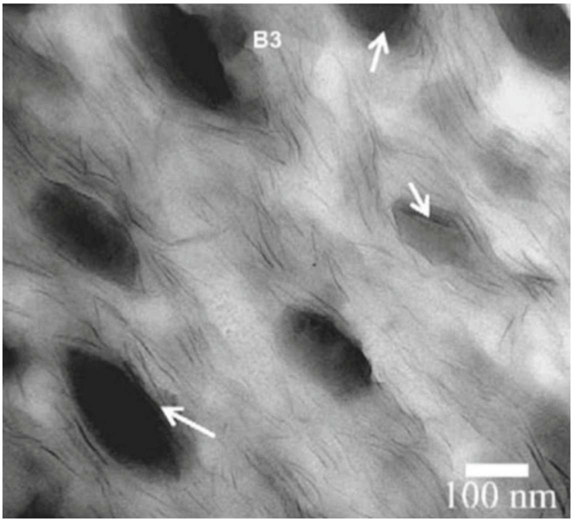

Fig. 14 Fine dispersion of T-POSS and clay in PA6 matrix. Adopted with permission from [59]. Copyright 2009 Elsevier

4.6 Rheological Properties

Rheological properties of polymer melt and POSS-containing polymer melts are crucial for processing. Therefore, it is essential to understand how POSS can be used to modulate rheological properties of polymer. Polymer viscoelastic properties are highly temperature dependent. At 225 °C, neat PA6 melt exhibits a constant dynamic modulus [60]. At higher temperature (285 °C), dynamic modulus changes with time. The incorporation of AB-POSS in PA6 increases the storage modulus with increasing AB-POSS concentration [60] (see Fig. 15). The plateau formation temperature also increased with AB-POSS incorporation. The tan δ is highly sensitive to POSS melting point ~267 °C where a second endothermic transition took place. At ~267 °C, slope of the tan δ decreases significantly for more than 1 wt% POSS-containing PA6 composites. This indicates that melting of POSS particles modifies the structure of PA6-POSS melt, and as a result, rheological properties changed. At lower POSS concentration (<3 wt%), POSS-polymer interactions lead to decrease the chain entanglement resulting in a lower viscosity of the composite. At relatively higher POSS loading (>3 wt%), the presence of solid POSS particles becomes significant, reinforces polymer, and as a result increases the storage modulus.

The rheological behavior of AB-POSS-containing PA6 multilayered film is similar to that of AB-POSS-containing PA6 blend. The influence of AB-POSS incorporation in PA6 think film was reported [61]. At lower temperature, the influence of AB-POSS on rheological properties is very subtle. At lower frequency, 5 wt% AB-POSS-containing PA6 film exhibited an increase in G' and plateau which indicates the presence of POSS aggregates. At higher temperature and lower POSS loading (2.5 wt%), loss modulus of the film decreases. POSS particles interact favorably with PA6 resulting in a decrease in polymer entanglement and increase in free volume

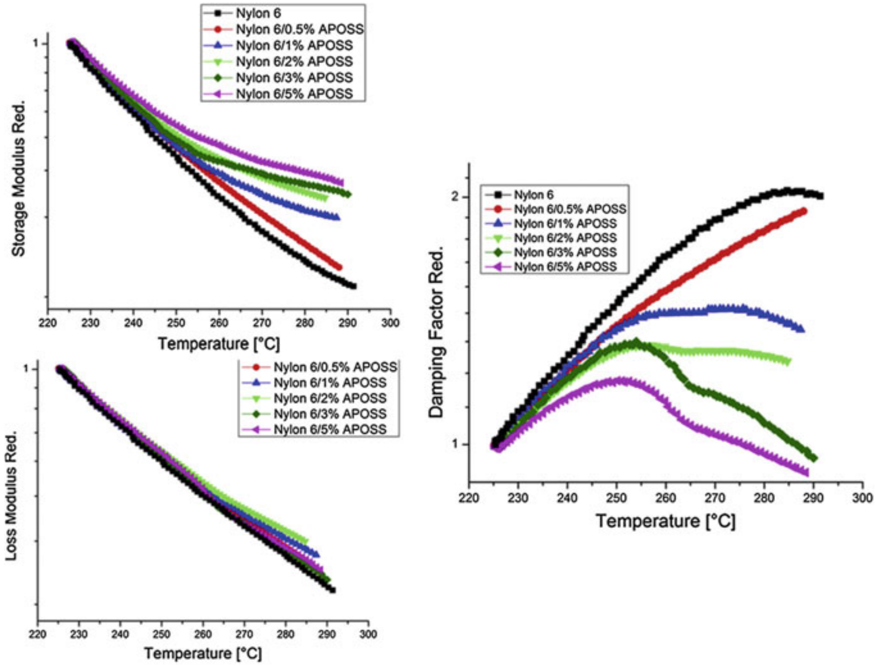

Fig. 15 Effect of POSS incorporation in PA6 on rheological properties. Reproduced with permission from [60]. Copyright 2014 Elsevier

which results in decreasing viscosity. At higher temperature and higher POSS loading (5 wt%), loss modulus increases. At higher concentration, POSS particles form aggregates which increased the G″.

5 Processing of POSS-Polymer Nanocomposites

In-depth understanding of the property improvement by POSS incorporation in polymers requires suitable processing method which can uniformly distribute POSS particle in desired location. POSS can be incorporated in polymer matrices by two ways: (i) chemical cross-linking and (ii) physical blending [12].

In the chemical cross-linking approach, POSS particles are covalently bonded with polymer either by grafting reaction or polymerization. Monofunctional POSS can bind covalently with polymer and form POSS-polymer nanocomposites. On the other hand, multifunctional POSS can react with reactive monomer and form network POSS-polymer composites. Chemical cross-linking provides precise control of nanoparticles distribution in polymer particles. However, chemical cross-linking involves complex chemistry which can pose serious challenges for commercialization [13].

The incorporation of POSS in polymer by physical blending, on the other hand, is advantageous over chemical cross-linking. Physical blending processes are fast, versatile, cost-effective, and easy to handle. The incorporation of POSS particles in polymer by physical blending requires favorable POSS-polymer surface interactions which are noncovalent in nature (van der Waals, hydrogen-bonding, polar, electrostatic, etc.). Strong particle–particle interactions often lead to particle aggregation and macrophase separation. Therefore, proper processing for physical blending is essential. Physical blending is of two types: (i) melt blending and (ii) solvent blending.

Incorporation POSS by melt mixing requires melting of polymers and mixing by applying high shear. Twin-screw extruder is one of the melt compounding techniques used for processing of thermoplastics. However, polymer melt viscosity is very high, and movement of POSS particles in polymer melt is very slow, and equilibration is difficult. POSS forms aggregates and macrophase separates. Also, POSS-containing polymer nanocomposites end up with kinetically trapped condition due to slow equilibration.

In case of solvent blend process, both polymer and POSS particles are dissolved in a suitable solvent; for example, THF is widely used for PA6 [62]. Dissolved polymer is allowed to mix well with POSS dispersion. Once, polymer and POSS particles are mixed well, solvent cast leads to final POSS-containing polymer nanocomposites. The incorporation POSS in polymer by solvent blending has several advantages over chemical cross-linking and melt mixing such as very fast equilibration (no kinetically trapped product), ease of processing, no heat treatment (problem of thermal degradation is absent), and cost effectiveness. However, solvent cast has one disadvantage of remaining residual solvent.

6 Other Polymer-POSS Nanocomposites

6.1 POSS-Homopolymer Nanocomposites

In general, polymer lacks thermal stability and mechanical strengths which restricted their applications in severe conditions. Reinforcement of polymer by incorporating POSS can improve both mechanical strengths and thermal stability, which make them beneficial for several other severe conditions. Property enhancement of POSS-containing polymer composites depends on (i) polymer-POSS surface interactions, (ii) amount of POSS, (iii) cross-linking, (iv) special organization of POSS in polymer matrices such as elongated morphology. The incorporation of POSS in epoxy resins exhibits improved thermal stability [63]. The presence of POSS can hinder polymer chain mobility and increase glass transition temperature [64]. POSS incorporation in various polymers can improve Young's modulus, strain, stress, elongation at break, izob impact strength, etc. POSS particles are inert in nature and are biocompatible which make them an ideal candidate for nanobiocomposites. POSS-containing nanobiocomposites can find applications in dental implant, drug delivery, tissue engineering, etc. [65, 66]. The incorporation of methyl functionalize POSS in polyvinyl chloride decreases the brittleness of the polymer [9]. Inclusion of POSS in poly(methyl methacrylate) helps improving their thermal stability [67]. POSS-containing polystyrene membranes show improved gas selectivity [68]. The incorporation of POSS in polyurethane provides superior mechanical behavior, hydrophobicity, and barrier property [69]. POSS-containing polymer nanocomposites possess several nanoscale structural and functional features which are not found in conventional composites.

6.2 POSS-Block Copolymer Nanocomposites

Amphiphilic block copolymer can self-assembled into order nanostructures which can be used for controlling POSS dispersion, location, and orientation in polymer matrices. Incorporation of octaphenol-POSS in ordered lamellar structure of poly(caprolactone)-poly(4-vinyl pyridine) (PCL-P4VP) block copolymer results order-to-order phase transitions such as cylindrical hexagonal-to-spherical cubic with increasing POSS loading [70]. The incorporation of octamaleamic acid and octaaminophenyl-POSS with solid poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) PEO-PPO-PEO block copolymer causes disorder-to-order phase transition [71]. Depending on the amount of POSS, various ordered structures such as cylindrical hexagonal (50% POSS loading) and spherical cubic (70 wt% POSS loading) are observed. Similar disorder-to-order phase transition occurs when PEO-PPO-PEO block copolymer is dissolved in water.

PEO-functionalized POSS is incorporated in hexagonal structure of solvated PEO-PPO-PEO block copolymers. PEO-POSS has a favorable surface interaction with PEO-rich domains which help localization of PEO-POSS in PEO-rich domains. Hexagonal structure of solvated PEO-PPO-PEO remained stable up to 15 wt% of PEO-POSS loading [21]. Beyond 15 wt% PEO-POSS loading, structure transforms from hexagonal to lamellar order-to-order structural transition took place. The incorporation of tetramethylammonium-POSS in hexagonal structure of hydrated nonaethyl glycol dodecyl ether ($C_{12}EO_9$) remains stable up to 5 wt% POSS loading.

Chemical cross-linking of phenyl-POSS on polybutadiene block of polystyrene-polybutadiene-polystyrene (SBS) block copolymers led to decrease in the degree of block segregation [72]. This decrease in degree of block segregation results in a decrease in lattice parameter of ordered SBS structure. Phenyl-POSS displays a favorable surface interaction with polystyrene which decreases the incompatibility between polybutadiene and polystyrene; thus, degree of block segregation decreases. When phenyl-POSS is substituted by cyclopentyl-POSS or cyclohexyl-POSS, or cyclohexenyl-POSS, effect of POSS on polybutadiene–polystyrene interface becomes insignificant.

7 Summary

This chapter presents the recent development of POSS-containing polyamide nanocomposites. POSS-PA nanocomposites exhibit improved structural and functional features which are not displayed by conventional PA composites. POSS particle possesses hybrid structure which contains a rigid silica core which is well defined and monodisperse. Diameter of POSS particles is typically in the range of 1–3 nm which is smaller than polymer radius of gyration.

Various POSS types and their influence on PA structure and functional properties were discussed with specific examples. POSS-containing PA composites can be obtained by chemical cross-linking, melt blending, or solvent casting method. Favorable interaction of POSS with PA enables physical blending (both melt mixing and solvent cast) feasible. POSS having surface functional group attractive to PA surface can distribute uniformly on PA matrices, and reinforces polymer. On the other hand, POSS with less attractive surface functional group can aggregate and cause macrophase separation without reinforcing polymer.

Incorporation of POSS in PA can improve several functional properties such as mechanical, rheological, thermal degradation, rheological, and membranes. Properties of POSS-containing PA nanocomposites depend on the state of POSS dispersion and composite structure. Further investigations on PA nanocomposites are required to gain deeper understanding of structure–property relations which will provide design rule for new materials. The incorporation of POSS would facilitate improved PA products in broad range of fields such as automobile, food packaging, reverse osmosis.

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