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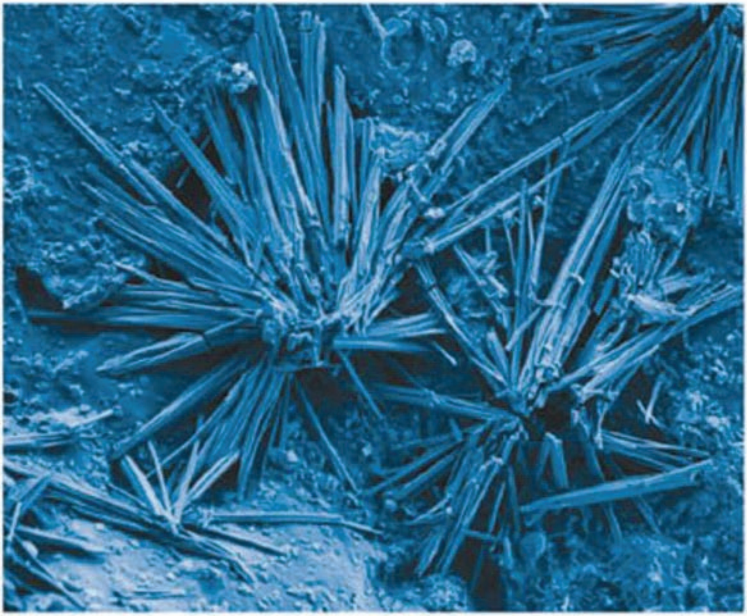
Functional Fillers for Plastics

Second, Updated and Enlarged Edition



23
Polyhedral Oligomeric Silsesquioxanes

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23.1
Introduction

Polyhedral oligomeric silsesquioxanes, known as POSS®, are a unique family of molecular fillers comprised of a central, silica-like core surrounded by covalently attached organic groups [1–5] (Figure 23.1). These molecules can be viewed as inorganic–organic hybrids where the silica core imparts rigidity and high temperature resistance and the organic moieties provide compatibility and functionality. As hybrid materials, POSS provide a spectrum of new properties. As an indicator of the global interest in POSS, there are now over 2500 articles and 900 patents dealing with this topic. POSS research continues to flourish and commercialization has taken off in recent years.

23.2
Production

POSS is produced by the condensation reaction of organosilanes [1, 3]. Interestingly, these are the same organosilanes [6] that are commonly used for the surface treatment of mineral fillers to improve dispersion in, and/or adhesion to, the polymer matrix (see Chapter 4). Either trichlorosilanes or trialkoxysilanes may be used to make POSS [1, 3]. Normally, such organosilanes self-condense into an amorphous network and POSS cage formation does not occur to any significant extent. Initial POSS syntheses suffered from extremely long reaction times (several months), coupled with very low yields of imperfect cage structures and resin formation necessitating arduous separation methods to obtain a pure product [7]. These problems were overcome and now short reaction times and good yields have enabled rapid commercialization of POSS in thermoplastics, thermosets, elastomers, and coatings [8].

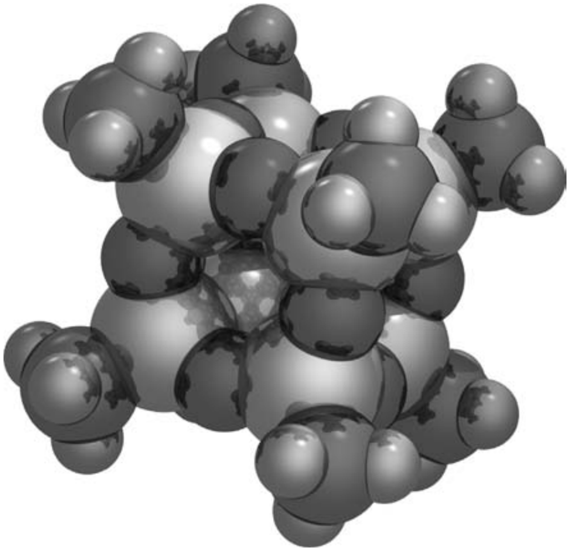

Figure 23.1 POSS molecule showing the central rigid cage and surrounding methyl groups.

23.3 Structure and Properties

For conventional mineral fillers such as calcium carbonate, dolomite, mica, and wollastonite, the chemistry of each is constant across all grades of a given material and the grades are differentiated by their particle size, size distribution, particle shape, and presence (or otherwise) of a surface treatment. In the case of POSS, every grade is chemically distinct and so properties such as density, polarity, refractive index, and so on, are different for each POSS [8] (Table 23.1).

Table 23.1 Overview of typical POSS properties.

Density range	0.9–1.3 g/cm^3 typical (up to 1.82 g/cm^3)
Refractive index range	1.40–1.65
Molecular size	1–5 nm
Form	Colorless, odorless crystalline solids, some waxes, and liquids
Polarity	Very low (fluoroalkyl), low (alkyl), phenyl (medium) to polyionic (high)
Chemical and pH stability	Molecular silicas (closed cage) very stable, trisilanols good stability
Thermal stability	250–350 °C typical (>400 °C for some types)
Safety	All testing performed has shown POSS to be safe
Purity	Standard purity >97% (higher purity and electronics grades are available)

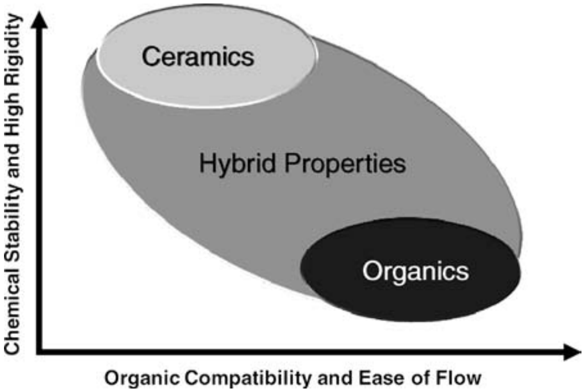

Figure 23.2 Organic–inorganic hybrid properties of POSS.

As the size of the organic groups on the POSS is increased, so the properties shift progressively from those resembling silica toward those of organic compounds. Thus, it is possible to access properties in between those of organic and inorganic materials (Figure 23.2).

As an example, the density of a POSS cage with hydrogen at the corners of the cage is 1.82 g/cm^3, which is much higher than the density of common organic compounds. For POSS with progressively longer alkyl substituents, the silica-like core dominates less and so the density decreases to lower values, ~1.0 g/cm^3, more common for organic molecules (Table 23.2). This change occurs for other properties such as thermal conductivity, modulus, dielectric constant, and so on. For instance, the Young's modulus of common organic polymers such as PE and PP is in the range 1–1.5 GPa, whereas the value for silica is ~70 GPa. The Young's modulus of octacyclopentyl POSS has been calculated to be ~12 GPa [9]. POSS with smaller organic groups are expected to have commensurately higher moduli, whereas larger organic groups such as *iso*-octyl chains lead to low modulus, liquid POSS types [8].

Table 23.2 Comparison of POSS densities with those of inorganic silica and organic molecules.

Material Type	Density (g/cm^3)
Quartz	2.60
Amorphous silica	2.18
Octa hydrido POSS	1.82
Octamethyl POSS	1.50
Octaethyl POSS	1.33
Octaiso-butyl POSS	1.13
Octaiso-octyl POSS	1.01
iso-Octane	0.69

The most prevalent POSS types may be divided into four categories:

1) **Molecular silicas**: a closed cage with an inert organic group at each vertex (e.g., alkyl, fluoroalkyl, phenyl, PEG). Usually all the eight groups are the same but alternatives exist with seven identical groups plus one different one.
2) **Functionalized POSS**: a closed cage with a reactive organic group at each corner (e.g., epoxy, amine, acrylate, methacrylate, alcohol, isocyanate, sulfonate, carboxylic acid, thiol, imides, silane, or nitrile.) It is also possible to have seven reactive groups and one unreactive or vice versa.
3) **POSS trisilanols**: where there are seven identical groups but one silicon atom is missing to leave an open corner with three reactive silanols.
4) **POMS**: where a metal atom has been reacted into the corner of a POSS trisilanol.

Conceptually, the inert POSS (type 1) can be viewed as molecular fillers. It can be shown that POSS are clearly molecules since

1) POSS are spontaneously soluble in solvents;
2) POSS can be analyzed by methods such as HPLC, GPC, and solution NMR;
3) POSS exhibit distinct molecular weights;
4) POSS can be crystallized;
5) pure POSS can be a solid, liquid, or gas.

Although POSS are molecules, they do look reminiscent of particles. This molecule–particle duality or "molicle" appearance leads to some interesting observations. For example, all particulate fillers tend to agglomerate [10] and, as the particle size decreases, the problem is greatly exacerbated such that it becomes very difficult to make nanocomposites with a proper level of particle dispersion [11]. That is one of the great challenges for nanocomposites. In stark contrast, POSS molecular fillers are able to dissolve into a solvent or polymer with perfect dispersion and no tendency to agglomerate (Figure 23.3). If the POSS polarity is chosen to match that of the solvent then the Gibbs free energy of mixing is negative and dissolution is spontaneous with no need for stirring.

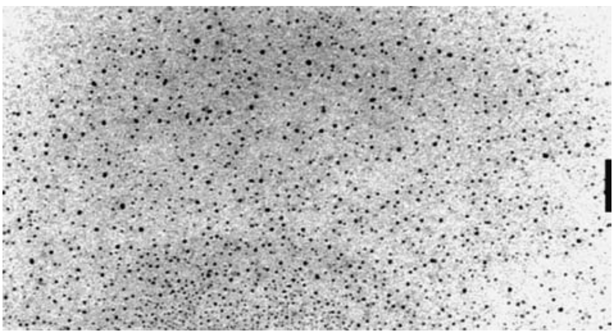

Figure 23.3 POSS dissolves molecularly and spontaneously; each black dot is a 1.5 nm POSS molecule (scale bar is 50 nm).

Traditional particulate fillers tend to agglomerate already during manufacture, and once agglomerated, it is difficult to subsequently disperse them. Dispersion requires addition of a dispersant additive (e.g., stearic acid or alkysilanes) and the input of energy to overcome the attractive forces between particles [6]. The correct selection of dispersant type and application method is crucial. In contrast, POSS as synthesized, already possesses its own intrinsic dispersant in the form of covalently bonded organic groups and dispersion is easy.

In order to ensure good compatibility between POSS and the matrix, one must match the polarity or solubility parameter of the POSS and the solvent, polymer or coating in which it is to be dissolved. POSS polarities span the whole gamut from extremely hydrophobic fluoroalkyl POSS used to make ultrahydrophobic surfaces [12], through progressively more polar variants such as alkyl POSS (low polarity), phenyl POSS (medium polarity), and water soluble types including PEG POSS, POSS trisulfonic acids, and octaammonium POSS.

POSS is usually found to be soluble up to around 5 vol% in thermoplastics such that up to that concentration, no light scattering occurs and the material remains optically clear. In thermoset resins and solvents, POSS can be mixed at all ratios if the polarities of POSS and medium are properly matched.

Instead of matching the polarity of the POSS to the matrix, one can also imbue compatibility through reaction of POSS with the matrix by choosing appropriate chemistry. Virtually all chemistries are available to facilitate reactions such as alcohol, carboxylic acid, sulfonic acid, epoxy, chloroalkyl, acrylate, methacrylate, isocyanate, amine, thiol, silanol, and several others.

23.4 Suppliers/Cost

Initially, extremely long reaction times (months) and very low yields meant that cost of the POSS was rather high, approximately $3000/lb (€4000/kg) and, therefore, the commercial appeal was limited at that time. However, the potential of POSS was such that effort was made to lower reaction times and to improve yields. Hybrid Plastics has worked to scale up POSS production and now has a capacity of several hundred tons per year (as of 2009) that is increasing steadily in line with demand. Correspondingly, the improved synthesis methods and scale-up have resulted in a 1000-fold reduction in POSS selling price to just $30–40/lb (€50/kg) for larger amounts of some of the most popular POSS variants [8]. Over 250 types of POSS have been synthesized, 80 types are presently available and of those, several have large-scale commercial availability.

Major commercial suppliers of POSS are Hybrid Plastics Inc., Hattiesburg, MS, USA. Distributors of POSS are Sigma-Aldrich Inc., Gelest and Toyotsu Chemiplas Corporation. Some POSS types are available in R&D amounts from Mayaterials Inc.

Suppliers of POMS are Hybrid Plastics Inc., Hattiesburg, MS, USA, Hybrid Catalysis BV.

23.5
Environmental/Safety Considerations

POSS are chemical compounds and should be handled with the normal precautions used for all other chemicals. Most POSS types are in the form of a crystalline white powder (typical size range 5–100 μm). Some types are colorless, viscous liquids.

Oral toxicity testing both in the United States and in Europe has shown that all three POSS tested are in the safest possible category [8] and do not require the risk phrase R22 "Harmful if Swallowed."

Octaisobutyl POSS	US	Category IV Oral $LD_{50} > 5000$ mg/kg (highest US method dose)
Octamethyl POSS	EU	Oral $LD_{50} > 2000$ mg/kg (highest EU method dose)
Dodecaphenyl POSS	EU	Oral $LD_{50} > 2000$ mg/kg (highest EU method dose)

Several of the larger production volume POSS types are TSCA listed. These include octaiso-octyl POSS, dodecaphenyl POSS, octamethyl POSS, octaiso-butyl POSS, *iso*-butyl trisilanol POSS, octaglycidyl POSS, aminopropyl *iso*-butyl POSS, and aminoethylaminopropyl *iso*-butyl POSS [8]. TSCA listing and FDA approval of other POSS types is ongoing.

23.6
Functions

23.6.1
Primary Function

The primary function of POSS depends upon the type of POSS chosen and the matrix. In thermoplastics, the most significant benefit of POSS is improved melt flow. In particular, improved flow for high temperature polymers, such as PEEK, PEI, COC, PA6, PPS, and PPO enables one to fill complicated, thin-walled parts. Flow aids for polymers are well established, however, conventional flow aids are not designed to withstand the high processing temperatures needed for these polymers. Also noteworthy is the finding that POSS does not degrade the mechanical properties, so for example, PEEK, PEI, PPS, PA6, and COC all retain full modulus and yield strength while melt flow is dramatically enhanced [13, 14]. The retention of yield strength indicates that the flow enhancement is achieved without molecular weight degradation, which has been further proven by gel permeation chromatography. Addition of chemically analogous hydrolyzed organosilane resin worsened melt flow so there is some particular attribute of the POSS structure responsible for its utility in melt flow enhancement (Figure 23.4).

POSS trisilanols act as highly effective dispersants to lower viscosity and improve mechanical properties. The POSS trisilanols have proven effective for many fillers

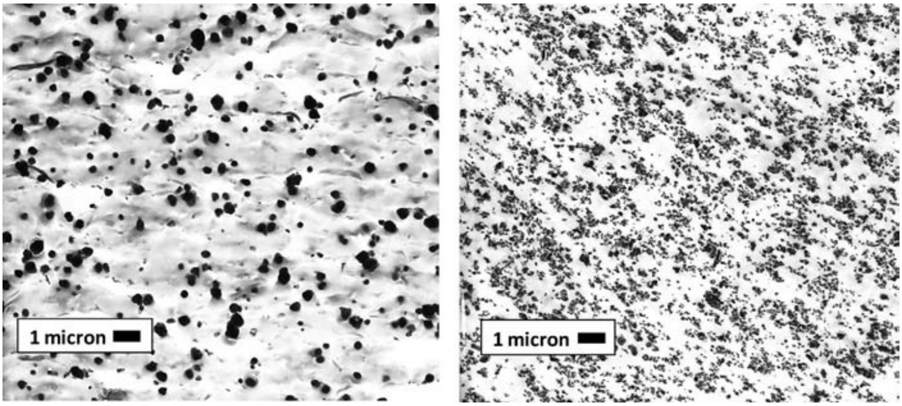

Figure 23.4 TiO_2 in PP with no dispersant (left) and the same TiO_2 in PP with POSS trisilanol dispersant added in the extruder (right) [15].

and pigments [14] including silica, titania [15], mica, alumina, and boron nitride. It comes as no surprise that the POSS trisilanols are effective on those materials because it is well known that organosilanes work well on the same materials [6, 10]. More surprising is that the POSS trisilanols are able to disperse fillers such as calcium carbonate, other carbonates, and barium sulfate, which are generally recognized as unsusceptible to organosilanes. POSS dispersants offer some advantages over traditional dispersants such as stearic acid and organosilanes. In particular, the reaction of POSS trisilanols with fillers leads only to the evolution of innocuous water. In contrast, organosilanes produce VOCs (usually methanol or ethanol) when reacted with fillers and pigments. Furthermore, the POSS has high thermal stability and binds strongly making POSS the obvious choice for pigments and fillers that need to be dispersed in polymers that have high processing temperatures [14]. For highly filled systems, the high flow effect in the matrix can be combined with the dispersant effect to provide a dual action flow improvement.

Addition of inert POSS molecular silica (MS0825, octaiso-butyl POSS) results in no significant change in viscosity because that POSS type cannot adsorb and cannot, therefore, act as a dispersant. The POSS trisilanols (SO1458, a phenyl trisilanol and SO1455, an isooctyl trisilanol) both adsorb strongly and act as efficient dispersants [14]. The POSS trisilanols coat the filler and reduce particle–particle interactions, and this accounts for the large drop in viscosity.

In thermosets, where POSS is reacted into the material, the primary advantage is excellent high temperature modulus retention beyond 300 °C [8]. For example, octa functional POSS epoxies or POSS amines can be added to conventional epoxy or BMI resins to provide very high temperature resins. While traditional resins lose rigidity at and above the glass transition temperature, the POSS modified materials retain modulus even under extreme temperature conditions. Such materials are in demand for oil well applications where the drive to deeper, hotter wells pushes existing

Table 23.3 Effect of POSS on swelling of silicone rubber.

Material type	Weight increase (%)
Silicone + 0% POSS	25
Silicone + 20% POSS	19
Silicone + 40% POSS	14
Silicone + 60% POSS	10

materials beyond their limits. The advantage of the POSS is attributed to two factors. First, the rigidity of the POSS cage [9] and second, the high cross-link density attainable due to the extraordinarily high functionality of the POSS.

In elastomers, the primary benefit of reacting POSS into the polymer is the improvement in solvent resistance. For example, while silicone elastomers are readily swollen when exposed to acetone, adding POSS reduces the solvent swelling dramatically (see Table 23.3). Two mechanisms are believed to be at work. The POSS allows a high cross-link density, which is well known to reduce swelling (in fact, solvent swelling can be used to estimate cross-link densities). The other mechanism is due to the structure of the POSS cage. The cage itself cannot swell, it is rigid with an immutable configuration. Thus, the POSS cage provides a volume of unswellable material analogous to conventional inorganic fillers.

23.6.2
Secondary Function

POSS exhibits several secondary effects which, when combined with primary or other secondary effects, can lead to commercial adoption. Thus, one may decide to use POSS for a primary benefit such as flow enhancement in a high temperature thermoplastic and see additional benefits such as improved mold-release, lower part friction [16, 17], and better surface finish. Another known benefit is flame retardance. POSS does not provide stand-alone flame retardance but it has been reported to be an effective synergist when used in conjunction with primary flame retardants. Under combustion conditions, the POSS vitrifies [18] to form a char that provides some intumescent flame inhibition (Chapter 17).

The vitrification of POSS has proven useful in other instances besides flame retardance. POSS has been used to protect polyimide used on satellites [19]. The aggressive radiation and atomic oxygen present in Low Earth Orbit combine to destroy standard polyimide. During testing, the regular polyimide was destroyed and only small traces of it remained. When POSS was added to the polyimide, the POSS formed a glassy protective coating upon exposure in space. This latter sample retained its mechanical integrity at the end of the test. The results were so encouraging that NASA is performing further space testing of POSS modified polymers. Similarly, it has been reported that, in the presence of oxygen plasma, POSS can vitrify and protect polymers from erosion [20]. Further work on POSS in polyimides resulted in a colorless polyimide sold as film by NeXolve Corp. under the trade name Corin XLS. The product won an R&D 100 Award in 2008.

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