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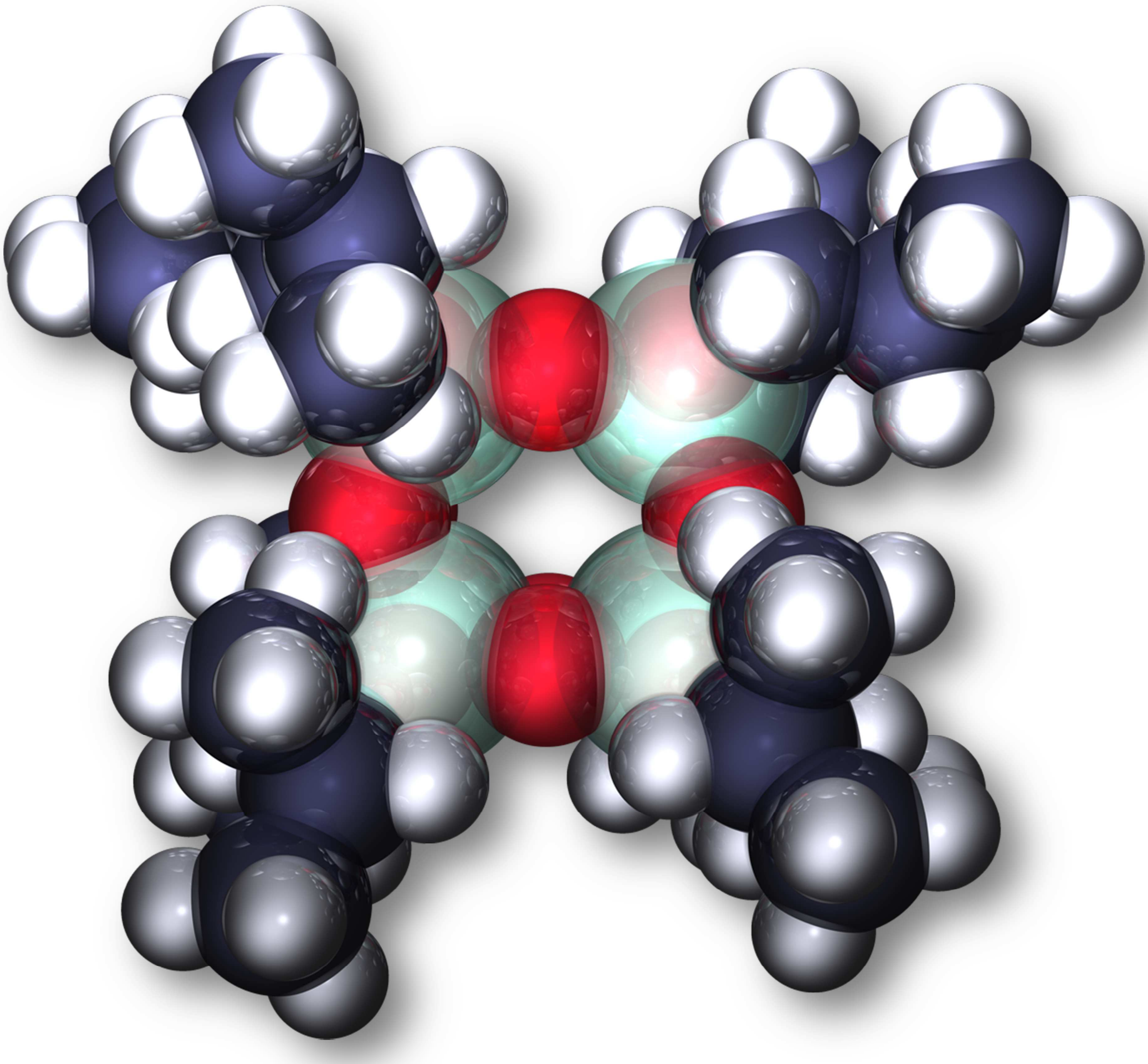

Phantom Plastics™

Polyhedral Oligomeric Silsesquioxane Handbook

www.phantomplastics.com

Preface

The aim of this book is to introduce polyhedral oligomeric silsesquioxanes (POSS®) and give an overview over what POSS are and what they can and cannot do. There is global interest in POSS and a definite need for a document that provides a starting place for people new to the field and a data source for those already acquainted with POSS. With hundreds of papers and patents already out there, it can be a bewildering task to get to grips with the topic, especially as the publications span so many different fields and because POSS is so different to other substances on the market.

During my time as Chief Scientist for Hybrid Plastics Inc., I sensed the need for a document on POSS and its application in plastics. Thus, the POSS User's Guide was born. The effort I put into writing that document was well rewarded as the number of downloads soon reached 700 per month and has remained steady since 2007. Given the success of that document, one may wonder why I have decided to create a new source for POSS information. Indeed, I have also recently authored two book chapters on POSS in plastics and there are numerous review articles already available.

There are three main reasons for this new POSS Handbook. Firstly, this document is an impartial source of information, written by someone very familiar with POSS but who no longer has any commercial connection to POSS, so that you can be sure that the information is technically sound and not tainted with marketing spin. A critical eye will be cast upon some of the claims made for POSS to see how they hold up to scrutiny and whether or not the proposed applications for POSS make technical and financial sense. Secondly, the POSS User's Guide is no longer up-to-date and I wanted to make people aware of recent developments. Lastly, this document is differentiated from scientific review articles in that it is intended as a place to find practical knowledge rather than having an academic tone.

About the author

As President of Phantom Plastics, Chris provides consultancy and training services to the plastics industry including multiple Fortune 500 companies. With years of experience from leading companies such as BASF (Germany) and Electrolux (Sweden & Italy), as well as a small start-up company, Hybrid Plastics (USA), Chris has a wealth of technical knowledge and international experience.

A recognized expert on plastics, composites and additives, Chris has given innumerable invited lectures, workshops and web seminars, chaired conferences and has over 40 patents, papers and book chapters to his name. He has authored two book chapters on POSS. Most recently, he was commissioned by Elsevier to write two chapters for the Plastics Engineering Encyclopedia.

In addition to technical expertise, Chris is a renowned innovator. He solved a major technical production problem that had confounded BASF for over 30 years. This was followed by the invention of a new class of smart materials, namely plastics that change opacity reversibly with temperature. In 2007, 2009 and 2010 he won substantial cash prizes for solving Innocentive open innovation industrial challenges. As well as his more established seminars and workshops in the plastics field, Chris now lectures to share his insights on innovating in an industrial setting and how to overcome obstacles to success.

Chris obtained his BSc, MPhil and PhD from the University of Sussex, UK. He is a Fellow of the Royal Society of Chemistry and a Chartered Chemist.

For more information visit:

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Introduction

Polyhedral oligomeric silsesquioxanes, now commonly referred to under the trade name POSS, were discovered in the 1940s. Although they were not pursued commercially at that time, there was a revival of interest in the 1990s and that interest has been sustained globally ever since. The cage-like shape of the molecule is visually intriguing and that is certainly part of the appeal. Conventional molecules tend to be more or less linear with perhaps some degree of branching and the behavior of those "normal" molecules is rather well understood. Molecules departing from that norm tend to attract substantial interest in the hope that they will provide revolutionary properties and technological breakthroughs. For example, hyperbranched polymers, and their structurally perfect analogues the dendrimers, have been the focus of intense research and their unconventional structures do indeed lead to unusual properties. Cage structured hydrocarbons are well-known and again have unusual properties. Cubane is one example, having a density higher than any other hydrocarbon (1.29 gcm^{-3}). Similarly, some POSS types display exceptionally high densities of up to 1.82 gcm^{-3} (see Table 1). Another family of cage-like hydrocarbons, the diamondoids, found naturally in petroleum deposits, was investigated by Chevron Technology Ventures in collaboration with Stanford for several years. The simplest diamondoid is adamantine with several other higher homologues reported and can be chemically derivatized to impart reactive groups. Interestingly, the diamondoids are also referred to as nanodiamonds, thus implying that they are nanoparticles of diamond. In much the same way, POSS is often referred to as "nano silica". In both cases however, the terminology is misleading. As will be illustrated later, these substances are all molecules that merely appear reminiscent of particles.

Material	Weight% Cage	Density (gcm^{-3})	Refractive index
Quartz (crystalline silica)	100	2.60	1.54
Octa hydrido POSS	98	1.82	1.51
Octa methyl POSS	78	1.50	1.51
Octa ethyl POSS	64	1.33	1.50
Octa iso-butyl POSS	48	1.13	1.48
Octa iso-octyl POSS	32	1.01	1.45
Iso-octane	0	0.69	1.39

Table 1 Property variations in POSS with changing side groups

As well as density and refractive index, other properties including modulus, thermal conductivity, solubility and so on are expected to vary systematically as one varies the ratio of inorganic cage to the surrounding organic groups. Therefore, POSS is able to span the gamut of properties from those associates with inorganic materials, to those found for organic substances.

Conceptually, one may consider each POSS molecule to be a filled polymer where there is a central "silica" filler bonded within an organic matrix. Thus, the properties of this molecular composite are expected to follow the same rules as for macroscopic composites so that for example, the modulus of the POSS would be dependent upon the moduli of the central "silica" cage, the organic phase and the volume fraction of each as described by the Halpin-Tsai equation. Other well established polymer composite equations could also be applied in order to estimate the properties of those POSS that already exist and to predict properties of POSS types not yet extant.

No discussion of cage-like molecules would be complete without mentioning C_{60}, Buckminsterfullerene (see Figure 1) and the other fullerenes. The discovery of these new forms of carbon was greeted with tremendous enthusiasm and much speculation about unique properties leading to new applications. I was studying at Sussex University in that exciting time period and was taught by Professor Sir Harry Kroto and the other members of that research team, Professors Dave Walton and Roger Taylor. Yet despite the momentous discovery, now, over 20 years later, there are no commercial applications.

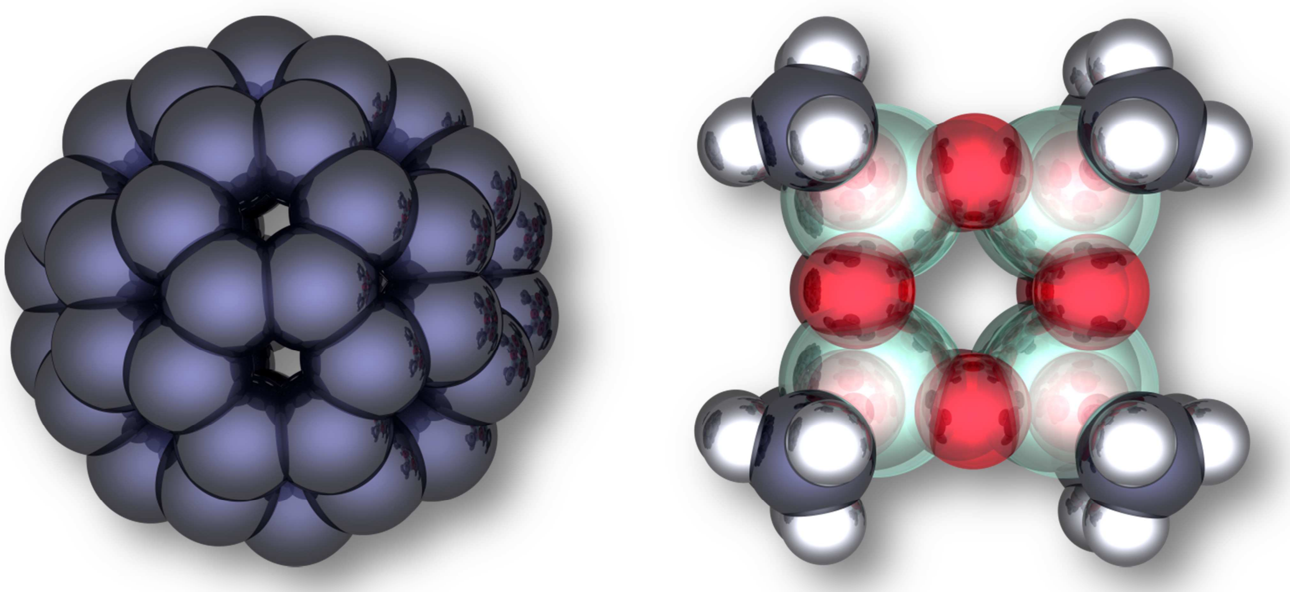

Figure 1 Buckminsterfullerene, C60 (left) and octamethyl POSS (right), both ~1nm across
Carbon – blue, silicon - green, oxygen – red, hydrogen - silver

While all of these cage molecules generated excitement and did indeed turn out to have unique properties, large commercial applications have not emerged for three reasons. It has proven difficult to synthesize larger amounts and to produce the diverse chemistries needed to facilitate adoption in a wide range of applications. Furthermore, the prices of these materials are too high to justify their use. Even though performance advantages may have been seen in some cases, they were simply not enough to make these new materials competitive with those already incumbent in the market.

Therefore, we can conclude that it is not enough that a molecule is intriguing or different. In order to have commercial success it must fulfill one or both of these criteria:

- Provide performance levels unattainable by any other route
- Lower the final cost (holistic, total system cost, not materials cost alone)

Furthermore, it is my experience that the best breakthrough technologies on the market today took 15-20 years to come to fruition. When one discovers a new material, it is both a blessing and a curse. Certainly, the material is likely to exhibit new properties but one must first find those properties, then work out how that can bring value and who the potential customers might be. Testing ensues, alliances are made and with luck, eventually a product reaches the market.

Chevron Technology Ventures' interest in the diamondoids has fizzled out and while academic research continues on those and hyperbranched polymers, dendrimers and of course C_{60}, there is little prospect for commercial applications. Looking at all these materials, it is my view that the POSS family of chemicals is, in fact, the most promising of all. They offer the whole range of chemistries and can be tuned easily to attain a spectrum of properties. Equally important, they can be made on a large scale using conventional chemical reactors, resulting in prices far lower than for those other materials.

The organic side groups on POSS span the whole range of chemistries: fluoroalkyl, alkyl, phenyl, alcohols, thiols, amines, vinyl, carboxylic acid, sulfonic acid, PEG, acrylate, methacrylate, epoxides, halides, imides, silanes and silanols. Interestingly, some organosilanes starting materials convert readily to POSS whereas other POSS types simply cannot be synthesized. As one example octaisooctyl POSS is available in bulk whereas octa n-octyl POSS cannot be made at all. There is at present no understanding as to why some kinds can be made and others cannot.

	POSS	Dendrimers	Hyperbranched polymers	Diamondoid Adamantane	C_{60}	Carbon MWNT
Available amounts	100s of tons	Kilo	Kilo	Tons	Kilo	100s of tons
Price (€/kg)	10s	100s	10s	100s	1000s	1000s
Solubility	Good	Good	Good	Good	Poor	None
Diversity of chemistries	Very good	Good	Good	Poor	Fair	Poor

Table 2 Pricing and availability for POSS and other high profile specialty additives
STARBURST® is a trademark of Dendritic Nanotechnologies, Inc.

As a comparison, a STARBURST® dendrimer with 8 functional (amino) groups per molecule costs $181 for 2.0g of a solution in methanol where the concentration of dendrimer is just 20 weight %. Thus, the effective price for the dendrimer is ~$450/g. Contrast that to an octafunctional (vinyl) POSS, also a spherical molecule of well-defined structure with pricing of $2/g, POSS octaamic acid for $24/g or the acrylates and epoxy POSS at only 60 cents per gram. Not to mention that those are the R&D, small order prices for the POSS which drop very significantly for larger orders.

Probably due to the diversity and relatively low POSS prices, some commercial POSS applications do exist and they continue to grow slowly as is the way with such new technologies. However, companies are often hesitant to use any technology that has only one supplier because it can lead to unfavorably high pricing and instability of supply. It could well be that such considerations have slowed the application of POSS.

Having set the scene in terms of what POSS is and how it fits into the landscape of other high profile molecules, we will now look in more detail at POSS types and how they can be used to modify the properties of polymers. Normally, scientific reviews simply look at what can be achieved. As stated in the preface, the aim of the POSS Handbook is to take a more pragmatic view. Thus, not only will the effect of the POSS be examined but also whether it offers an attractive solution compared to those already known or on the market.

POSS - Molecule or Particle?

POSS appear spherical or cubic to the eye and somehow this makes the viewer think that POSS are particles. They are often described in the literature as nanoparticles with all the good and the bad associations that come with that nomenclature. Nano has, in recent years been a buzzword and research on all things nano has been popular and well-funded. On the downside, the term nano now invokes concerns over safety and lack of commercialization means nano has lost much of its shine.

As mentioned earlier, POSS are in fact molecules and that can be proven categorically in several ways. POSS can be analyzed by the following techniques which only apply to molecules:

- Solution NMR spectroscopy (^{1}H or ^{29}Si)
- HPLC
- Mass spectroscopy
- Dielectric spectroscopy
- Some POSS types are liquid at room temperature
- POSS can be melted and recrystallized
- POSS can be recrystallized from solution

POSS dissolves molecularly in solvents if the polarity of the solvent is matched to that of the POSS. The POSS can then be recrystallized from solution to purify it, just as with other solid chemical substances. Suitable solvents for POSS can be predicted using the Solubility Parameter concept, which is also useful for example when one needs to predict the solubility of an as yet unsynthesized POSS type. POSS can be dissolved in solvents in high concentrations, approaching 100 weight percent in some cases. POSS can also be dissolved in polymers but in that case the solubility limit is normally around 5 weight percent.

There are four main types of POSS configuration:

- Eight identical side groups
- A statistical mixture of two different ligands totaling eight
- Seven identical units with one corner of the cage open exposing three silanol groups
- Seven identical groups with one different group inserted in one corner of the cage

So, POSS are molecules that just look reminiscent of particles and that is why they are sometimes referred to as "molicles" to reflect their dual nature. The fact that POSS are molecules is a great advantage because it means they dissolve. In contrast, nanoparticles are notoriously difficult to disperse and that has held back their use in commercial applications. Furthermore, as POSS are not nanoparticles they avoid the safety uncertainties associated with nano materials.

Properties of POSS

Naturally, with well over 200 POSS types in existence, one cannot detail the properties for each and every one. It is more convenient to take an overview (Table 3).

Property	Value or typical behavior
Density range	0.9-1.3 gcm^{-3} typical (up to 1.82 gcm^{-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 and PEG (medium) to polyionic (high)
Chemical & aqueous pH stability	Molecular silicas (closed cage) very stable, trisilanols good
Thermal stability	250-350°C typical (> 400°C for some types)
Safety	All three POSS tested so far were shown to be safe
Purity	Standard purity >97%

Table 3 POSS properties overview

When trying to identify applications for POSS, it is appropriate to start by looking at the unusual and unique properties arising from the POSS molecular structure. These can be summarized as follows where each of the features results in consequences in terms of properties:

- Rigid cage structure
- High thermal stability
- Relatively high molecular weight
- Fully tunable solubility
- Fully tunable reactivity

Special Properties and Applications

In order to have a chance in the marketplace, a product needs to present an attractive value proposition to the customer. Specifically, the following three criteria must be fulfilled:

- The product must produce an effect
- The effect must be useful in some way
- The product must be competitive in terms of cost and performance compared to products incumbent in the marketplace

In order to have a metric of the viability of each proposed application for POSS, these three criteria will be applied in each case.

Modulus and Yield Strength

The rigid cage means that POSS has higher modulus than normal organic molecules. So, when POSS is added to polymers, the modulus of the polymer is not lowered, whereas adding low molecular weight organic molecules usually results in lower modulus. That is, they act as plasticizers. Because POSS has little to no effect on modulus of polymers, unlike fillers, it is not added to improve modulus.

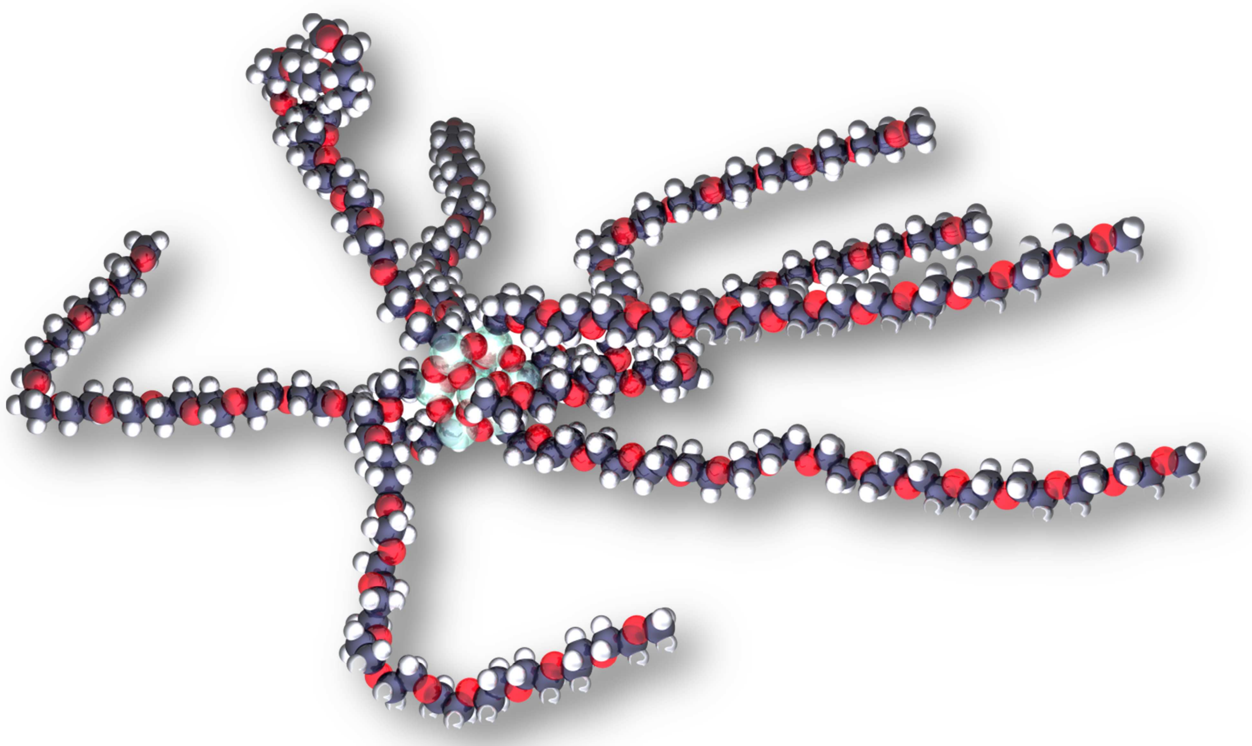

Figure 2 PEG POSS with 14 ethylene oxide units per arm

The modulus of the cage is high (silica is ~70GPa). However, the surrounding organic groups are not nearly as rigid. Therefore POSS types span a wide range of moduli depending upon the ratio of cage to organic groups. Octahydrido POSS can be expected to have a very high modulus whereas, as the organic groups become larger, they have more and more influence on the modulus of the entire POSS molecule. Some POSS, for example octa iso-octyl POSS and PEG POSS, are liquid at room temperature. In these latter cases, large flexible organic groups in the POSS cage dominate the modulus.

Effect Present?	Performance Advantage?	Competitive?
✘	✘	✘

HDT & Vicat Softening Temperature

The cage has a locked conformation and size so it does not deform or soften when heated. In consequence, copolymers of POSS and POSS homopolymers in particular, retain modulus at elevated temperature. Thus POSS can be copolymerized to raise HDT and Vicat softening temperature. POSS epoxies can retain almost full modulus to 300°C. Unfortunately, their continuous use temperature is far lower than that because oxidative degradation sets in leading to embrittlement and failure. The thermal stability of the central cage is very good however, for two reasons. Firstly, it is composed of silicon – oxygen bonds which are intrinsically stable. Secondly, to break up the POSS cage requires cleavage of multiple bonds. It is well-recognized that ladder polymers have excellent thermal stability for just that reason.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	✘

Permeability

POSS can be thought of as molecular silica and it is often assumed that, like silica and traditional fillers, addition of POSS will be impermeable and furthermore that addition of POSS to polymers will render them impermeable. While it is true that the cage itself is impermeable, the surrounding organic groups are not. Taking octa iso-butyl POSS as a typical example, the cage only accounts for around 50 volume percent of the molecule as a whole. Thus, only half the molecule is impermeable to gases and liquids. Consider that typical POSS loadings in polymers are in the range 5-10 volume percent. That means that only 2.5 to 5 volume percent of the total POSS-polymer mixture is impermeable. Thus, it turns out that addition of POSS is ineffective at lowering permeability. In fact, adding POSS can actually increase permeability in some cases.

Effect Present?	Performance Advantage?	Competitive?
✗	✗	✗

Molecular Weight Effects

The molecular weight of POSS spans an unusual range. Normal organic molecules typically have molecular weights in the range ~50-500 Daltons whereas polymers are in the range from around 10 000 Daltons and upward into the millions. Furthermore, synthetic polymers even so-called "monomodal" polymers, are comprised of a mixture of molecules with differing molecular weight. POSS are the only family of chemicals that have molecular masses in the range from ~1000-5000 Daltons and where the molecules are well-defined with single molecular weights rather than a distribution. POSS has generated interest as molecular weight calibration standards for certain types of mass spectroscopy where no well-defined standards exist for the 1000-5000 Da range.

Another potential use of POSS is for GPC (SEC) calibration because unlike polymer standards, the POSS are truly monodisperse and the volume of the POSS standard is solvent independent whereas the polymer standards vary widely in molecular volume depending upon the solvent used.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	✓

A more mundane effect of POSS's relatively high molecular weight is that POSS are a lot less volatile than most additives for plastics. Thus, loss due to evaporation is low, even at elevated temperature. Migration of POSS is also slow because of the molecular weight and the bulky rigid cage which cannot diffuse by reputation as polymers do.

Surface Area

Many of the notable properties of nanoparticles are attributable to their high surface area. Silicas and carbon blacks can have surface areas in the hundreds of meters squared per gram. This means that when properly dispersed, such particles have a huge amount of contact with the surrounding matrix leading to good adhesion and a boost in some properties, most notably the yield strength of such composites.

Hybrid Plastics correctly state that POSS is a molecule, not a particle. It is therefore surprising that they then go on to calculate a surface area for POSS of 3600 m^2g^{-1}. This figure is arrived at by summing up the external surface of each molecule as if it were a particle. Clearly, this is both preposterous and misleading. The actual surface area is far lower, as shown below (Figure 3).

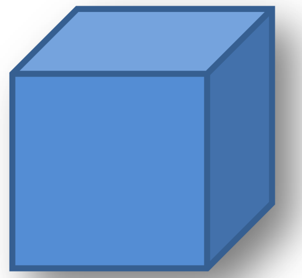

Figure 3 POSS cube of 1cm^3 volume – claimed surface area 3600 m^2g^{-1}, actual area 6 cm^2

Solubility

Fillers and other particulates, especially nanoparticles are notoriously difficult to disperse and can lead to opacity in otherwise transparent polymers. POSS on the other hand dissolves spontaneously and does not induce haze because the POSS molecules are far too small to scatter visible light. However, in order to ensure solubility of the POSS, one needs to match the polarity of the POSS organic groups to that of the matrix polymer, or solvent. This is done by choosing the correct organic ligands and fortunately, the whole gamut is available from low polarity perfluorocarbons through hydrocarbons, to higher polarity water-soluble groups like PEG, sulfonic acids and quaternary ammonium salts. Thus, one can tailor the POSS to suit the intended use.

POSS made with a statistical mixture of two or more different side groups increases the ability to tune POSS solubility and reactivity. A side-effect is that crystallization is inhibited in such POSS mixtures because the irregularity of molecular shapes prevents good packing. This can help solubilization. For crystalline materials, one needs to first overcome the latent heat of crystallization to separate the molecules in order to then solvate them. Amorphous materials have no such requirement and therefore dissolve more easily.

Lubrication

Quite some time ago, the US Air Force proposed that POSS could make good high temperature lubricants for jet aircraft. The thermal stability of the POSS cage and the low volatility of the molecule as a whole were thought to make it an ideal candidate. As those were the early days and the desired POSS types were not yet commercially available, the

Air Force set about synthesizing them. The project did manage to make some high molecular weight POSS with 8 hydrocarbon arms but the properties as lubricants were not investigated at that time. Presumably the project time and money was expended solely on the synthesis.

More recently, while I was working at Hybrid Plastics, I decided to test POSS as lubricants. With the help of a local entrepreneur, we borrowed a Falex Film Strength Tester which simulates bearing wear. A bearing is pressed against a rough, rotating wheel which spins through the lubricant to be tested. Weights are added to increase the pressure on the bearing until the lubricant film is displaced causing a sharp rise in wear rate and noise. We were surprised that the hydrocarbon POSS types such as octa iso-octyl POSS originally proposed by the Air Force were not effective. Instead, thanks to the tenacity of my team members, we discovered that PEG POSS was extremely potent. In fact it was on a par with the industry leading Royal Purple brand automotive lubricant. This was extremely surprising in light of the fact that the PEG POSS was tested neat, with no additives whatsoever whereas the Royal Purple was a fully formulated commercial product. As PEG POSS costs around $30-50/lb it cannot compete with for example automotive lubricants. However, PEG POSS has the unique property that it is water-soluble. If an application can be found that requires water-solubility, for example to facilitate easy cleaning, then the price premium of the PEG POSS could be justifiable. As the person who conceived PEG POSS and managed its development, I would like to see it find such a commercial application. PEG products are normally very safe and are even approved for oral consumption so it may be that the PEG POSS proves to be very safe and that could also be a selling point in certain applications.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	?

Applications for POSS

The academic interest in POSS is undeniable. However, this in no way assures commercial success. Academic interest in Buckminsterfullerene, dendrimers and hyperbranched polymers is also immense but with no commercialization. On the plus side, POSS combines the rigid cage of C_{60} with the high functionality of hyperbranched polymers and all at a lower cost than either one. This has helped POSS find some small initial applications. We shall look at the applications real and potential to evaluate the commercial potential of POSS.

POSS Enhanced Dental Restoratives

The oldest reported commercial application of POSS is by Pentron Clinical Technologies who incorporated POSS into a self-etching adhesive named Nano-Bond. It is claimed that POSS helps reduce tooth sensitivity by blocking tooth nanotubules. This application was a nice early win, however, the POSS is only an additive in the formulation and dental materials are only used in low quantities so the commercial significance of this use for POSS is minimal.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	✓

POSS for Chorizo Packaging

A much touted application for POSS is in food packaging. Cellulose had traditionally been used to make Chorizo packaging. The wish was to use nylon because it is cheaper, but the barrier properties of nylon were not suitable. By adding POSS it is claimed that the barrier properties are adjusted, thereby allowing a doubling of product shelf-life. The company Convertidora Industrial (http://www.conver.com.mx/) has been making this POSS modified packaging for several years.

This would appear to be an excellent example of a good volume, value added application for POSS. However, in light of the fact that no POSS are approved for food contact, the existence of this application for POSS is, in fact, rather startling. POSS in the nylon is in direct contact with the Chorizo meat which contains both water and fatty substances providing an environment ideal for migration of additives from the packaging into the meat. It remains to be seen whether the authorities take an interest in this and, if so, what actions result.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	✓

Colorless Polyimide

Polyimide is a transparent, high temperature polymer with a characteristic orange tint. A copolymer of fluoropolyimide and POSS gives a colorless material with increased resistance to etching from atomic oxygen in Low Earth Orbit (important for satellites) or from oxygen plasma. When exposed to strongly oxidizing conditions, the POSS vitrifies to make a protective glassy layer.

The colourless polyimide is called Corin XLS and is sold by NeXolve (a subsidiary of ManTech International Corporation) as either a powder or a film. Proposed applications include solar cell covers for satellites where the weight saving compared to glass is a huge advantage.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	✓

Friction Reduction in Polymers

It has been reported that POSS reduces the coefficient of friction when added to thermoplastics including PP and nylon. When the POSS is added in concentrations above its solubility limit, usually around 5 weight %, it phase separates from the polymer in small domains and blooms to the surface. This effect has been studied in detail on the micro and macro-scale.

It is bewildering that this effect has garnered so much attention. After all, addition of any oil or wax will do exactly the same thing, i.e. phase separate and lower the friction. Products such as oil filled nylon have been available for decades and are widely used commercially. Not only are they far cheaper than the POSS alternative but the oil approach is FDA and USDA approved. Similarly, additives such as erucamide are used to lower the COF of polyolefins. Typical dosage is in the 1 % range and the cost of such slip aids is in the $1-5/lb region. As POSS requires over 5 weight % loading and costs $30-50/lb, there is clearly no appeal in using POSS for friction reduction.

Hybrid Plastics has attempted to direct sell guitar picks made of nylon with POSS added to reduce friction. Needless to say, this has not been a big hit. Marketing a product that delivers no performance edge, using more expensive materials than the alternatives and of unproven safety, does not constitute a recipe for success. As guitar picks are frequently placed in the mouth, it is probably advisable to use only additives of proven safety.

Effect Present?	Performance Advantage?	Competitive?
✓	✗	✗

Hydrophobic and Oleophobic Surfaces

This is another topic that has received an inexplicable amount of academic interest. Hydrophobic surfaces created using POSS are neither surprising from a scientific standpoint nor interesting from a commercial standpoint. Any surface that is hydrophobic and microscopically rough will show ultra-hydrophobicity. Examples abound in the patent literature from the last several decades. Possibly the simplest and cheapest method for making such ultra-hydrophobic, Lotus-Effect surfaces is to simply paint and substrate and dip it in hydrophobically modified silica while the paint is still wet. The paint acts as an adhesive binding the silica onto the surface giving both the hydrophobicity and roughness required at a fraction of the price compared to using POSS.

The same applies to the ultra-oleophobic surfaces which have been made using extremely expensive perfluorinated POSS. The same effect has been reported using far less expensive routes.

Effect Present?	Performance Advantage?	Competitive?
✓	✗	✗

Flow Aids

Addition of low molecular weight substances generally leads to increased polymer melt flow, i.e. a reduction in viscosity. However, such additives normally act as plasticizers such that the modulus and yield strength of the final material are lowered. POSS is able to improve melt flow but without sacrificing either modulus or yield strength. Although the effect works in most thermoplastics including PP, using POSS in such inexpensive polymers is nonsensical. However, POSS has been shown effective in PEEK, PEI and other high price polymers where expensive additives such as POSS could make financial sense. Masterbatch concentrates are available and only time will tell whether commercial success ensues.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	?

Dispersants

Dispersants are a class of surfactants. They operate by binding to the particle surface such that two adjacent particles cannot approach closely. This reduces the interparticle forces and aids dispersion. The mechanism by which dispersants operate in low polarity media is called steric stabilization, the details of which can be found in colloid science text books.

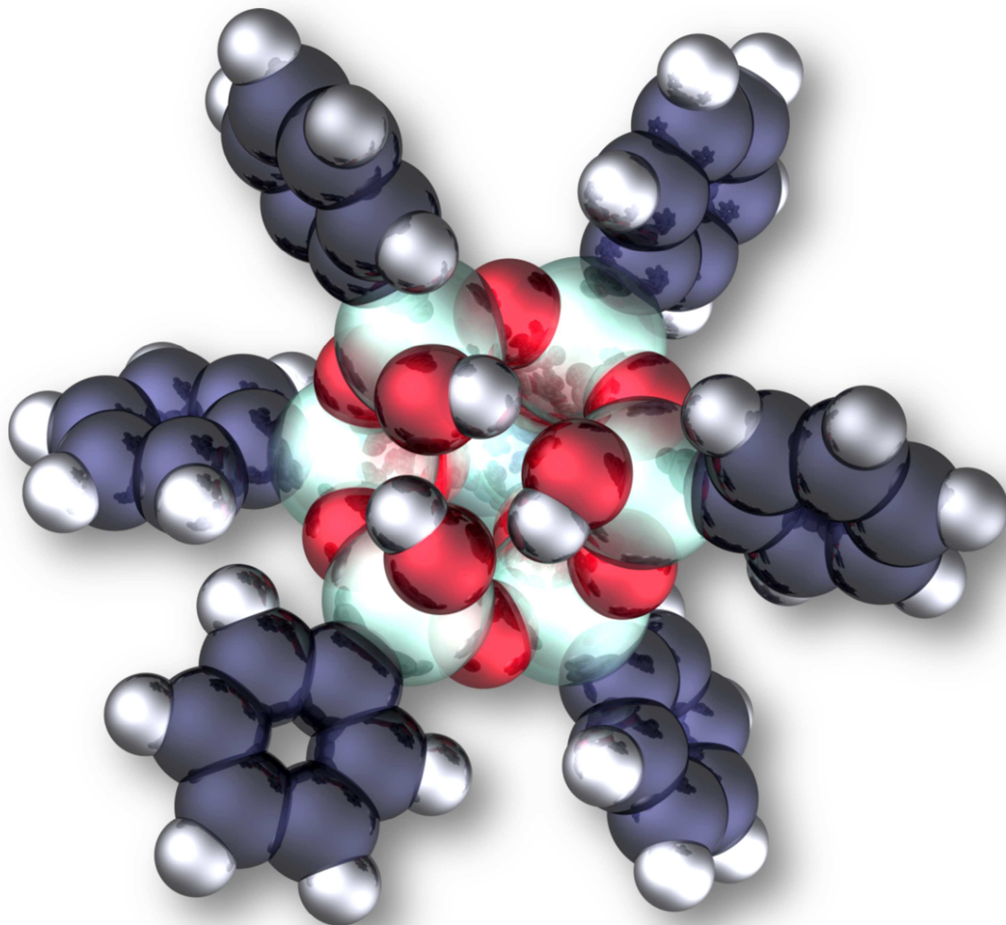

Figure 4 Trisilanolphenyl POSS showing the three acidic protons in the center

Dispersants are big business. They are selected to have chemistry allowing strong attachment to the particles and organic groups that are compatible with the surrounding matrix polymer, solvent or coating. Clearly, POSS cannot compete in applications where cheaper alternatives such as stearic acid or alkyltrimethoxy silanes costing $1-10/lb are effective. Instead, POSS dispersants are targeted at niche applications where those traditional dispersants founder. For example POSS dispersants have proven effective for formulations containing specialty fillers and pigments compounded into high temperature polymers including PEEK. In these instances, stearic acid and other related dispersants do not possess sufficient thermal stability to survive the high processing temperatures where the POSS trisilanols are able to operate under those demanding conditions. As the price of PEEK is in the same range as that of the POSS dispersants, namely $40-50/lb and are used at around 1 weight %, their use makes commercial sense. Due to their unique chemistry, they are able to bond to a very wide range of fillers and other inorganic materials.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	✓

Catalysts

It is possible to bind metal atoms into the corner of a POSS trisilanol, thus solubilizing the metal and giving a route to new catalysts. A very wide range of metals have been successfully chelated by POSS. The POSS trisilanols are very acidic, with roughly the same electron withdrawing effect as a CF_3 group. The POSS silanols exhibit a delta shift of 7-8 in the proton NMR, again indicating very high acidity.

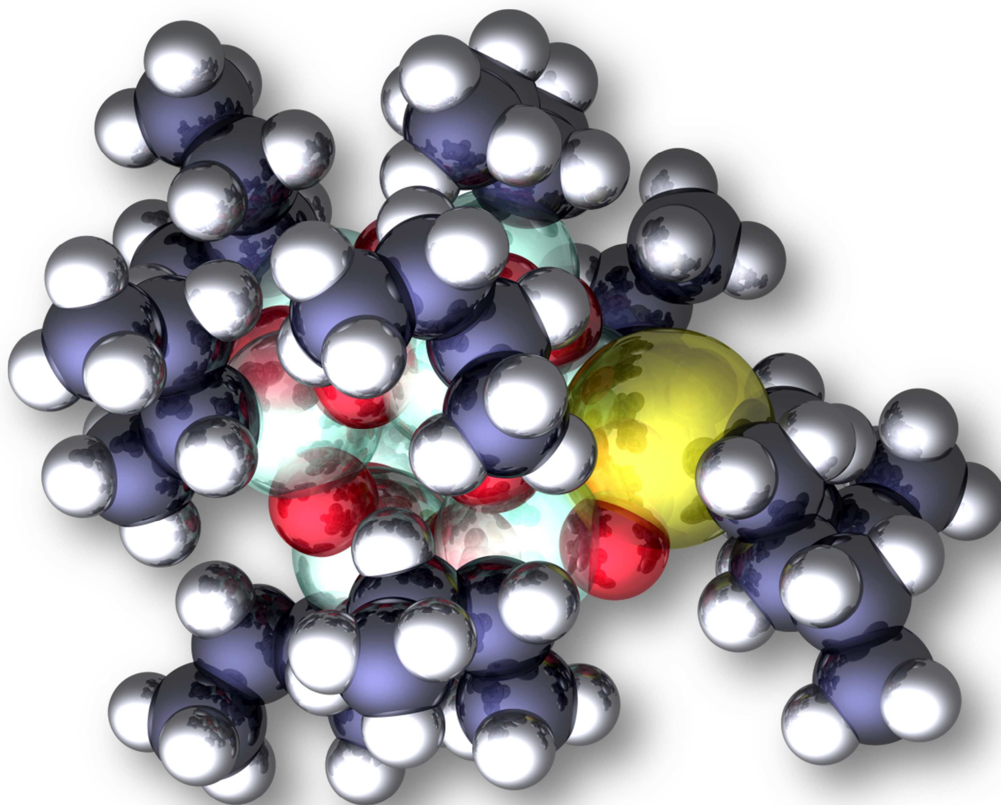

Figure 5 Tin POMS used as catalyst for polyurethane cure (tin shown in yellow)

Despite the potential for POSS catalysts, there has been very little work done on the area. Perhaps due to the lack of availability of such POSS types. One paper did show that tin POMS can catalyze the polymerization of polyurethanes. However, the POSS was no more effective than the industry standard tin octoate (tin 2-ethylhexanoate) and was of course dramatically more expensive.

Effect Present?	Performance Advantage?	Competitive?
✓	✗	✗

Metal Deactivator

The role of a metal deactivator is to protect polymers and coatings from the oxidative degradation that occurs when organic materials are left in contact with transition metals such as iron, copper, chromium and vanadium. Such metals catalyze the degradation of trace levels of hydroperoxides in these materials leading to a chain reaction whereby the organic material is progressively attacked with ensuing loss of mechanical properties.

A prime example is found in the wire and cable industry where copper wires come into contact with the plastic insulator. This causes degradation and early failure of polyolefin based insulation if an appropriate metal deactivator is not used. Similarly, transformer oils are attacked by copper and other metals, a problem exacerbated by warm conditions.

Formulation	DSC Pan Type	OIT Stability (mins)
No antioxidant	Aluminium	< 1
Irganox 1010 antioxidant	Aluminium	12
Irganox 1010 antioxidant	Copper	5
Irganox 1010 + octaisobutyl POSS	Copper	11
Irganox 1010 + octaisooctyl POSS	Copper	12

Table 4 OIT heat stability in squalane showing POSS trisilanols as metal deactivators

During my time at Hybrid Plastics, I decided to look at POSS trisilanols as potential metal deactivators. DSC experiments using the well-known oxidation induction time method showed the POSS trisilanols were very effective at just 200ppm concentration, binding to the copper and shielding the oil from it even at 190°C. Crucially, the POSS trisilanols outperformed the industry standard additive Irganox MD 1024 which proved to be insoluble and ineffective in the test. Metal deactivators are used in ppm levels and are relatively expensive ~ $10 / lb so POSS could well be competitive in terms of cost and performance.

Effect Present?	Performance Advantage?	Competitive?
✓	✓	✓

Conclusions and Future Outlook

As we have seen, the POSS family of molecules is interesting and has been the focus of a great deal of research. One or two very niche applications exist already and it can be expected that new applications will gradually be found over the coming decades. Unfortunately, the commercial potential of POSS very much limited in three ways. Firstly, the high cost, which cannot be further lowered because the raw materials used to make POSS are themselves expensive ($10-20 / lb in bulk for the least expensive types). Secondly, as discussed, the marketing efforts are focused on applications that make no sense in terms of cost or performance. Lastly, commercial exploitation of new technologies takes in the order of 10-20 years. Even if Hybrid Plastics can somehow survive that long, by that time, the key patents will have expired and other companies could step in and take over the market for POSS. Should a market for POSS have developed by that time, the natural outcome would be for the producers of the organosilanes raw materials to step in and produce POSS themselves and at a price that would be impossible to match.

POSS FAQ

This FAQ gives a concise list of POSS attributes and answers to typical questions about pure POSS and POSS enhanced products.

General Questions

Q. What is POSS?

A. POSS are chemicals that bridge the gap between ceramic and organic materials in a single molecular composition. The unique structure of POSS means it can provide performance attributes not attainable using standard chemical additives.

Q. Is POSS commercially available?

A. POSS is commercially available in large, multi-ton scale. Smaller amounts can also be purchased from Hybrid Plastics, Mayaterials, Gelest and Aldrich.

Q. Are POSS nanoparticles?

A. No, it has been shown definitively, using several methods, that POSS are chemicals. For example POSS have distinct molecular weights and can be measured by molecule specific techniques such as solution NMR, HPLC and GPC.

Q. Is POSS safe to use?

A. Of the 80+ types of POSS available only three have had any safety testing done (as of 2009). Those three POSS were all closed cage, non-reactive types and were all shown harmless in oral toxicity LD50 tests on rats.

Q. Can Hybrid Plastics provide me with a free sample?

A. Their company policy is not to provide free samples, instead they sell samples through the POSS R&D Chemicals Catalog.

Q. Is POSS difficult to disperse like nanoparticles are?

A. No, because POSS are molecules, they dissolve spontaneously if you use a solvent / media of the correct polarity (solubility parameter).

Q. Is POSS abrasive to my processing equipment?

A. No, because POSS are molecules there is no abrasion whatsoever.

Q. Is an MSDS available?

A. Yes, an MSDS for each POSS chemical is available for download at the Hybrid Plastics website www.hybridplastics.com

Q. Are POSS REACH or FDA approved?

A. POSS are neither REACH nor FDA approved which is surprising because Hybrid Plastics have sold POSS commercially for use in food packaging for several years.

Q. What is the purity of POSS?

A. Standard purity is greater than 97%.

Q. Can I get help to select a POSS for my application?

A. Yes, Hybrid Plastics can help you formulate and they have a laboratory to support development work.

Q. I don't see the POSS I want, what can I do?

A. Contact Hybrid Plastics about custom synthesis of new POSS. They may even have what you need already in stock.

Q. Is POSS stable to acidic and basic conditions?

A. POSS is stable to aqueous acid and base.

Q. What is the thermal stability of POSS?

A. Each POSS has its own unique stability. As determined by TGA, the most stable types survive to around 400°C for short periods.

Q. Is POSS soluble in my solvent?

A. POSS solubility guidelines are given in the POSS R&D Chemicals Catalog. If you need testing in another solvent, Hybrid Plastics can give advice or check for you.

Q. What concentration of POSS is normally used?

A. POSS can be effective from ppm levels to 100% POSS depending on the application. In thermoplastics 1-5 weight % loadings are typical. In thermosets loadings of 10-40% are common.

Q. How much does POSS cost?

A. Bulk orders (ton scale) see pricing as low as the $30-50 / lb range for some POSS types.

Q. What physical form does POSS come in?

A. The vast majority of POSS are white, crystalline solids. Some are greases or liquids.

POSS Application Questions

Q. Can you tell me about commercial applications for POSS?

A. POSS has been commercial for many years in dental materials and packaging. Emerging potential applications include air filtration, optical property tuning, colorless polyimide, high temperature epoxy resins, flow aids and dispersants for high temperature polymers like PEEK, PEI, PPS, COC and PA6.

Q. What are the POSS Flow Aids?

A. POSS Flow Aids increase melt flow without sacrificing any mechanical properties so you can get the performance of high molecular weight polymer with the high flow normally found only in lower molecular weight grades. The POSS Flow Aids are supplied in masterbatch concentrates providing for a drop-in solution.

Q. Why do I need POSS Flow Aids?

A. Good flow improves:

- Mold filling for lower scrap
- Ability to make complex parts
- Thin-walled parts
- Lower frozen-in stresses

Q. Will POSS Flow Aids work in my polymer?

A. POSS Flow aids are validated in PEEK, PEI, PPS, COC and PA6 with additional engineering polymers imminent.

Q. What can you tell me about the POSS dispersants?

A. Proper filler dispersion is paramount for good flow, high loadings, impact resistance, elongation to break and gloss. POSS dispersants deliver all these benefits at high temperatures where traditional dispersants degrade and fail.

Q. What fillers and pigments do POSS dispersants work for?

A. Due to their unique chemistry, POSS dispersants are effective on a wide range of fillers such as boron nitride, titanium carbide, titanium dioxide, yttria, calcium carbonate and many more.

Q. How are the POSS Epoxies unique?

A. The cycloaliphatic POSS Epoxies that retain modulus to 300°C (572°F), have high solvent resistance and ultra-low cure shrinkage (as low as 1% shrinkage for an unfilled epoxy). However, their stability at these high temperatures is unproven.

Q. When should I consider the POSS polyimides?

A. POSS adds oxidation resistance to colorless polyimide. This is potentially useful, for example, in solar cell covers used in space. Free-standing films or aerosol spray versions are available.

Q. Is POSS useful in other polyimides?

A. Yes, other polyimides can be improved. For example, POSS incorporation will enable improved oxidative stability via in-situ vitrification of POSS to form a passivating surface layer of glass.

Q. Can I put other molecules inside the hole in the POSS cage?

A. The hole turns out to be extremely small so only the smallest entities such as H• and F• can fit inside the cage.

Q. How can POSS do so many different things?

A. POSS is not one chemical but a family of over 250 different molecules. The versatility of POSS comes from the diversity of compositions and molecular topologies that can provide hydrophobic, hydrophilic, inert, or reactive groups.

Q. What else can POSS do?

A. There are thousands of articles and patents mentioning POSS. It has been tested in polymers, coatings and microelectronics and even in biological systems. Hybrid Plastics tracks all POSS publications so you can get up to date information from them.

Appendix

Refractive Index and Density

Refractive indices can be accurately calculated from using the method proposed by Vogel. Value have been taken from the CRC Handbook 68th Edition except for values marked with a star which were taken from examining the original Vogel work and the value for Si determined by fitting experimental and calculated RI values. It should be noted that calculated RI values for solid and liquid POSS agree well with measured values reported by H.W. Oviatt. This method is especially useful for calculating refractive index of POSS that are, as yet, unsynthesized.

C = **2.591**	**H** = **1.028**	**phenyl** = **25.463**	**naphthyl** = **43.00**
–O– = **1.764***	**Cl** = **5.844**	**N primary** = **2.376**	**–S–** = **7.729**
=O = **2.122**	**Br** = **8.741**	**N secondary** = **2.582**	**=S** = **7.921**
–OH = **2.553**	**I** = **13.954**	**Si** = **5.10**	**C≡N** = **5.459**

Such values can be used to calculate the molar refractivity from which the refractive index can be obtained. For example, for C_2H_5COOH: Rcalc = 3(2.591) + 5(1.028) + 2.122 + 2.553 = 17.588 in close agreement with the experimental value of 17.51.

$$n^2 = (V_m + 2R_m)/(V_m - R_m)$$

Where n is the volume refractive index, V_m is the molar volume (molar mass/density) and R_m is the molar refractivity.

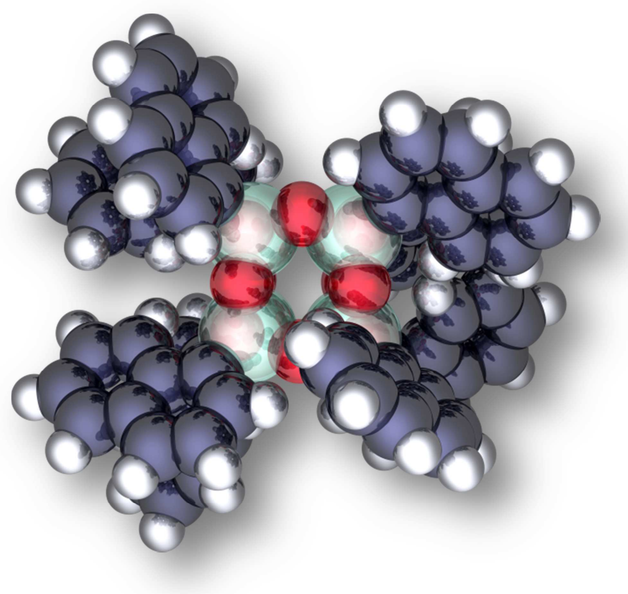

Figure 6 Shown to the right is octanaphthyl POSS which has not yet been made, but is expected to have a very high refractive index

POSS® Type	Density (gcm^{-3})	RI
SH1311 (octahydrido) - solid	1.82	1.51
MS0830 (octamethyl) - solid	1.50	1.51
SO1458 (trisilanolphenyl) - solid	1.42	1.65
AMO285 (octaammonium) - solid	1.40	---
OL1160 (octavinyl) - solid	1.38	1.47
MS0840 (octaphenyl) - solid	1.35	1.61
MS0822 (octaethyl) - solid	1.33	1.50
SO1444 (trisilanolethyl) - solid	1.33	1.50
AM0273 (aminopropylphenyl) - solid	1.31	1.58
SO1460 (tetrasilanolphenyl) - solid	1.31	1.60
MS0802 (dodecaphenyl) - solid	1.26	1.56
EP0417 (glycidylethyl) - solid	1.25	1.47
EP0409 (glycidyl cage mixture) - liquid	1.25	1.51
EP0408 (epoxycyclohexyl cage mixture) - semi-solid	1.24	1.52
PM1285MV (vinyl silsesquioxane resin) - liquid	1.24	---
SH1310 (octasilane) - solid	1.23	1.43
MS0860 (octaTMA) - solid	1.23	---
MA0736 (acrylo cage mixture) - liquid	1.23	1.45
MA0735 (methacryl cage mixture) - liquid	1.20	1.46
AM0281 (N-phenylaminopropyl cage mixture) - liquid	1.20	1.57
AM0275 (aminoethylaminopropyl i-butyl) - solid	1.17	1.50
EP0402 (epoxycyclohexyl i-butyl) - solid	1.17	1.50
MS0813 (phenyl i-butyl) - solid	1.17	1.50
AM0265 (aminopropyl i-butyl) - solid	1.16	1.49

POSS® Type	Density (gcm^{-3})	RI
MS0865 (octatrimethylsiloxy) - solid	**1.16**	**1.43**
TH1550 (mercaptopropyl i-butyl) - solid	**1.15**	**1.48**
EP0418 (glycidyl i-butyl) - solid	**1.14**	**1.47**
OL1118 (allyl i-butyl) - solid	**1.14**	**1.48**
SO1450 (trisilanol i-butyl) - solid	**1.13**	**1.48**
AL0130 (1,2-propanediol i-butyl) - solid	**1.13**	**1.47**
MA0701 (acrylo i-butyl) - solid	**1.13**	**1.47**
MA0702 (methacryl i-butyl) - solid	**1.13**	**1.47**
OL1123 (monovinyl i-butyl) - solid	**1.13**	**1.46**
OL1163 (octavinyldimethylsilyl) - solid	**1.12**	**1.41**
PG1190 (PEG POSS cage mixture) - liquid	**1.09**	**1.45**
EP0423 (trisglycidyl i-butyl) - liquid	**1.08***	**1.47**
TH1555 (mercaptopropyl i-octyl) - liquid	**1.02**	**1.47**
MA0719 (methacryl i-octyl) - liquid	**0.995**	**1.45**
AM0270 (aminopropyl i-octyl) - liquid	**0.99**	**1.46**
EP0419 (glycidyl i-octyl) - liquid	**0.99**	**1.45**
MS0805 (i-octyl cage mixture) - liquid	**0.97**	**1.45**
SO1455 (trisilanol i-octyl) - liquid	**0.97**	**1.45**

POSS® Densities (all values as reported by Hybrid Plastics using a pycnometer except * measured by H. W. Oviatt SwRI). Refractive indices calculated by Dr. Chris DeArmitt.