Chapter 5  
Polyhedral Oligomeric Silsesquioxanes in Plastics

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5.1 Introduction

Polyhedral oligomeric silsesquioxanes (POS or POSS®) were first synthesized as long ago as the 1960s. Since that time, global interest has grown considerably as indicated by the many articles and patents in the field [1,2,3,4,5]. The reason being that POS, with a unique three dimensional cage structure composed of silicon and oxygen (Fig. 5.1), is an unusual type of molecule with correspondingly unusual properties. The discovery of the cage form of carbon, called buckminsterfullerene (Fig. 5.1), was awarded the 1996 Nobel Prize for Chemistry, and other cage structure hydrocarbons such as adamantane and other diamondoids have attracted considerable interest. However, time has shown that POS is far more commercially important for several reasons. Firstly, POS is extremely versatile. It is possible to attach any chemistry to the silica-like core. Such customization of POS is simple and can be easily controlled, whereas in the case of C\textsubscript{60}, there are many equivalent carbons so controlled derivatization is more challenging. Secondly, POS is rather straightforward to make using standard chemical reactors, which facilitates scale-up. Thirdly, because the raw materials are relatively inexpensive and yields can be as high as 90% or more, the price of POS is low enough to place it under consideration for multitudinous application areas from packaging [6] through to sensors [7,8,9] and fuel cell membranes [10,11,12].
This chapter describes the varieties of POS and how they can be incorporated into polymers to enhance the polymer properties, along with a description of applications already extant and expected. Hundreds of different POS molecule types have been reported, and naturally each has its own unique set of properties. An overview of the range of typical properties is therefore helpful (Table 5.1).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value or typical behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density range</td>
<td>0.9-1.3 \text{ g cm}^{-3} \text{ typical (up to } 1.82 \text{ g cm}^{-3})</td>
</tr>
<tr>
<td>Refractive index range</td>
<td>1.40-1.65</td>
</tr>
<tr>
<td>Molecular size</td>
<td>1-5 nm</td>
</tr>
<tr>
<td>Form</td>
<td>Colorless, odorless crystalline solids, some waxes and liquids</td>
</tr>
<tr>
<td>Polarity</td>
<td>Very low (fluoroalkyl), low (alkyl), phenyl (medium) to polyionic (high)</td>
</tr>
<tr>
<td>Chemical and pH stability</td>
<td>Molecular silicas (closed cage) very stable, trisilanols good stability</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>250-350 °C typical (&gt; 400 °C for some types)</td>
</tr>
<tr>
<td>Safety</td>
<td>All testing performed has shown POS to be safe</td>
</tr>
<tr>
<td>Purity</td>
<td>Standard purity &gt;97% (higher purity and electronics grades are available)</td>
</tr>
</tbody>
</table>

5.2 POS are Molecules

Similarly to norbornane, bornane, adamantine and the fullerenes, POS are also molecules rather than particles. This can be proven categorically by experiment:
- POS have distinct molecular weights
- POS are spontaneously soluble in solvents
POS can be recrystallized from the melt or from solution
POS can be characterized by solution NMR (solids have no solution NMR spectrum)
Soluble POS can be distinguished from POS agglomerated into domains by dielectric spectroscopy [13]
Soluble POS can be distinguished from POS domains by wide-angle X-ray diffraction (WAXD) [14]
Some POS types are liquids even in pure, undiluted form (particles are not liquid at 100% concentration)

When POS is added to transparent polymers, it is often observed that transparency is retained up to 5-10 wt % (or vol %) POS because the POS is soluble. Above that threshold however, turbidity sets in because additional POS is no longer soluble, forming domains that scatter light. This makes for an easy way to detect solubility, but caution must be exercised because the test is not infallible. Turbidity will only be detected if the POS domains have a different refractive index to the host polymer, and if the domains are of the right size to scatter visible light.

Although POS are clearly molecules, the POS cage conveys the visual impression that the substance is a particulate, due to the spherical / cubic shape. Indeed, some of the properties are reminiscent of particles and conceptually POS can be considered the smallest possible form of silica with a built in surface treatment, namely the organic moieties surrounding the central cage.

In physics parlance, light is referred to as a wavicle because it displays the properties of both a wave and of a particle. POS can therefore be considered “molicles” since they are molecules that display properties and appearance reminiscent of particles [5].

Often, siliceous fillers are surface treated with organosilanes to enhance their performance in polymers and coatings. Trialkoxysilanes, such as iso-octyltrimethoxysilane, react with the surface silanols on silica, whereby the iso-octyl groups protrude away from the surface, preventing agglomeration by sterically hindering close approach of adjacent particles. Thus, the non-reactive POS types such as octa-iso-butyl POS, octa-iso-octyl POS and octaphenyl POS can be considered minute silica particles with a perfectly applied layer of dispersant. Viewed from that perspective, it is no wonder that the POS are so easy to “disperse” in solvents, coating and polymers.

The other type of organosilane surface treatment applied to siliceous fillers such as talc, mica, wollastonite and silica, is the reactive sort commonly referred to as a coupling agent. These also contain a trialkoxy function which can react with the filler surface but they also contain a second functional group which can react chemically with the matrix coating or polymer. Typical functionalities include virtually the complete spectrum of organic moieties from amines, through alcohols, carboxylates, epoxides, urethanes, thiols and so on. Such coupling agents help with filler dispersion, and by increasing filler-matrix adhesion, yield strength in particular is enhanced, along with retention of matrix adhesion after exposure to
heat and humidity.

When used in their conventional role as coupling agents, they react with the filler surface, and at the same time they self-condense in a non-ordered manner to produce an amorphous resin. In contrast, under POS synthesis conditions, these same coupling agents are directed to self-condense into ordered cage structures. Rather remarkably, high yields of single cage types are now possible, making purification easier and lowering manufacturing cost. However, early syntheses were fraught with problems including low yields, product mixtures that were hard to purify and multi-month reaction times [15] (see also Frank Feher’s Foreword). POS varieties made from these coupling agent-type organosilanes include acrylate, methacrylate, vinyl, epoxy, thiol and amino compounds [6]. It should come as no surprise that these compounds, which are conceptually composed of molecular silica surrounded with a shell of coupling agent, are able to react and bond with polymers and coatings.

The properties of POS such as density, modulus, refractive index and so on fall between the properties of silica and those of organic compounds. Organic polymers such as polyethylene have Young’s modulii in the 1-2 GPa range, whereas silica has a value closer to 70 GPa. Octacyclopentyl POS has been calculated to have an intermediate value of 11.8 GPa [16]. POS with shorter alkyl groups are expected to have higher modulii, whereas POS with long organic groups such as octa iso-octyl POS and PEG POS are found to be liquids at room temperature, implying a rather low modulus (Table 5.2).

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight% cage</th>
<th>Density (g cm$^{-3}$)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (crystalline silica)</td>
<td>100</td>
<td>2.60</td>
<td>1.54</td>
</tr>
<tr>
<td>Octa hydrido POS</td>
<td>98</td>
<td>1.82</td>
<td>1.51</td>
</tr>
<tr>
<td>Octa methyl POS</td>
<td>78</td>
<td>1.50</td>
<td>1.51</td>
</tr>
<tr>
<td>Octa ethyl POS</td>
<td>64</td>
<td>1.33</td>
<td>1.50</td>
</tr>
<tr>
<td>Octa iso-butyl POS</td>
<td>48</td>
<td>1.13</td>
<td>1.48</td>
</tr>
<tr>
<td>Octa iso-octyl POS</td>
<td>32</td>
<td>1.01</td>
<td>1.45</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>0</td>
<td>0.69</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Interestingly, cubane, a carbon-based cage structured molecule, has the highest density of any hydrocarbon (1.29 g cm$^{-3}$). It seems then that cage structures such as POS and cubane confer unusually high densities and other related properties.
5.3 POS as Plastics Additives

The success of plastics is due in large part to the use of an array of additives including stabilizers, plasticizers, mold-release agents, antistatics, anti-blocks, flow aids, dispersants and acid scavengers to name just a few. Usually, such additives are low molecular weight compounds which have the advantage that they can easily be solubilized in the polymer. However, being low molecular weight, they also suffer disadvantages including:

1. Volatility – leading to loss through evaporation (the additive may be lost during polymer processing at high temperature), odor and safety concerns
2. Extractability – giving rise to unwanted taste and safety concerns when the additives migrate into food or water supplies
3. The combination of 1 and 2 above leading to loss of the additives, and thus loss of efficacy, causing plastic embrittlement and failure
4. Low molecular weight additives acting as plasticizers with a corresponding and undesirable loss of modulus and yield strength

For example, it has been shown that in hot water pipe applications, over 99% of the antioxidant is lost via evaporation and extraction, and less than 1% is chemically consumed, i.e., doing its job protecting the polymer from degradation [17]. The costly antioxidant is wasted, and the lost additive ends up burdening the environment where it pollutes water and soil. In the case of plasticizers used to keep plastics pliable, loss of additive leads to brittle plastics that break in use. There has been great interest in polymeric additives such as antioxidants [18,19] and plasticizers because their high molecular weights are expected to prevent volatility or migration. However, the stumbling block has been that polymers do not usually mix with one another, so it is difficult to incorporate such additives into the plastics.

POS bridges the molecular weight gap, having sufficient molecular weight to retard evaporation and migration, but having low enough molecular weight to enable it to dissolve molecularly into polymer melts and in the final fabricated part. In order to assure solubility, one must be able to fine tune the polarity of the additive so that it is similar to, and thus soluble in, the plastic or coating. This is where the customizability of POS comes to the fore. Similar to dendritic and hyperbranched structures, which can give higher molecular weight antioxidants with enhanced stabilization [20], POS antioxidants have also been synthesized and found to be effective [21]. POS is less expensive than the dendritic options, and has other advantages such as stability to high temperature processing.

Typical solubility for a POS with a polarity matching that of the host polymer is approximately 5 wt %, which is more than adequate for many polymer additive applications including antioxidants, plasticizers, flow aids, dispersants and lubricants.

The effect of POS upon a polymer depends upon many factors.

1. Addition of up to ~5 wt % of a soluble POS often leads to improved melt flow, but with no loss in modulus or yield strength [22]. Indeed, in some
cases, the POS acts as an antiplasticizer [23,24] filling free volume and raising modulus. Because the POS is molecularly dissolved, such systems retain full transparency.

2. Addition of ≥ 5-10 wt % soluble POS (or less for an insoluble POS) results in the formation of POS domains. This results in a loss in transparency but the domains on the surface give significantly reduced friction [25] and change the contact angle [26].

3. When POS is chemically bound to a polymer, the glass transition temperature is raised, and therefore the heat distortion and Vicat temperatures, because the rigid, bulky POS cages restrict chain mobility [27].

From the preceding discussion, it is clear that solubility and reactivity of POS are key factors. Therefore, we will now consider those aspects in more detail.

## 5.4 POS Solubility

Solubility follows the rule that “like dissolves like”, meaning that the solvent must be similar to the substance being dissolved (solute). Specifically, the polarity of the two substances must be similar. So, how does one quantify polarity? Well, some common indicators are contact angle (although often misleading), surface energy, or testing the solubility of the new substance in solvents of known solubility parameter. For substances that have not yet been made, or have not yet been measured, the Solubility Parameter concept [28] offers a convenient method to calculate the polarity of a substance and its propensity to dissolve in different media. There are established tables which can be used to calculate the polarity, Solubility Parameter and many other attributes with some degree of confidence. The method is based on group contributions whereby each organic group has a fixed tabulated value, and the contribution from each group is assumed to be independent of the other groups in the molecule. The contributions for each group are summed and adjusted for the density of the substance. As the polarities and Solubility Parameters of POS have not yet been measured, calculating Solubility Parameters offers a way to predict solubility, thus saving considerable time and money (when compared to trial and error experimental work such as compounding).

## 5.5 Effects of POS on Polymer Properties

The precise effect of POS depends on many factors including whether the POS is miscible with the polymer, what type of polymer is being modified, the properties
of the POS being added, and whether or not the POS is chemically bonded to the polymer.

### 5.5.1 POS Solubilized in the Polymer

To begin with, let us consider the case of an unreactive POS added to a polymer of similar polarity such that the POS is soluble. In such instances, the solubility of the POS normally has an upper limit at around 5-10 wt % POS, beyond which precipitation occurs and cloudiness is observed. We consider the case where POS is added at 5 wt % so that it remains molecularly dissolved.

**Table 5.3** Typical response to different additive types (note that exceptions do exist)

<table>
<thead>
<tr>
<th>Property</th>
<th>Solvent or plasticizer</th>
<th>POS</th>
<th>Polymer</th>
<th>Spherical filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td></td>
</tr>
<tr>
<td>Yield Strength</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
</tr>
<tr>
<td>Heat Distortion Temperature</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td></td>
</tr>
<tr>
<td>Impact resistance</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
</tr>
<tr>
<td>Transparency</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
</tr>
<tr>
<td>Flow / processability</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
<td>‡</td>
</tr>
<tr>
<td>Leachable</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

Key: ‡ Property increases strongly, ‡ Property decreases strongly, ‡ Property unchanged, ‡ Property increases, ‡ Property decreases

It is interesting to note that at low addition levels, POS can actually increase modulus somewhat, since it acts as an antiplasticizer. The POS cages are molecularly dissolved and fill in the free volume in the polymer, thereby increasing stiffness. Above the solubility limit, the POS forms domains of insoluble material, and since these have low cohesive strength, the POS acts as a plasticizer, thus softening the polymer.

Similarly, the effect of POS on transparency is different above and below the solubility limit. At low concentrations, where the POS is soluble, there is no loss in transparency even in cases where the refractive index of the POS and the polymer differ. This is because the POS molecules are too small to scatter visible light, being only 1-2 nm in diameter (and visible light having wavelengths in the range ~380-750 nm). As the POS concentration is increased above the solubility limit, turbidity sets in and one can often see at a glance that the POS is no longer soluble because of this haziness.
In other cases, POS acts as a plasticizer. It has been shown that POS is just as effective as conventional plasticizers like dioctyl phthalate on a per molecule (molar) basis in PVC [29] and PMMA [14]. Hence POS could find application as a non-volatile plasticizer in specialty applications that can bear the cost of using POS instead of standard plasticizers.

Dissolved POS was reported at a process aid, enhancing the melt flow in poly(phenylene oxide). Normally PPO is blended with polystyrene (PS) in order to improve the melt flow of the former, but an unwanted consequence is that the PS lowers the HDT and Vicat temperatures of the PPO. Any lower molecular weight additive would be expected to reduce the melt viscosity, but normally there would be a reduction in the modulus and yield strength of the polymer, in this case PPO.

However, it was found that POS, while improving the melt flow, did not have any detrimental effect on mechanical properties, and even gave some additional property enhancements. For instance, the color of the PPO was significantly reduced and the flame retardance was enhanced [30]. This initial proof of concept on PPO lead to subsequent investigations whereby it was shown that POS can also improve the melt flow of high performance polymers such as polyetheretherketone (PEEK), polyetherimide (PEI), polyphenylenesulfide (PPS) and cyclic olefin copolymer (COC) with no loss in mechanical properties [6,22] or degradation of molecular weight.

5.5.2 POS Insoluble Present at Concentrations Above the Solubility Limit

It would be natural to think that solubility of the POS is always desirable. However, it is found that some properties are only affected above the solubility limit. For example, addition of POS to PP or nylon 6 has little effect on the coefficient of friction until around 5 wt %, at which point additional POS is no longer soluble and blooms to the surface to give a strong lubricant effect [25,26,31] (see also Section 7.8, Chapter 7). The friction reduction has been reported in the literature with much fanfare, which is rather surprising given that oil filled nylon (for reduced friction) has been available commercially for decades, and at prices far more attractive than one can expect for POS-modified nylon.

Similarly, substantial work has been reported whereby fluorinated POS has been added to polymers, resulting in increased contact angles [32-35] (see also Chapter 6). Addition of POS above the solubility limit gives rise to high contact angles with water, although again, the same would be found for addition of any perfluorocarbon. Observation of a high contact angle should be interpreted with caution; it is assumed that contact angle is directly related to hydrophobicity of the bulk material, but that is only true under a strict set of conditions [36,37].

1. The surface must be completely smooth
2. The surface must be homogeneous with no domains of varying polarity
3. The surface must represent the bulk material (i.e., be chemically similar to the bulk material)

4. The test liquid must not swell or penetrate into the polymer under examination

It has been shown that condition 1 is not met because POS forms crystalline domains on the surface, thereby increasing roughness and resulting in a higher contact angle. This is the same phenomenon as seen in so-called ultrahydrophobic surfaces where the roughness boosts the contact angle to values higher than those arising from the hydrophobicity of the material itself.

In the case of POS in polymers, it is known that condition 2 is not fulfilled because POS above the solubility limit has been shown to form domains at the surface [25] which completely alter the contact angle measurements. Condition 3 is also unlikely to be satisfied, since the insoluble POS is expected to bloom to the surface as the system acts to achieve the lowest overall energy configuration; for example, the fluoro POS, having the lowest surface energy, will accumulate at the polymer surface. Thus it is possible to observe a high contact angle, but still find that the bulk polymer is hydrophilic and adsorbs water.

The interest in ultrahydrophobic and ultraoleophobic surfaces is fueled by the observation that Lotus plants have ultrahydrophobic surfaces, and are self-cleaning. Rainwater runs off them, taking dirt particles with it. There has been much effort expended to reproduce and commercialize this effect in artificial materials, but attempts to use such ultrahydrophobic surfaces in everyday life have failed for fundamental reasons. First, the effect depends upon the fine structure at the surface, and is easily destroyed by contact. Furthermore, the effect only works in the case of pure water without surfactants. So what works well with rainwater will not work well, for example, in a dishwasher.

5.5.3 POS Chemically Attached to the Polymer

Reactive POS types may be either polymerized into the polymer backbone or post-grafted onto a preexisting polymer. For instance, polymerization of a POS monomethacrylate with methyl methacrylate has been reported [38]. As expected, incorporation of such a bulky group into the polymer chain resulted in a significant increase in heat distortion temperature because the bulky groups restrict chain mobility, thus increasing the glass transition temperature \( T_g \) (see also discussion in Chapter 4). The incorporation of stiff, bulky groups is used commercially to increase HDT/Vicat, for example copolymerization of poly(styrene-stat-acrylonitrile) (commonly known as SAN) with a third monomer, either alpha-methyl styrene, or \( N \)-phenyl maleimide gives a high \( T_g \). SAN used to make specialty high heat ABS. Although POS is far larger and stiffer than those monomers, it is not cost-competitive with them. Use of POS to increase \( T_g \) would only be worth considering in the case of ultra-high temperature polymers such as PEEK, PAI (polyamide
imide, e.g., Torlon®) and the like where the cost of POS might be tolerated.

### 5.5.4 POS Network Thermosets

Having looked at unbound POS and then POS bound chemically to the polymer backbone or pendant to it, we now consider the effect of making a network from POS. In this case, a highly functional POS is cross-linked to form a three dimensional structure. A conventional thermoset, for example an epoxy, will typically consist of monomers that are tetra-functional. POS epoxies, either the glycidyl type or the cycloaliphatic kind (Fig. 5.2), consist of POS cage mixtures whereby T8, T10 and T12 cages are intermingled, typically in the ratio 15:65:30, arising from the POS synthesis conditions (see also Section 4.6.1, Chapter 4).

Thus, the average number of epoxy groups is near to 10 and one can form an extraordinarily strong network. There are several advantages to POS epoxy systems.

1. They display low cure shrinkage, as low as 1% for the cycloaliphatic POS epoxy
2. Reduction in coefficient of thermal expansion (CTE) owing to the immutable structure of the POS cage
3. Retention of high modulus up to 300°C (cycloaliphatic type)
4. Resistant to solvent swelling due to high cross-link density and also because the POS cage acts like an unswellable molecular filler

As they share polarity similar to conventional epoxy monomers, the POS epoxies are miscible with them. Thus formulation is rather easy, as mixing is simple. Because the POS epoxies are viscous liquids, they can be blended with other epoxies at room temperature.

Curing of POS epoxies can be performed using the normal routes such as amine
cure, anhydride cure or the use of imidazoles as appropriate for the epoxy chemistry, either glycidyl (aliphatic and aromatic amines) or cycloaliphatic (anhydrides and amines).

Gel time is the time at which an essentially infinite network is formed and that is critically dependent upon the average functionality of the system [39]. Adding just a small amount of highly functional monomer significantly reduces gelation time, thus giving a faster cure and increased productivity. As mentioned, POS epoxies have extremely high functionality and are therefore ideal for reducing cure time and thereby improving productivity.

The incorporation of POS epoxies often lowers the viscosity of the formulation, which is clearly advantageous in many instances, especially when there is a need to wet out a fiber tow or fabric. Another benefit is that the POS increases the high temperature modulus. The room temperature modulus remains unaltered, but at elevated temperatures the POS cage is so effective at restricting motion that there is often a complete absence of the glass transition temperature as measured by DMA [40].

5.6 POS Dispersants

Dispersants are an important class of surfactant because achieving good dispersion is often critical in commercial materials. Pigments when fully dispersed give higher tinting strength. Thus, for a given pigment concentration, more intense colors can be achieved. Alternatively for a given desired color, less pigment is required, thereby saving money on pigment, which tends to be expensive. Thus both plastic and coating formulations often contain some type of dispersant.

Agglomeration of pigments and fillers leads to problems. Specifically, the impact resistance of thermoplastics and thermoset materials is dramatically lowered by the presence of agglomerated particles. The other mechanical property most affected by agglomerates is elongation to break. Modulus and yield strength are not significantly altered however.

It is not just the mechanical properties that are affected. Electrical and thermal conductivity are both very much dependent upon the degree of dispersion. Agglomerated conductive particles can form a continuous pathway through the material, at which point (the so-called percolation threshold), the conductivity increases by several orders of magnitude.

The processability of materials can be as important as their final properties. Increasing the particulate concentration, be that fillers, pigments or other additives, increases the viscosity of the system. Progressively smaller particles have a stronger and stronger tendency to agglomerate and thereby raise viscosity. Thus, with the recent attention on nanoparticles, there is more need than ever for effective dispersants.
At low particle concentrations, the viscosity increase may be negligible, but some materials contain very high filler loadings. For instance, flame retardant fillers such as aluminum hydroxide and magnesium hydroxide are often used at 60 wt % or more. PVC tile contains 80 wt % of calcium carbonate, and polymer magnets can contain over 85 wt % filler. At such high loadings, the viscosity of the material becomes an issue. Extruder throughput and mold filling suffer appreciably. High gloss is difficult or impossible to attain. Sometimes one desires to add more filler, but the viscosity limits the filler amount that can practicably be used. All of these issues can be mitigated, or avoided outright, by the use of an optimal dispersant. So, how do dispersants work and what constitutes an ideal dispersant for a given material? Dispersants coat particles and prevent them from adhering to one another.

The ubiquitous van der Waals forces attract particles together. Once they approach closely, those forces become very strong and the particles come into contact. Once agglomerated, they are hard to separate. By coating the particles, a dispersant prevents close approach and lessens the attractive forces. In non-aqueous systems, the primary mechanism for dispersant action is steric stabilization. The criteria [41] for effective steric stabilization are:

1. The surfactant must adhere well to the particle surface so that it is not displaced when two particles approach each other.
2. The portion of the surfactant not adsorbed must be soluble in the surrounding medium, i.e., the solvent, coating or polymer as the case may be.
3. The surfactant “tail” must be long enough to prevent the particles getting too close where van der Waals attractive forces dominate and cause strong agglomeration.

AB and ABA type block copolymers make excellent dispersants whereby an insoluble block (B) adsorbs onto the particle and the other, soluble block (A), provides the particle separation. However, polymeric block copolymer stabilizers have disadvantages such as being relatively expensive. Furthermore, they are not ideal for nanoparticle dispersion because the size of the polymeric stabilizer is significant compared to the particles; hence one needs a lot of stabilizer and the effective particle size (the particle plus the layer of adsorbed polymer) is large, resulting in an increase in the effective filler loading and thus a concomitant increase in viscosity.

Small molecule surfactants have also been used as dispersants to good effect. Stearic acid is the standard dispersant for calcium carbonate because the carboxylic acid group adsorbs strongly to calcium carbonate and the aliphatic tail is compatible with low polarity polymers such as polyethylene and polypropylene. While stearic acid is highly efficacious on calcium carbonate, it is known to be ineffective on silica and other siliceous fillers (Fig. 5.2) because the acid group does not adsorb onto the surface [42].
In some cases, there are no places for the dispersant head to “dock”. For fillers such as silica and related fillers, organosilanes (Fig. 5.3) are a good choice because the head group can bond well to the filler. Thus, one must pick the appropriate dispersant in each case where the head group bonds well and the tail group is soluble in the medium. One large study investigated nine different mineral fillers and pigments to determine the optimal dispersant for each [43]. It was found that the surface chemistry, that is, the affinity of the surface for dispersants, was unique for every type of particle tested. Contrary to popular perception, it was shown that minerals do not behave as either acids (e.g., silica) or bases (e.g., calcium carbonate) but each were amphoteric, adsorbing both acid and basic dispersants. The unique surface chemistry of the minerals means that the quest for a universal dispersant is challenging.
Most POS are symmetrical and therefore do not display surfactant properties. However, there are exceptions. In particular, the POS trisilanols are surface active due to the highly polar silanol groups on the one hand and the less polar alkyl groups on the other (Fig. 5.4). Other POS expected to show strong surface activity are the new POS trisulfonic acids.

Indeed, POS trisilanols have proven to be effective dispersants for fillers and pigments [6,44,45]. Unusually, the POS trisilanols work well as dispersants for many different types of fillers including calcium carbonate, bismuth subcarbonate, yttrium oxide, titanium dioxide, hexagonal boron nitride, titanium carbide, magnetite and silica. As mentioned previously, a universal dispersant that functions on fillers as different as calcium carbonate and silica has hereto proven elusive. The broad applicability of POS trisilanols is probably due to their unique nature. They are highly acidic and therefore effective on basic fillers including carbonates, but also contain silanol functional groups that can bond to free silanol groups on the surface of silica, other siliceous fillers and metal oxides. Furthermore, because there are three reactive groups per molecule (Fig. 5.5), the POS trisilanols can chelate to surfaces forming bonds that survive even under extreme temperatures. Thus, particles can be dispersed using POS trisilanols in an extruder even in the case of PEEK which is extruded at rather high temperatures.
5.7 POS Metal Deactivators

A related application, relying upon the ability of POS to adsorb strongly to surfaces, is the use of POS trisilanols as metal deactivators [6]. Transition metals attack organic substances including coatings and polymers so for example, the copper in a copper cable tends to attack the polyethylene insulation causing oxidation and premature failure. Metal deactivators adsorb strongly to the metal, thus preventing it from coming into contact with and degrading the surrounding material. POS trisilanols were tested as metal deactivators for copper and it was found that they were able to reduce the detrimental effect of the copper even at high temperature approaching 200°C under pure oxygen. Metal deactivators are rather expensive and
are only needed in monolayer amounts so using POS may be commercially viable from a cost perspective.

5.8 New Applications and the Future

The utility of POS relies upon its special properties, namely:

- A rigid, bulky cage
- High degree of functionality
- Defined and intermediate molecular weight (between solvents and polymers)
- Defined molecular size
- Unique chemistry, i.e. the POS trisilanols
- Their unique chemistry offers possibilities for new patents and marketing

As well as those applications of POS already alluded to, there are other assorted applications either already commercialized or being explored. Some of those are mentioned here.

POS has been suggested for novel cosmetic formulations [46,47] where it could serve as a dispersant, emollient or viscosity modifier. Recently POS has been copolymerized to create a new, colorless and transparent polyimide [48] which can be solution cast or applied as a spray. The POS serves two vital roles in the polyimide which was developed to be a solar cell cover for space applications. Firstly, normal polyimide is colored, blocking some portion of the light and thereby reducing the efficiency of the solar panels. The copolymerization with POS results in a colorless film with improved solar cell efficiency. Presumably, the POS changes the intermolecular spacing, thereby disrupting the electronic interactions that normally result in color. Secondly, polyimides are attacked by atomic oxygen in Low Earth Orbit. Testing has shown that where a standard polyimide is first etched, and then destroyed, a POS enhanced polyimide is much more robust. Attack by atomic oxygen vitrifies the POS to form a protective glassy film, dramatically improving survivability of the material in space [48] (see Also Chapter 8).

POS molecules reside in an intermediate molecular weight range between solvents and plasticizers on the one hand, and polymers on the other. This has led to interest in using POS as calibration standards for mass spectroscopy. POS are also intermediate in size and are ideally suited to use as absolute calibration standards for gel permeation chromatography (GPC or SEC). GPC calibrations are normally performed using polystyrene standards but that method has serious drawbacks. Firstly, such calibration standards and expensive and are not truly monodisperse whereas POS is truly monomodal in size and also cheaper than polystyrene standards. Furthermore, solvated polystyrene coils change dimensions with temperature and with solvent type. POS on the other hand is rigid and does not change size with
temperature or solvent polarity. This gives a tremendous advantage compared to traditional standards.

5.9 Conclusions

The POS family of molecules extends into the hundreds, but they are all based upon a rigid, inorganic, central core composed of silicon and oxygen. This characteristic structure makes them visually intriguing, but more importantly, it imparts a unique property set distinct from that of small molecules, polymers or particles. POS are immensely tunable, from non-reactive types to highly functionalized versions, and from hydrophobic to highly hydrophilic and water-soluble examples.

The scale-up of POS manufacture has brought prices down dramatically, thus opening up the possibility of using POS in new applications. However, POS is still relatively expensive compared to other chemicals and additives, so commercialization will remain limited to niche applications where POS can deliver what no other additive is able to.

5.10 References


