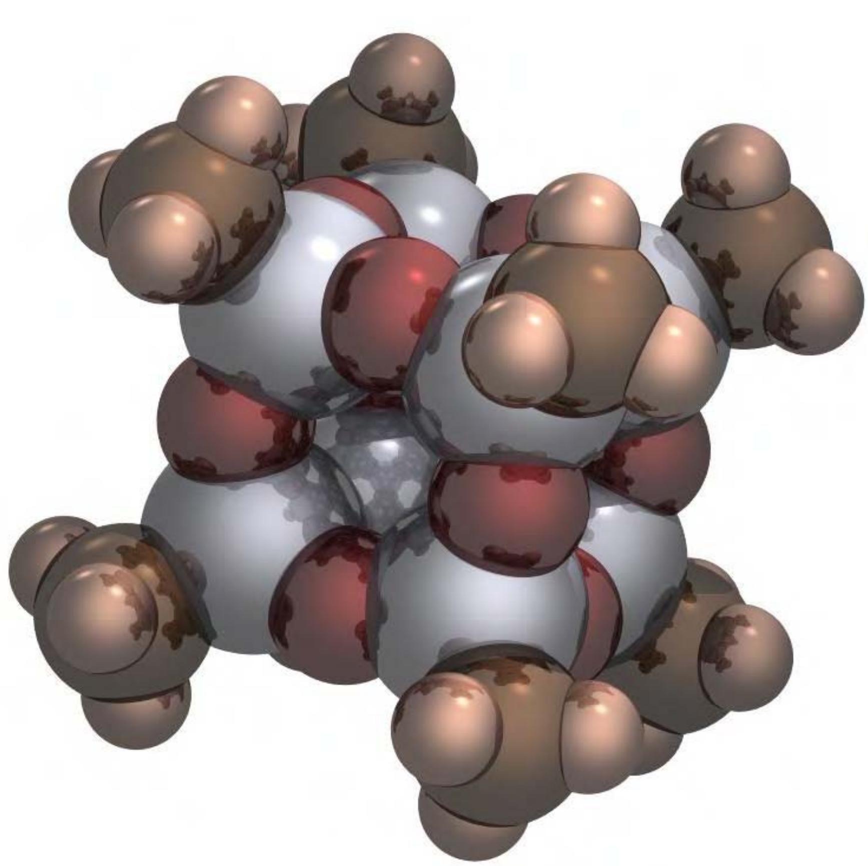
Version 2.06

POSS® User's Guide

A guide to developing new products with POSS®



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Introduction

Polyhedral oligomeric silsequioxanes (POSS®) are used to impart unique properties to thermoplastics, thermosets, elastomers and coatings. This revolutionary Nanostructured® Chemical Technology is foundational in nature and possesses broad utility within the consumer products, aerospace, biological, pharmaceutical, agricultural, transportation, and construction industries. At present, Hybrid Plastics offers for sale over 80 different POSS® types including alkyls, olefins, alcohols, esters, anhydrides, acids, amines, imides, epoxies, thiols, sulfonates, fluoroalkyls, silanols, siloxides and POMS® (where a metal is incorporated into the cage structure). As with any new technology, there is a great potential to make advances by judicious use of these products. Because these are new and fundamentally unique molecules, it is not trivial to use them. In order to be successful in exploiting its full potential, one must understand that POSS® behaves differently than conventional additives. We provide this POSS® User's Guide so that companies new to POSS® can get a feeling for what they can expect POSS® to deliver and to give some hints on how to go about making POSS® enhanced products.

Occasionally, companies are able to do this alone. However, we have found that commercialization invariably comes about more quickly and easily when Hybrid Plastics works together with the customer under an NDA to achieve the target performance.

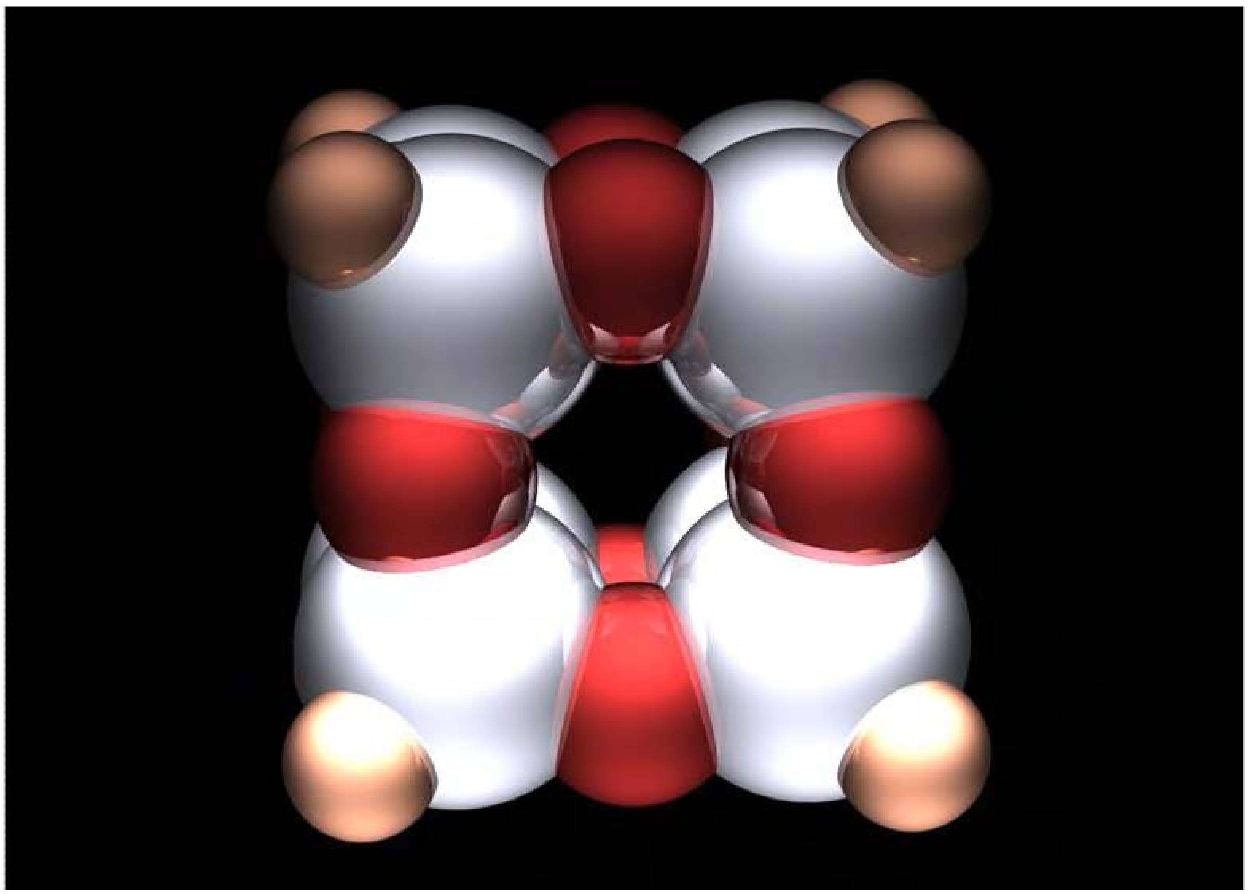


Figure 1 Octahydrido POSS® (SH 1311) showing the POSS® cage with hydrogen at the corners

POSS® Nanostructured® chemicals

The basic POSS® structure can be thought of as a cage of molecular silica comprised of 8 silicon atoms linked together with oxygen atoms. At each of the 8 corners is a substituent which can be just about any chemical group known in organic chemistry. Therefore, there are potentially an unlimited number of POSS® variants. The Hybrid Plastics catalog lists the POSS® compounds which have proven to be of most interest to our customers. Moreover, Hybrid Plastics has a large "tool chest" selection of other, more exotic POSS® types which are not shown in the catalog, that may be used for special applications. These other POSS® compounds may be made available to interested customers under certain circumstances. New POSS® molecules are made frequently and we can even perform custom synthesis under contract.

How to work with Hybrid Plastics

There are two ways to work with Hybrid Plastics' POSS® materials

1. Buy the POSS® directly from Hybrid Plastics or from one of our distributors
2. Develop a tailored solution in conjunction with Hybrid Plastics via an NDA / JDA

The first approach may be preferred in cases where the client wants to try POSS® and get a feeling for what it can do. Perhaps the goal is not yet clearly defined and some preliminary experiments are needed to see what POSS® can offer. When positive results are found, then the company can choose to work with Hybrid Plastics to develop and commercialize the solution.

In the second approach, the company either begins working closely with Hybrid Plastic right from the outset or transitions from the first approach. For example, based on its fundamental and wide ranging understanding of POSS®, Hybrid can often predict whether POSS® is likely to deliver what the client wants. If the match between POSS®'s known effects and the targeted result is very close, then it invariably saves time and money to collaborate early under an NDA. In cases where the goal is not clearly defined, then Hybrid Plastics is quite willing to give advice and let the customer buy POSS® to conduct their own experiments.

The technical staff at Hybrid Plastics hold either a PhD or Masters degree in polymer science. When you contact Hybrid Plastics, you will be working with a dedicated team of scientists and engineers who will assist you to identify where POSS® may be of benefit. If we see no match between POSS® capabilities and your goals then we will tell you so. If, on the other hand, we do see potential to help you then a contact person will be assigned to you. We have extensive equipment onsite for quality control of POSS® and for development work. Current on-site analytical capabilities include:

HPLC – Quality control

GPC – Molecular weight determination and quality control

NMR – R&D and quality control

DSC – Crystallinity, nucleation, Tg, Tm, decomposition, thermoset cure

TGA – Thermal stability, volatility

DMA – Thermo-mechanical characterization

FTIR – Chemical characterization

MALLS (DAWN®) - Light scattering method to determine absolute molecular weights

MFI / MFR – Polymer melt viscosity

Twin-screw extruders – Masterbatching POSS® concentrates in polymers

Injection molding – Preparation of test specimens

Instron – Tensile testing of polymers

Rheometer – Testing of POSS® dispersants and POSS® Flow enhancers

In addition, we have a close collaboration with the highly regarded School of Polymers and High Performance Materials at the University of Southern Mississippi. We have access to their expertise and facilities including multi-nuclear NMR for QC and new product development.

Patent Aspects

Hybrid Plastics owns or controls the basic composition of matter and synthesis patents covering POSS® compounds. Moreover, we hold numerous application patents for specific uses of POSS®. Due to this wide patent coverage, the only source of POSS® for commercial use is Hybrid Plastics. This extensive IP portfolio allows us to support our customers commercializing POSS® in their products.

When does POSS® make sense?

The POSS® family of additives are specialty chemicals. POSS® will never compete on a cost basis with conventional fillers and other commodity additives for the simple reason that the starting materials for making POSS® are relatively expensive. Consequently, POSS® makes sense where there is a specific need for improved performance and the final product or system can bear the cost of high performance additives. In these instances, either the POSS® provides performance levels that cannot be reached in any other way, or the total system cost is acceptable because the POSS® is effective at low usage levels.

Where can I get POSS®?

POSS® may be ordered directly from Hybrid Plastics (www.hybridplastics.com), or from one of our distribution partners, such as Aldrich (www.sigmaaldrich.com), Gelest (www.gelest.com) or Toyota Tsusho (www.toyota-tsusho.com).

What are typical loading levels for POSS®?

There is no universally applicable optimum dosing level. POSS® catalysts or surface treatments may be used in ppm or sub 1% levels, whereas in some applications more than 50 weight % of POSS® is used. Mainly though, we see POSS® being used at 1-10 % by weight. As an indication, for thermosets, elastomers and coatings POSS® is used in the 10-80 weight % range. For thermoplastics between 0.5 and 10 weight % is typical, and for POSS® dispersants 1-5 weight % versus the particles is usual.

How do I disperse POSS®?

Unlike particles, POSS® can actually dissolve if there is proper compatibility between the POSS® and the matrix. For example, many POSS® can be dissolved in common solvents such as THF, acetone, methanol and so forth. Similarly POSS® can molecularly dissolve in polymers and coatings if there is a good match between the polarity of the POSS® and the medium. An indication of likely solubility can be determined using the Solubility Parameter concept as described in books such as the Polymer Handbook or Properties of Polymers by Van Krevelen. Naturally, as the POSS® is dissolved to give 1-2nm entities, the material remains transparent as the POSS® is too small to scatter visible light.

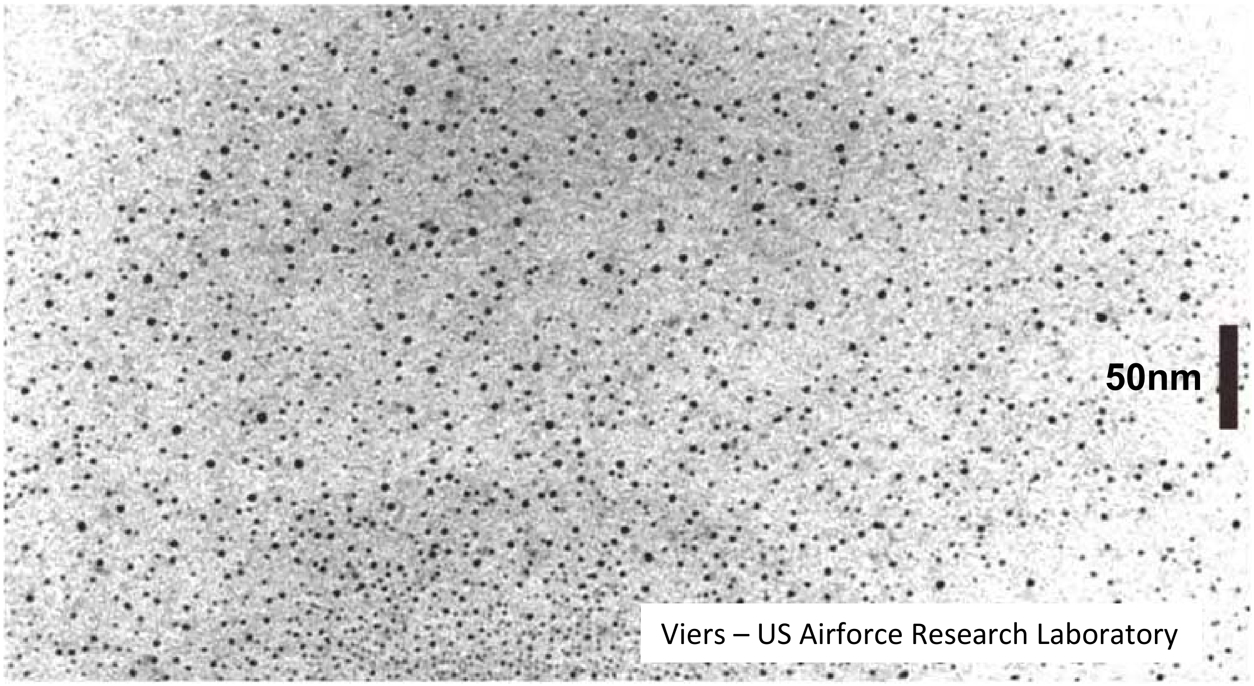


Figure 2 POSS® molecularly dissolved in PP, each black dot is a 1.5nm POSS® cage

If the polarity of the POSS® and the matrix do match exactly, then the POSS® will form domains in the polymer or coating. For mixtures that are almost miscible the domains will be nanoscopic, becoming microscopic for even less compatible mixtures. The less compatible the POSS® is with the formulation, the more mixing energy will be needed. Normally, POSS® can be dispersed using a high speed mixer (coatings, thermosets) or a twin screw extruder (thermoplastics). For customers who prefer the POSS® predispersed, we provide POSS® masterbatch concentrates.

Will the POSS® be abrasive to processing equipment?

Mineral fillers can be abrasive to processing equipment. Softer fillers like talc and calcium carbonate with low Mohs hardness do not cause problems. In contrast, harder fillers, especially silica and glass fiber can cause serious problems over time. A rule of thumb is that wear on standard steel occurs when the filler has a Mohs hardness over 4. As POSS® contains a silica cage, one might fear that there could be an abrasion problem but in reality this is not the case. The Mohs hardness of POSS is approximately 1, like talc, and so there is no abrasive wear on metal processing equipment. We run POSS® at high concentrations through our extruder all the time and there has been zero wear caused by the POSS®.

What physical form is the POSS® provided in?

Most POSS® are solid white powders and some are colorless liquids. It is important to note that the powders are not nanopowders, but rather micron sized agglomerates typically in the 1-100 micron range. The nanoscopic dimensions of the POSS® are only obtained once it is dispersed in the plastic, rubber or coating. Like all additives, proper dispersion is the key to good performance so Hybrid Plastics delivers concentrates of POSS® predispersed in polymer to form masterbatches. Masterbatches of POSS® in generic thermoplastic grades are available. We are also able to compound the POSS® into polymer supplied by our customers.

Figure 3 POSS® Solid, grease and oil

Safety and bulk availability

Several of the larger production volume POSS® types are TSCA listed. POSS® are not nanoparticles. POSS® are molecules that have melting points, boiling points and, unlike particles, POSS® can dissolve spontaneously in solvents.

Regarding toxicity testing, all results so far, both in the USA and in Europe, have shown that acute oral toxicity of POSS® is in the lowest possible category. Testing is underway on other some POSS® types.

Octaisobutyl POSS® MS0825	US	Category IV Oral LD50 > 5000 mg/kg (highest US method dose)
Octamethyl POSS® MS0830	EU	Oral LD50 > 2000 mg/kg (highest EU method dose)
Dodecaphenyl POSS® MS0802	EU	Oral LD50 > 2000 mg/kg (highest EU method dose)

Does **not** require the risk phrase R22 "Harmful if Swallowed."

POSS® Compounds	Bulk Production Status	TSCA Approval Status
MS0802	Confirmed	Registered and approved
MS0805	Confirmed	Registered and approved
MS0825	Confirmed	Registered and approved
MS0830	Confirmed	Registered and approved
SO1450	Confirmed	Registered and approved
SO1455	Ramp-up phase	
SO1458	Confirmed	LVE accepted, PMN pending
MA0735	Ramp-up phase	In progress
EP0408	Ramp-up phase	In progress
EP0409	Confirmed	Registered and approved
OL1160	Ramp-up phase	In progress
AM0265	Ramp-up phase	Registered and approved
AM0275	Ramp-up phase	Registered and approved

LVE – Low volume exemption, PMN – Premanufacture notice

Can we ship POSS® to your location?

We ship R&D samples of POSS® globally, to just about every country in the world. The only exception is that we do not ship to India. Customers in India can order through Aldrich.

Are there price breaks for larger orders of POSS®?

Prices listed in the R&D catalogue apply only to small orders and are not at all indicative of pricing for commercial amounts. Pricing on commercial orders is subject to volume discounts. As an example, bulk orders of the less expensive POSS types may see pricing as low as $30-50 / lb (around €50 / kg).

Can Hybrid Plastics supply large quantities of POSS®?

We make POSS® at our Mississippi manufacturing facility with capacity in the hundreds of metric tons per year range for neat POSS® and far larger capacity for masterbatches. Several products have already been scaled-up and others are presently in the scale-up process. If you require large quantities please contact us for availability and pricing.

Does Hybrid Plastics provide free samples of POSS®?

Company policy is to not provide free samples.

How long has Hybrid Plastics been in business?

Hybrid Plastics is a spin-off from the US Air Force Research Laboratory at Edwards Air Force Base, California. The company was founded in 1998 and relocated its headquarters and principal manufacturing facility to Hattiesburg, Mississippi in 2004.

Figure 4 The Hybrid Plastics Offices, Laboratories and Production Facility in Mississippi USA

POSS® in Thermoplastics

The following comments are applicable to unreactive POSS® compounded into thermoplastics where there is no chemical bond between the POSS® and the polymer chain. If the POSS® is reacted with the polymer then the property changes are akin to those summarized below for thermosetting systems.

Modulus

Solid POSS® types have a high modulus (around 10GPa) and thus increase the modulus of polymers. Liquid POSS® can act as an antiplasticiser, thus at low addition levels (5 weight%) the modulus increases and then decreases progressively as more POSS® is added.

Yield Strength

POSS® is neutral with respect to yield strength.

Impact resistance

POSS® leaves impact resistance unchanged or improved especially in intrinsically brittle polymers.

Elongation to Break

In some cases, POSS® improves elongation to break.

Melt Flow

POSS® can give marked improvements in melt flow. In particular POSS® can be used in high temperature polymers to improve their processability. In the case of PPO/PPE, the polymer is not melt processable without addition of POSS®. For other polymers, like COC, addition of POSS® allows injection molding of very intricate, thin-walled parts without defects. Multi-functional, reactive POSS® can rebuild molecular weight and increase viscosity, an example would be octa-epoxy POSS® in polyesters. See our commercial POSS® Flow additives.

HDT / Vicat

POSS® does not directly affect HDT but may affect it indirectly through changes in crystallinity.

Friction

POSS® can be used to lower the coefficient of friction by as much as 70% by adding 10 weight % POSS® to PP resin. The effect is also apparent in nylon and should apply to a wide range of polymers. Other friction reducing aids are well-known in the marketplace, however they lead to loss in transparency in the polymer. POSS® can reduce friction while retaining transparency. Mold release is also improved.

Color

Several cases have been noted where POSS® reduces or totally removes color from a polymer. Probably the most impressive example is the recently reported manufacture of colorless polyimide using POSS®. The colorless polyimide, named Corin XLS Polyimide is shown on our web site. The color of PPO/PPE is also reduced markedly.

Permeability

POSS® is used commercially to tune the permeability of polymers. POSS® may increase or decrease permeability to a moderate degree. There is some data to suggest that POSS® gives films with selective permeability to different gases.

POSS® in Thermosetting Polymers

The following comments are applicable to reactive POSS® compounded into thermosets where there is a chemical bond between the POSS® and the polymer chain. If the POSS® is not reacted with the polymer, then the property changes are akin to those summarized above for thermoplastic systems.

Modulus

POSS® is neutral with respect to room temperature modulus. POSS® gives significant enhancement of high temperature modulus (see HDT / Upper use temperature) because the modulus of the cage is constant upon heating whereas polymers soften.

Impact resistance

POSS® leaves impact resistance unchanged or improved especially in intrinsically brittle polymers.

Elongation to Break

In some cases, POSS® improves elongation to break.

Viscosity

Addition of low viscosity POSS® may improve resin flow and aid fiber wet-out in composites. Fibre wet-out is essential in order to prevent voids that weaken the material.

HDT / Upper use temperature

POSS® can result in a large improvement in heat distortion temperature (HDT) & Vicat. For example, in the case of epoxy or BMI resins, addition of POSS® extended the Tg of the polymer to near the decomposition temperature. As a result, the maximum usage temperature of the polymers was greatly extended because the modulus and strength was retained even at very high temperatures.

Friction

POSS® can be used to lower the coefficient of friction by as much as 70% by adding 10 weight % POSS® to PP resin. This is expected to work in thermosetting resins as well. Other friction reducing aids are well-known in the marketplace, however they lead to loss in transparency in the polymer. POSS® can reduce friction while retaining transparency.

Color

Several cases have been noted where POSS® reduces or totally removes color from a polymer. Probably the most impressive example is the recently reported manufacture of colorless polyimide using POSS®.

Chemical resistance

The POSS® cage is very robust against chemical attack and can withstand strong acids and alkali for long periods. For example molecular silicas (MS series products) can withstand 2M $NaOH(aq)$ for at least 10 days without degradation. Acid resistance is even better. POSS® trisilanols (SO series products) are somewhat less resistant to hydrolysis. Adding POSS® decreases water uptake, solvent swelling and improves corrosion resistance.

POSS® in Cross-linked Elastomers / Rubbers

The following comments are applicable to reactive POSS® compounded into elastomers where there is a chemical bond between the POSS® and the polymer chain.

Modulus

POSS® increases the modulus of elastomers due to the stiffness of the cage and the high cross-link densities attainable using polyfunctional POSS cross-linkers.

Yield Strength

POSS® is neutral with respect to yield strength.

Impact resistance

POSS® leaves impact resistance unchanged.

Elongation to Break

POSS® is neutral on elongation to break.

Melt Flow

POSS® may increase the viscosity somewhat but not enough to cause problems in handling.

Curing time

Especially when there are several, highly reactive groups on the POSS®, the POSS® will act as a multifunctional cross-linker. This increases cure speed and results in a higher final cross-link density.

HDT / Vicat

HDT is not applicable to elastomers as they are already above Tg.

Friction

Neutral effect on friction unless fluorinated POSS® is used.

Color

Several cases have been noted where POSS® reduces or totally removes color from a polymer.

Permeability

POSS® is used commercially to tune the permeability of polymers. In elastomers, POSS® generally decreases permeability. The POSS® acts as a nano, spherical and non-permeable filler so reductions in permeability are limited.

Solvent resistance / swelling

Polymers swell when exposed to plasticizers and solvents. In contrast, the POSS® cage cannot swell because it has a fixed conformation and size. Therefore, when bound into an elastomer, POSS® replaces the swellable elastomer with non-swellable POSS®. The net result is a dramatic reduction in swelling. This is essential for o-rings and seals. As an example, a silicone elastomer swells by 22% when exposed to acetone for four days. The same elastomer with 70 weight % bound POSS® swells by less than 6%.

POSS® in Coatings

POSS® has been formulated into several different types of coatings. Due to its high molecular weight, POSS® does not contribute to VOC emissions. The high functionality, up to 8 reactive groups per POSS® moiety, means that high cross-link densities can be attained. Varying the type of side groups on the POSS® gives true molecular solubility of the POSS® in the coating formulation. As the POSS® is only 1-3 nm in diameter there is no loss of transparency as long as the POSS® is dissolved.

Solid POSS® types have sharp melting points and this may be used to advantage in coatings. As an example, low temperature cure powder coatings for wood or plastic can be made. The POSS® is a solid powder at room temperature but needs to flow well when heated to 100°C. This is achievable by choosing a POSS® that melts at the right temperature range.

Advantages of POSS® in coatings include improved hardness, scratch resistance, reduced friction and reduced color. Another important advantage is increased chemical & solvent resistance.

A new colorless polyimide coating containing POSS® is available under the Corin™ XLS brandname. See our web site and the POSS® Thermosets Brochure for more information on Corin™ XLS.

Another exciting new product is Short-Stop™ conformal coating which is specifically designed to mitigate tin-whiskers that are formed when lead-free solders are used. The patented active ingredient is a POSS® thiol that is able to bind to the solder surface and pin whisker growth. The product has a dual action as the POSS® slows whisker formation and the polymer coating inhibits whisker growth.

Examples of POSS® Enhancement

The first part of this guide was a brief overview to give a flavor of what POSS® is, what it can do and how Hybrid Plastics works with customers to commercialize new POSS® enhanced materials. Examples were left out in order to keep the overview concise. This section provides data to exemplify the claims presented in the overview.

Hybrid Properties

POSS® allows the creation of materials exhibiting hybrid properties. The silica core of the POSS® is inert and rigid whereas the surrounding organic groups provide compatibility with the matrix and processability. Conceptually, POSS® may be thought of as an organic-inorganic hybrid (Figure 5).

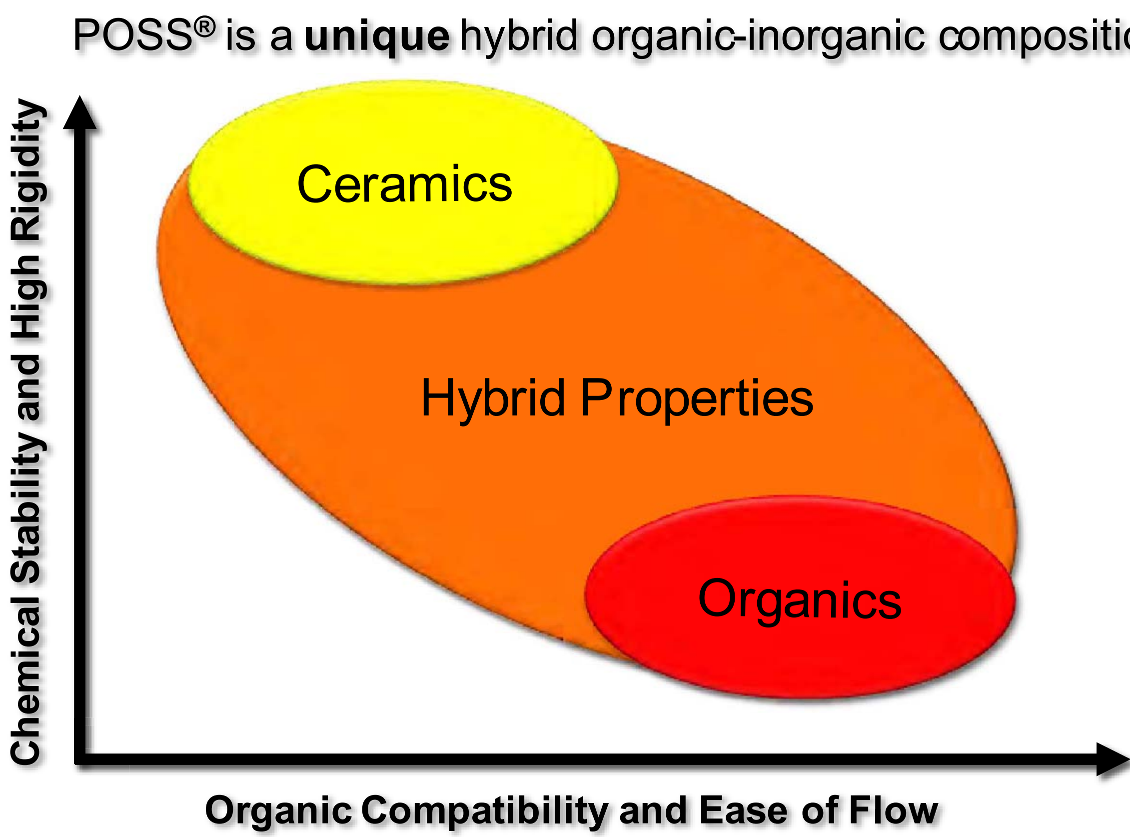


Figure 5 The hybrid nature of POSS® give rise to materials with hybrid properties

Similarly, POSS® is sometimes considered to be a filler and sometimes a molecule. For example, POSS® is rigid and inert like inorganic fillers, but unlike those conventional fillers, POSS® can molecularly dissolve in a polymer. Normal fillers and especially nanofillers suffer from agglomeration. The agglomerates formed when using conventional fillers lead to weak points in the polymer (stress concentrations) and this gives poor impact resistance and elongation to break. As a molecule, POSS® dissolves in polymer as 1-3nm cages and this gives performance advantages not seen with fillers.

When normal organic molecules are added to a polymer they act as plasticizers, reducing modulus, yield strength and HDT / Vicat softening temperature. Due to the rigid (high modulus) silica cage structure, POSS® addition does not have a detrimental effect on modulus and normally we see retention of yield strength. The modulus of octacyclohexyl POSS® has been calculated as 10-12 GPa. Polymers are normally 1-3GPa and mineral fillers 15-40 GPa.

Dissolving POSS® in Polymers

As mentioned, POSS® can dissolve in polymers under the right circumstances. Not all solvents are miscible. Similarly, not all POSS® types will dissolve into a given polymer. The side groups of the POSS® must be chosen to match the polarity of the polymer. Incorrect choice will lead to phase separation between POSS® and the host matrix (Figure 6).

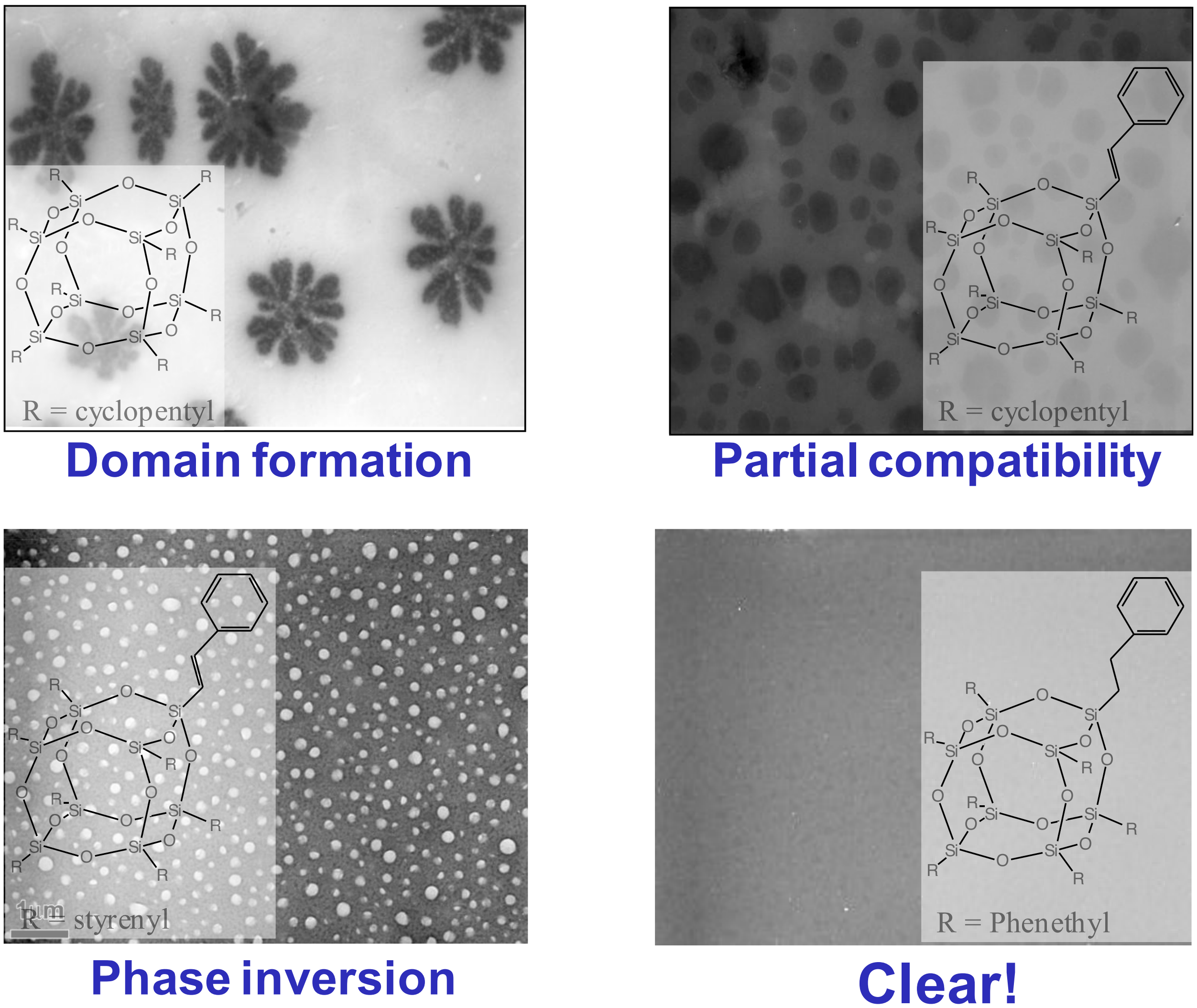


Figure 6 Compatible POSS® types dissolve, incompatible types phase separate

The octa phenethyl POSS® is compatible with the polystyrene resin and dissolves with no phase separation. Because the POSS® is truly compatible, this is the thermodynamically stable state and there are no concerns about agglomeration of the POSS®. This level of dispersion is not possible with nanofillers and nanoparticles.

Reduction of Friction and Flow Improvement using POSS®

There are many well known additives for reducing friction and improving mold release. Simple stearates work well and so do stearamides. More recently, ultra-high molecular weight silicones have entered the market and show promise. The low molecular weight additives are volatile and may degrade at high temperature. The UHMW silicones work well and are not extractable but when used in transparent polymers (PS, SAN, PMMA, PC), they lead to haze because the silicone is present as immiscible droplets in the polymer. Where the conventional friction reducing additives and flow promoters work well enough, they should be used as they are less expensive than POSS®. However, we have several clients who have needed a flow aid or friction reducing additive that is non extractible, highly temperature stable and which does not reduce transparency. In these instances POSS® is a good solution. Reduction in friction has also been demonstrated in nylon and work is ongoing to investigate the effect in other polymers.

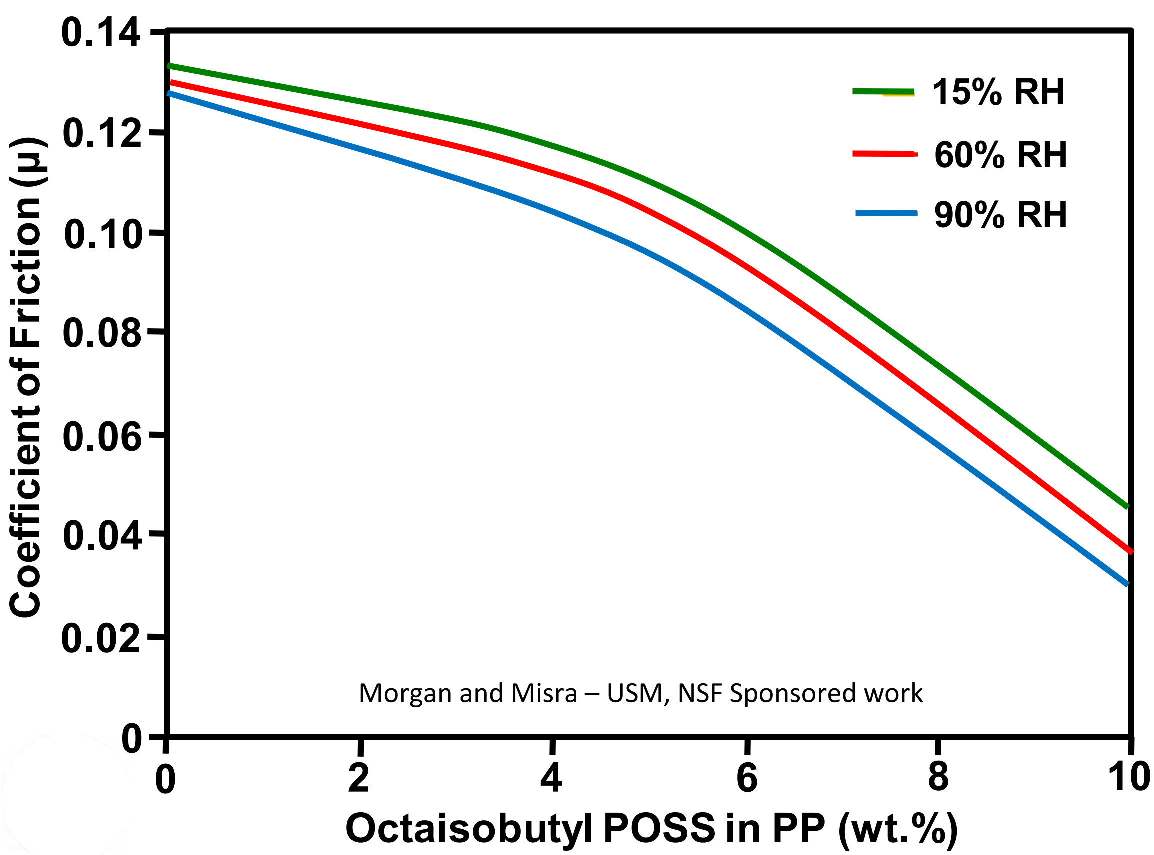


Figure 7 Friction reduction for MS0825 in PP: 3N load 20 minutes at 20rpm

In addition to friction reduction, we also have data to show that POSS® can improve melt flow and mold release in thermoplastics. As an example, cyclic polyolefin flow is improved by addition of POSS® so that very thin walled, delicate parts may be molded without flaws.

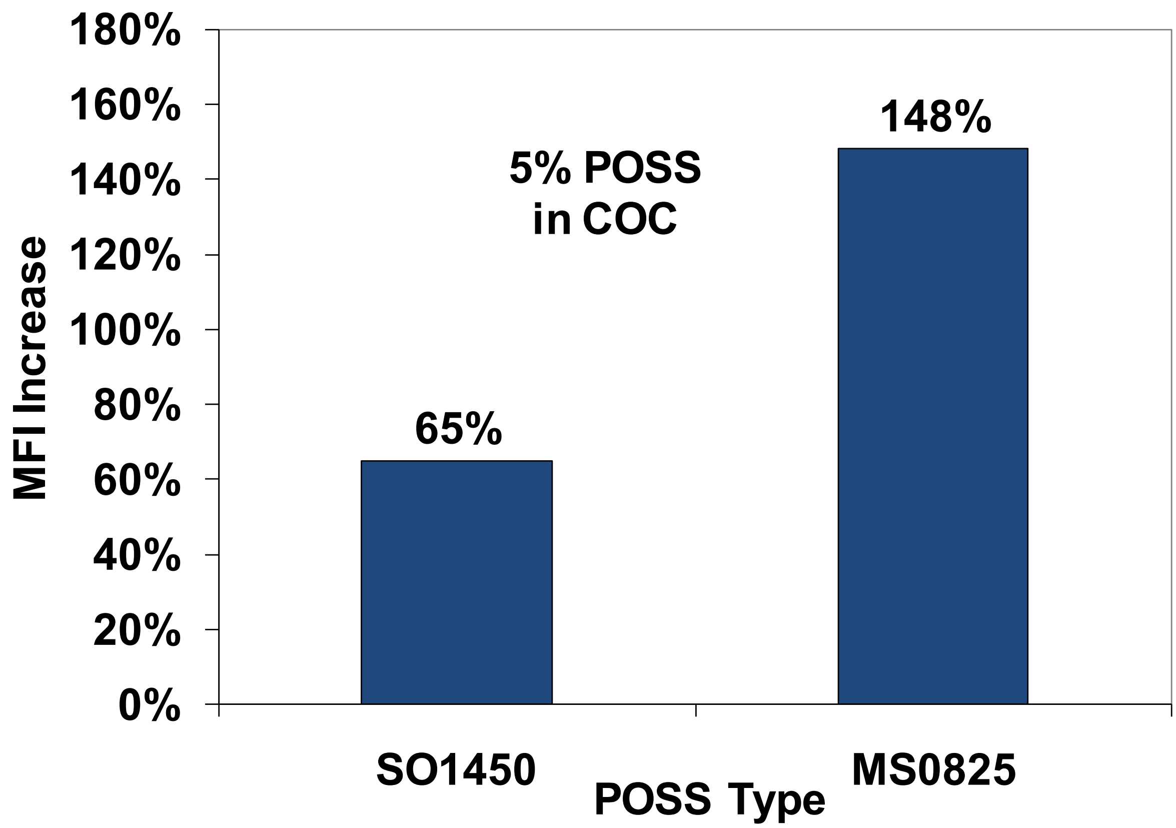


Figure 8 Melt flow enhancement using POSS® in COC (Topas®)

The parts could not be made successfully without POSS® in the formulation. This application of POSS® is in commercial production.

An even more dramatic effect is seen when POSS® is added to PPO (also known as PPE). PPO is a high temperature polymer but has poor processability so it cannot be injection molded. The usual solution is to blend PPO and polystyrene where the polystyrene acts to reduce the melt viscosity. Naturally though, adding polystyrene reduces the HDT / Vicat, so some of the advantage of the PPO is lost. Several different POSS® types were added to PPO (Figure 9). Significant flow enhancements were seen for all types but the POSS® AM0275 (Aminoethylaminopropylheptsisobutyl POSS®) was particularly effective and enabled injection molded parts of neat PPO to be made (results are taken from Asahi Chemical patents).

Ask for information on our POSS® Flow products comprising a series of masterbatches to improve flow of high temperature polymers whilst retaining mechanical properties.

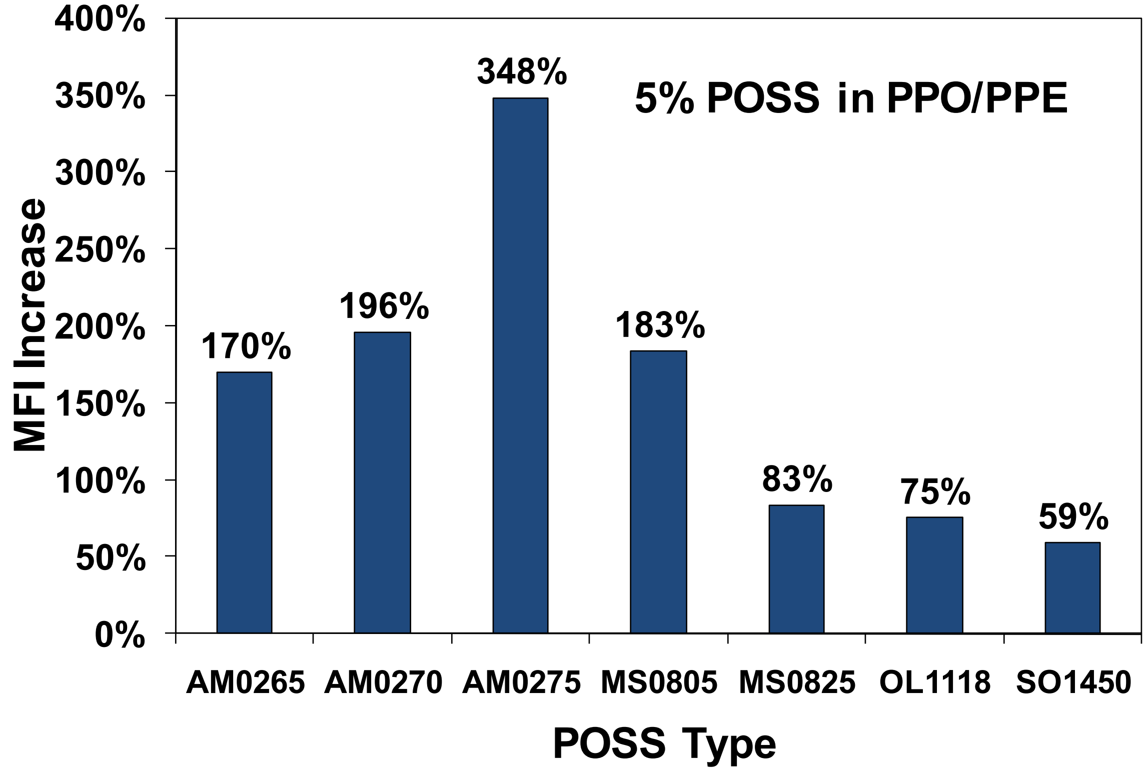


Figure 9 POSS® as a flow aid for PPO/PPE

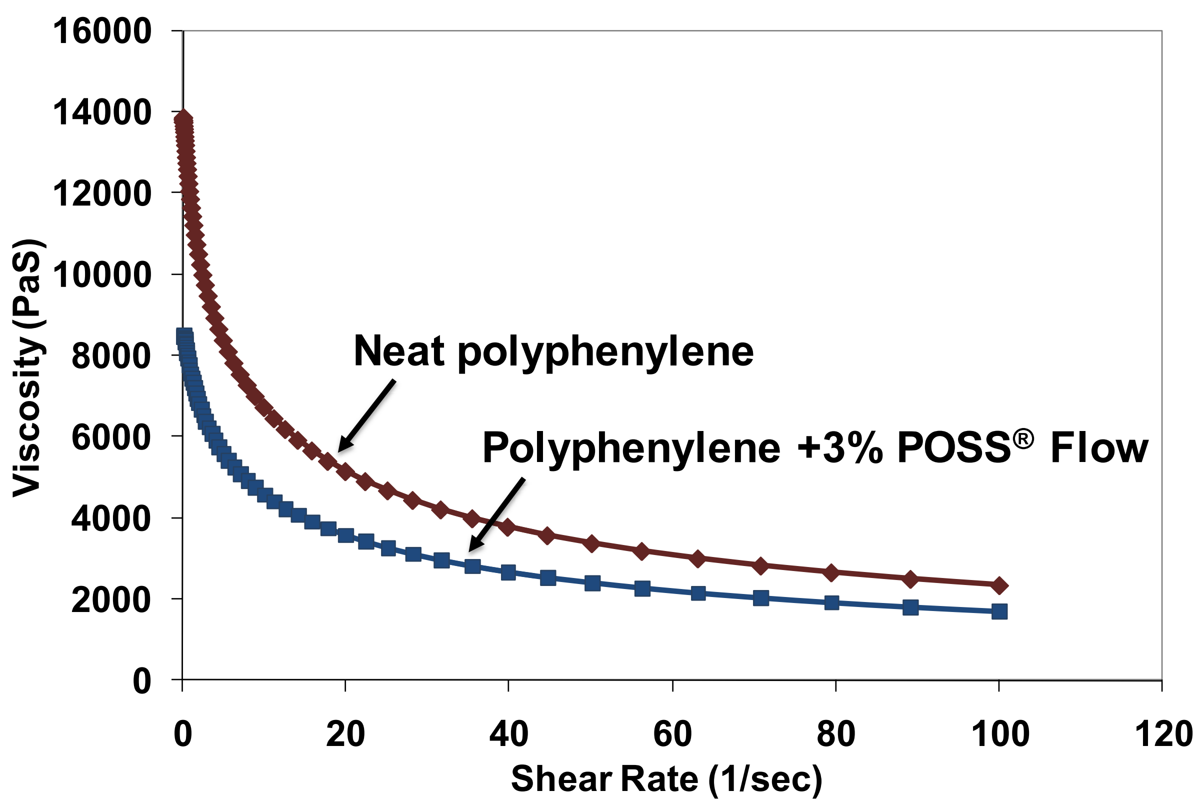


Figure 10 Flow is effective across a range of shear rates

When testing flow aids it is quick and simple to use MFI as a screening method. However, MFI is not an ideal method as it is performed at low shear rates, much lower than those used in typical polymer processing techniques such as extrusion and injection molding. To be sure that the POSS® Flow works at higher shear rates we tested the viscosity using a parallel plate rheometer at 350°C (Figure 10). Clearly the POSS® is able to impart lower viscosity across a range of shear rates and indeed it is found to work well in injection molding and extrusion.

There is ongoing work using POSS® as a flow aid, particularly for high temperature, hard to process polymers. More information can be found in the POSS® Flow Brochure.

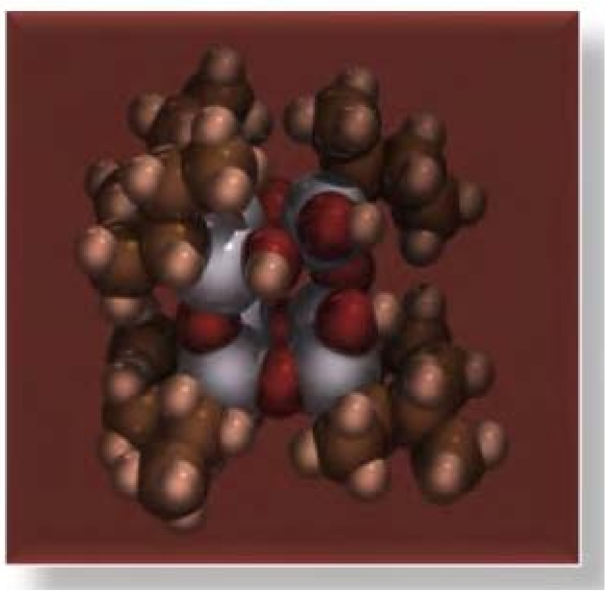
POSS® as Surface Modifiers

Surface active materials are an essential part of everyday life. Surfactants are added in small amounts to aid in cleaning. Minerals are surface treated to provide dispersion in polymers. Primers are used to tune adhesion and corrosion inhibitors are applied to protect metals in harsh environments. Typically, surface modifiers comprise only 1 weight % or less of a formulation but bring big benefits to properties.

POSS® Dispersants for particulates and pigments

It has already been shown that POSS® can be used to reduce friction. As friction is a surface phenomenon, we can deduce that the POSS® is present at the surface. In that instance, the POSS® is not chemically attached to the surface but in other cases, chemical attachment or at least strong adsorption is needed. One example is passivation of metals. Metals are oxidized leading to corrosion. POSS® can be reacted with the M-OH on the surface to provide an inert, protective coating. The reaction of Si-OH groups with M-OH containing surfaces is well documented and is an important reason for the widespread success of organosilane surface treatments. Organosilanes are very useful additives for surface treatment of mineral fillers, especially silicates, for example for treatment of silica used in car tires. However, the organosilanes have well known drawbacks. Firstly they self condense with neighboring organosilane molecules and that reaction competes with reaction onto the metal or filler surface. Another problem is volatile organic compound (VOC) emissions. Organosilanes give off ethanol or methanol as they react and there is increasing environmental pressure to reduce those emissions. Low VOC silanes are just appearing on the market as an attempt to alleviate the VOC problem, but conventional organosilanes with zero VOC do not exist. POSS® trisilanols (Figure 11) react cleanly with the surface and cannot form multilayers. Furthermore, the reaction gives off only water, no VOC at all is created.

Figure 11 Generic structure of a POSS® trisilanol



Such POSS® trisilanols have been shown to be excellent dispersants for nanoparticles. As an example, TiO_2 has been dispersed using this approach. Pigment dispersion is critical to ensure homogeneous color and also because proper dispersion increases tinting strength so that less pigment is need to achieve the desired color. The trisilanol bonds the POSS® to the surface and the –R groups on the POSS® are chosen to be compatible with (similar polarity to) the polymer or coating. Thus alkyl –R groups are suitable for polyolefins like PE, PP and COC whereas for more polar polymers a more polar –R group may be beneficial. For reactive coatings and thermosets, a reactive –R group on the POSS® may be best.

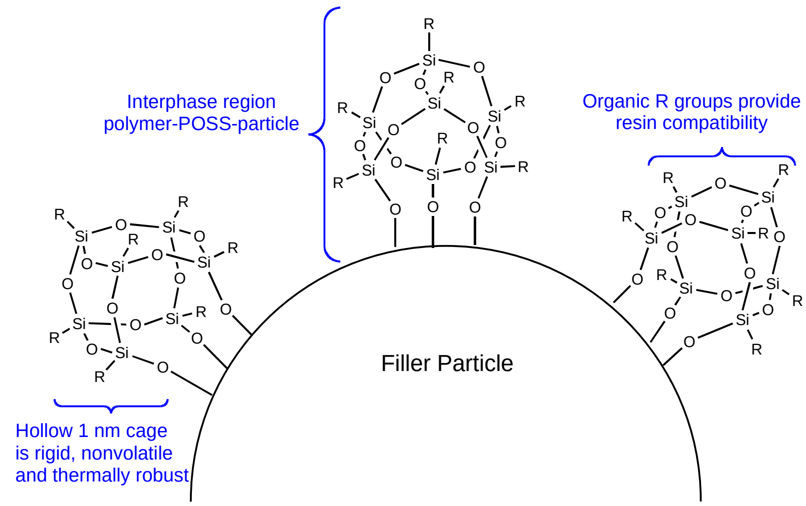


Figure 12 POSS® Trisilanol dispersant bonded to a filler or pigment particle

The dispersion imparted by the POSS® is impressive. The particle size of the TiO_2 is reduced from 100nm down to 30nm. This results in better impact resistance in the pigmented polymer and less TiO_2 is needed to achieve the desired whiteness level.

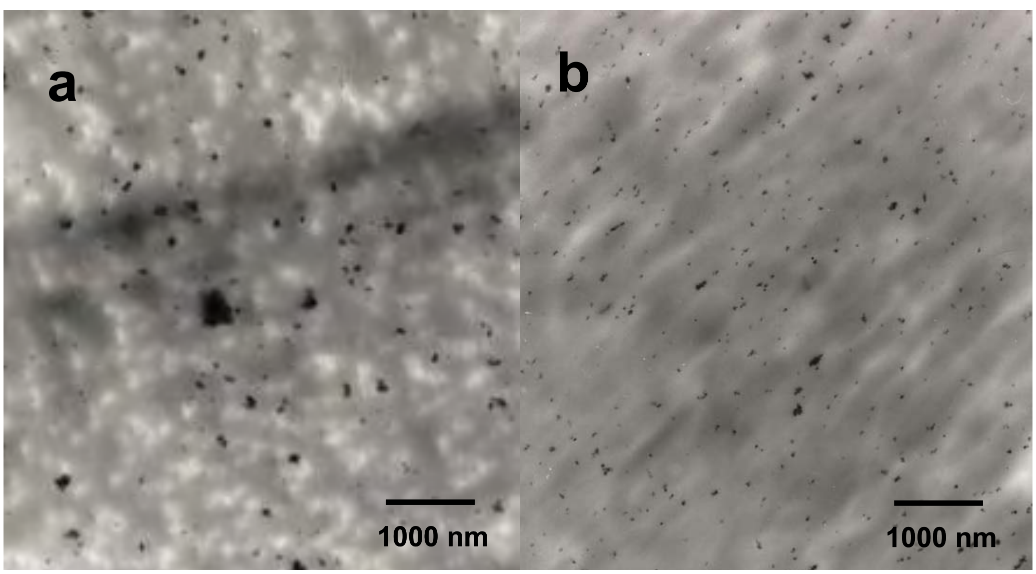


Figure 13 TEM images of TiO_2 in PP a) untreated TiO_2 and b) POSS® treated TiO_2

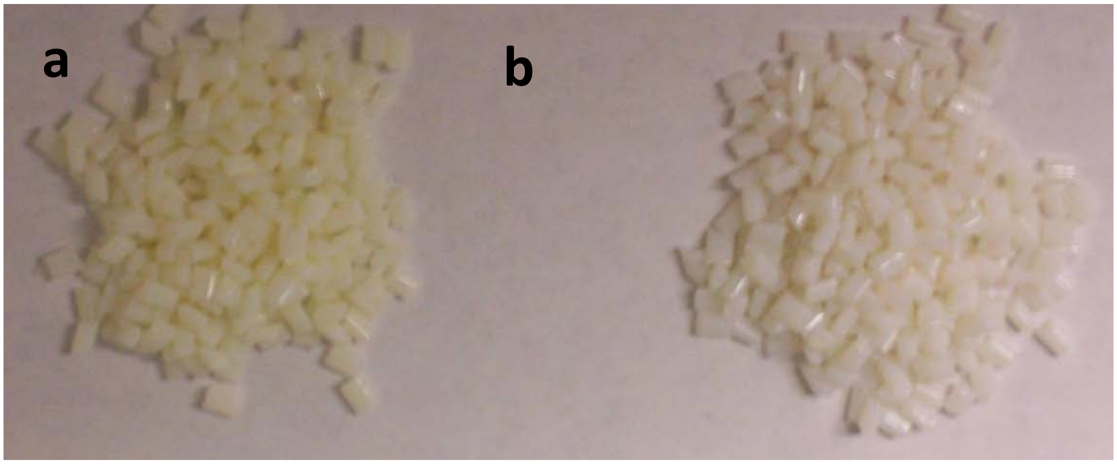


Figure 14 Photograph of TiO_2 in PP a) untreated TiO_2 and b) POSS® treated TiO_2

POSS®® Titania* is sold as a dry white powder and available in R&D, bulk pail and drum sizes.

*This product utilizes Degussa AEROXIDE® TiO_2 P 25 powder. The anatase/rutile ratio is approx. 80:20.

POSS®® Silanols compatibilize many metal, metal oxide, ceramic, and inorganic particles. If you have a different material preference, please inquire at info@hybridplastics.com to see whether we can help.

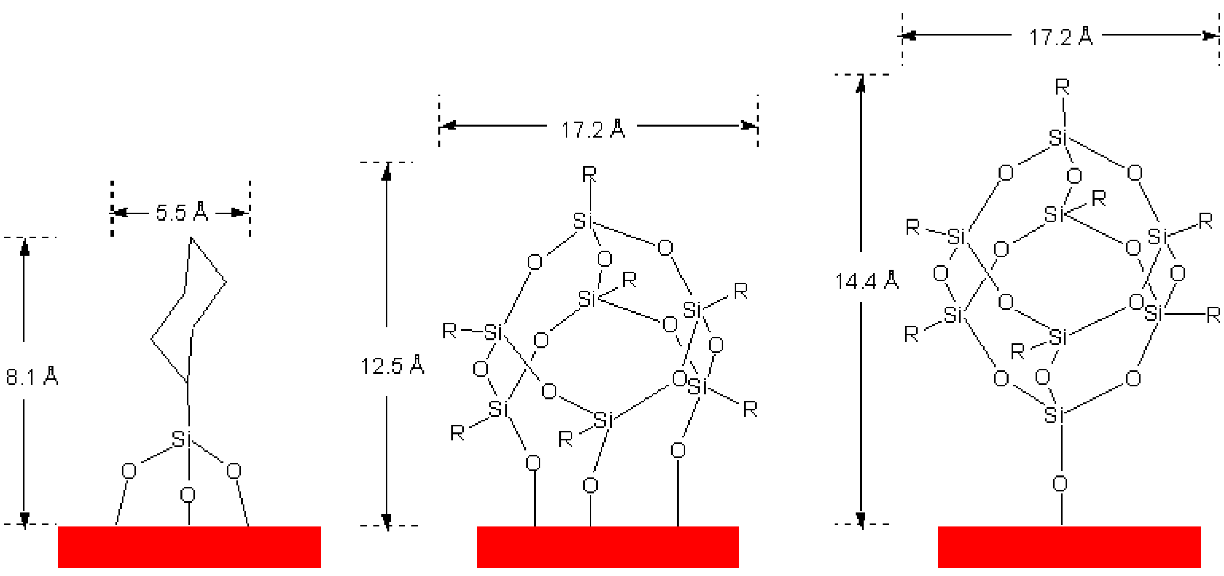


Figure 15 Bonding of POSS® Silanols onto a reactive surface showing the "footprint" area

POSS® to modify wetting behavior – Ultra hydrophobic and ultra oleophobic surfaces

Ultrahydrophobic surfaces occur when a surface has a combination of low surface energy (hydrocarbon) and micro or nanoscopic roughness. Such surfaces exhibit self-cleaning behavior whereby water droplets roll off the surface taking any dirt particles with them. This has been termed the Lotus-Effect, named after the Lotus plant that uses the effect to keep its leaves clean.

Ultraoleophobic surfaces are an extreme example of the above effect where an even lower surface energy surface (e.g. fluorinated hydrocarbon) combined with roughness provides a surface that even oil cannot wet. Such surfaces repel oil and water.

Published data has shown POSS® to be particularly effective in providing the necessary surface energy reduction and roughness.

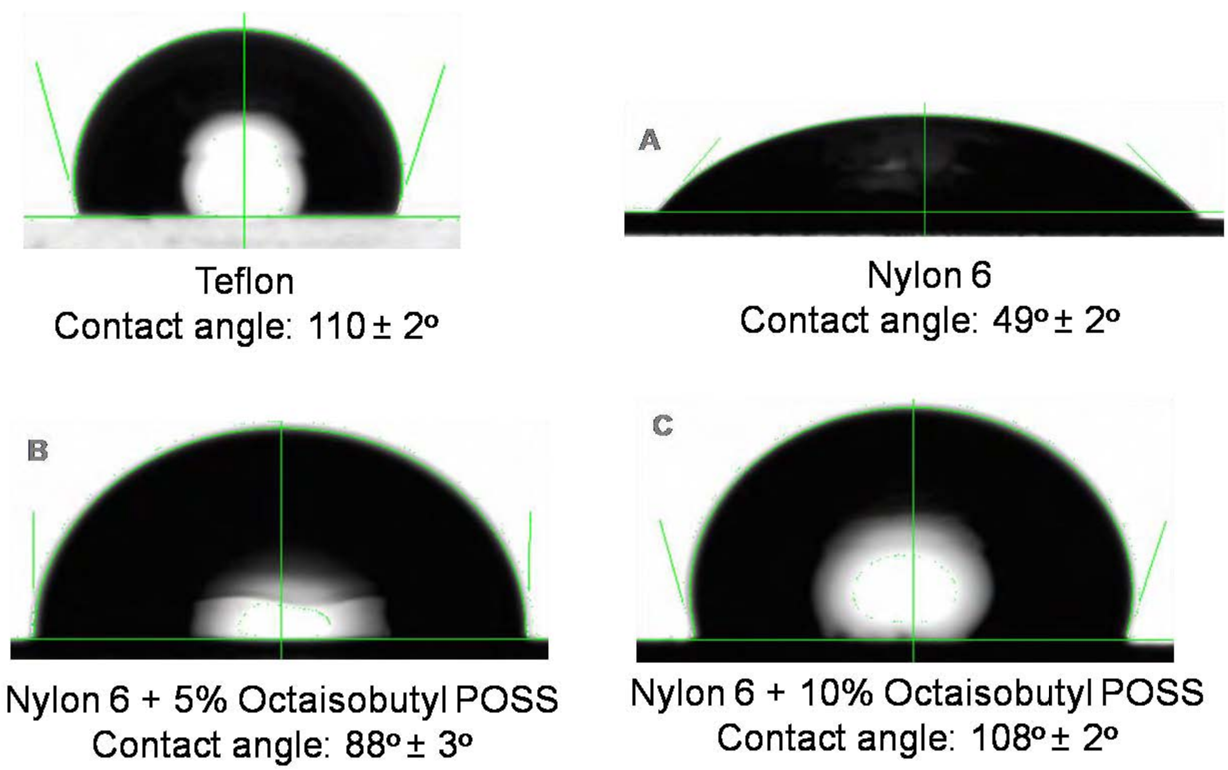


Figure 16 POSS® used to alter wettability of nylon 6

POSS® to Protect and Passivate Metals

We decided to look into POSS® as a surface treatment for metals because metal deactivation is important in various commercial applications such as electrical cables and transformer oils.

A common problem is for products in which copper or other transition metals like iron, vanadium or chromium are in contact with polymers. The metals catalyse degradation of the polymers by promoting decomposition of hydroperoxides in the plastic. Even ppm levels of transition metals have an effect. As an example, copper wires coated with polyethylene degrade rapidly so that they cannot be used without additives to protect the PE from the copper. We tried the POSS® trisilanols as copper deactivators. The concept was that the trisilanol should bond the POSS® firmly to the copper and the rest of the POSS® cage would block the copper surface from reaction.

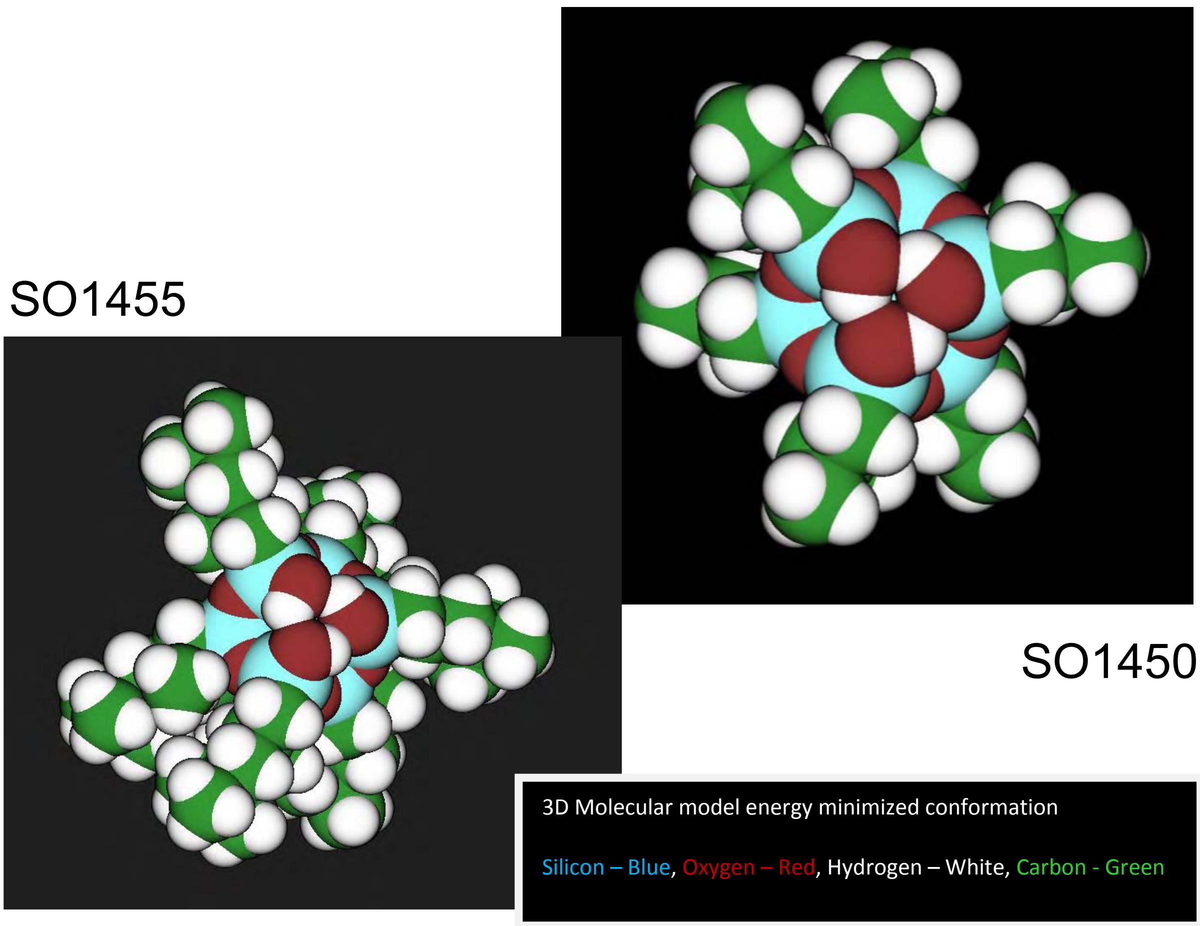


Figure 17 Space-filled Molecular models of POSS® Trisilanols showing availability of the silanol groups

This was checked by oxidation induction time based on the ASTM method D3895-06. The sample is heated in an (inert) aluminium pan under nitrogen using a differential scanning calorimeter (DSC). We chose 190°C as the test temperature. Without additives the sample oxidizes immediately, giving off heat (exothermic) so that the heat flow becomes positive (increase in the y axis direction).

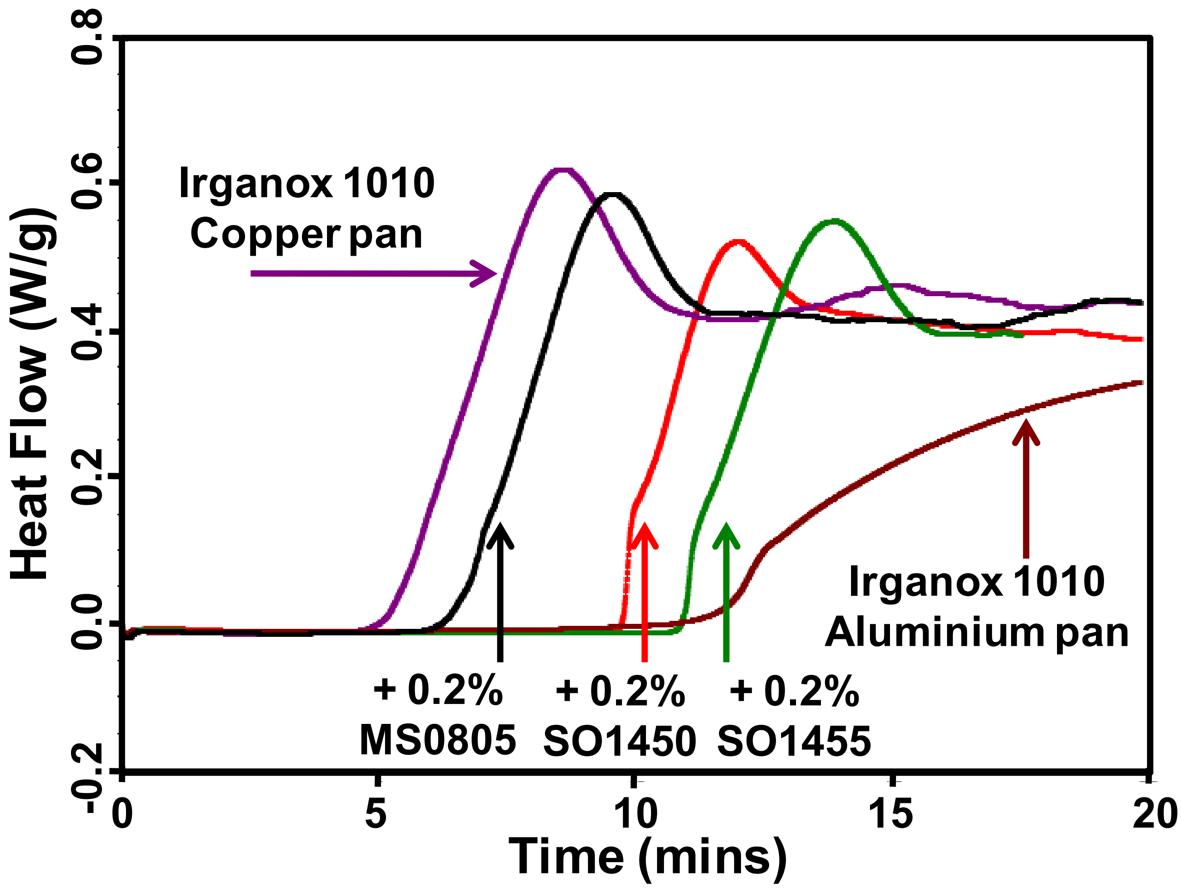


Figure 18 OIT of Squalane hydrocarbon oil stabilized with Irganox 1010 at 190°C by DSC

Adding a hindered phenolic antioxidant, Irganox 1010, increases the stability to 12 minutes on the diagram (Figure 18). However, when the same measurement is run in a copper pan instead of an inert aluminium pan, we see that the exotherm starts at 5 minutes so the copper is destabilizing the system. Adding 200ppm of POSS® SO1450 coats the copper pan and improves the stability to 10 minutes and 200ppm of POSS® SO1455 passivates the copper so well that the result is 12 minutes like it is for the aluminium pan. This means that the POSS® trisilanols bond to the copper and the bonding is so strong that it prevents the POSS® from debonding even at 190°C.

Having established that POSS® trisilanols such as SO1455 are excellent metal deactivators, we decided to benchmark them against an industry standard product. We selected the commonly used Irganox® MD1024 material. We were surprised to find that Irganox® MD1024 is insoluble in squalane (and therefore insolubility is expected in polyolefins). Furthermore, the Irganox® MD1024 failed to function as a metal deactivator in this test.

Due to the encouraging results we are now optimizing the POSS® trisilanols and testing them together with end-users requiring metal deactivation.

Upper use temperature enhancement in thermosets

It is well known that thermosets lose strength and rigidity when heated to their glass transition temperature (Tg). Although the polymer is not chemically degraded, it is no longer able to bear a load and so the polymer or composite cannot be used above Tg. By adding multifunctional POSS® with appropriate chemistry, it is possible to vastly increase the Tg so that the polymer can be used at much higher temperatures.

POSS® in Epoxy Resin

The unmodified epoxy shows typical behavior in that it loses modulus (stiffness) as it is heated near its Tg of 100°C. A composite based on that epoxy would not be useable above ~70°C. In contrast, the epoxy made using EP0409 (octafunctional glycidyl epoxy) retains most of its modulus all the way up to 300°C.

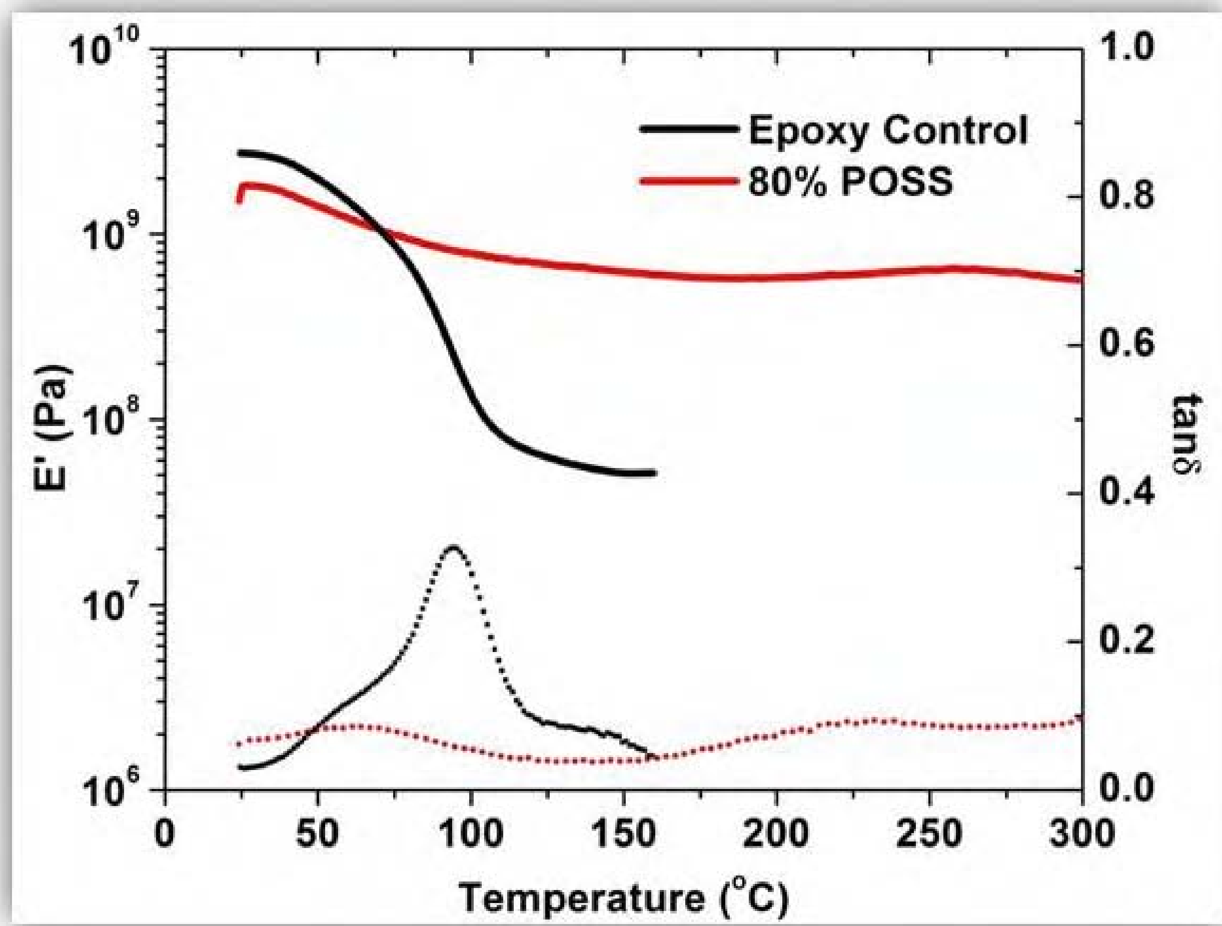


Figure 19 DMA of standard epoxy and POSS® enhanced epoxy

POSS® BMI Resins

Multifunctional POSS® reacts into thermosets to increase cross-link density resulting in composites with very high upper use temperature. This was initially shown in epoxies and more recently the idea was extended to BMI resins. The approach is general and is expected to work for any thermoset as long as the correct POSS® is selected for the cure chemistry in use.

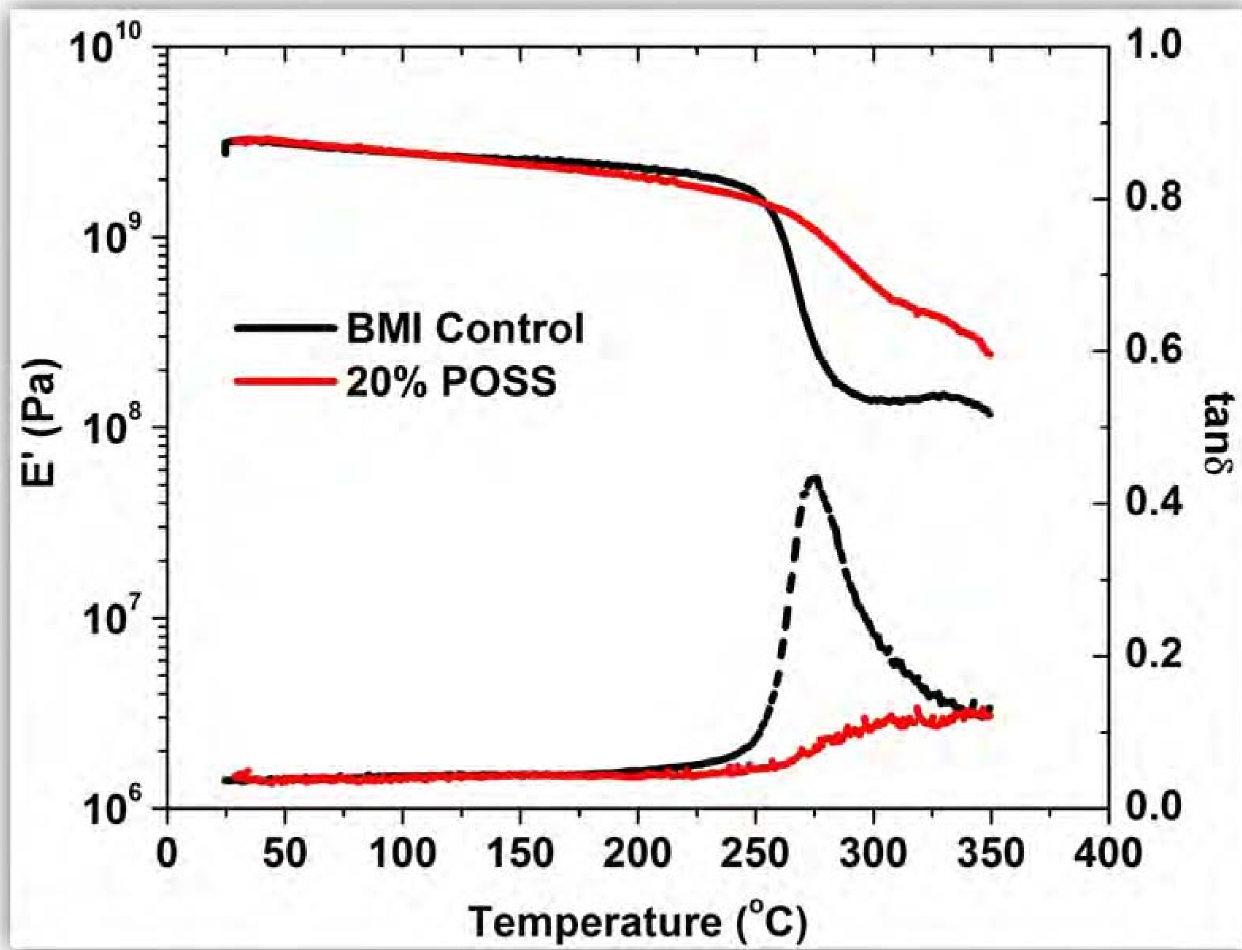


Figure 20 DMA of Standard BMI resin and POSS® enhanced BMI

BMI resins are used in applications with very high temperature requirements. A standard BMI resin softens as its Tg around 275°C. Addition of just 20 weight % of octafunctional epoxy POSS® extends the Tg and thus increases the maximum use temperature. POSS® based cure accelerator can also be added (an aluminium POMS).

More information about POSS® thermosets can be found in the POSS® Thermosets Brochure on our web site.

Commercial Products Using POSS®

So far there are over 800 patents and about 2300 published papers on POSS®. These numbers indicate a very high level of interest in POSS®. The publications reflect academic interest and the patents indicate the level of commercial interest. Commercial applications have increased steadily over the years and we see new applications all the time. Applications are in diverse areas including packaging, dental, aerospace, electronics and adhesives. More information can be found on the Hybrid Plastics homepage.

Future POSS® Enhanced Products

There are some exciting new products on the way. Many are under evaluation and several are close to commercialization on a large scale. Our web site is updated regularly to reflect new developments. Some of the most promising areas for POSS® are expected to be POMS catalysis, POSS® to improve flow of high temperature thermoplastics, reduction of friction while maintaining transparency and POSS® in biological systems, namely to improve soft tissue healing (FibroPOSS®) and bone growth (OsteoPOSS®).

POSS® Data Reference Tables

Over the last decade, Hybrid Plastics has gathered a considerable amount of data on our products. Some information is presented here for the benefit of our customers.

POSS® Density Data

Material Type	Density (gcm^{-3})
Quartz	2.60
Amorphous silica	2.18
SH1311 (octa hydrido)	1.82
MS0830 (octa methyl)	1.50
MS0822 (octa ethyl)	1.33
MS0825 (octa i-butyl)	1.13
MS0805 (octa i-octyl)	1.01
Iso-octane	0.69

Table 1 POSS® density compared to inorganic silica and organic hydrocarbon

Densities have been reported for several POSS® and are generally in the range 1.0-1.2 gcm^{-3}. As the organic component on the POSS® cage increases in size, the density progressively decreases from a very high value for SH1311 to a value more typical of organic compounds for MS0805 (Table 1). Densities for other POSS® compounds are shown here, other POSS® will be added as we collect the data. Customers may also request density data from us.

POSS® Type	Density (gcm^{-3})
SH1311 (octahydrido) - solid	1.82
MS0830 (octamethyl) - solid	1.50
SO1458 (trisilanolphenyl) - solid	1.42
AM0285 (octaammonium) - solid	1.40
OL1160 (octavinyl) - solid	1.38
MS0840 (octaphenyl) - solid	1.35
MS0822 (octaethyl) - solid	1.33
SO1444 (trisilanolethyl) - solid	1.33
AM0273 (aminopropylphenyl) - solid	1.31
SO1460 (tetrasilanolphenyl) - solid	1.31
MS0802 (dodecaphenyl) - solid	1.26
EP0417 (glycidylethyl) - solid	1.25
EP0409 (glycidyl cage mixture) - liquid	1.25
EP0408 (epoxycyclohexyl cage mixture) - semi-solid	1.24
PM1285MV (vinyl silsesquioxane resin) - liquid	1.24
SH1310 (octasilane) - solid	1.23
MS0860 (octaTMA) - solid	1.23
MA0736 (acrylo cage mixture) - liquid	1.23
MA0735 (methacryl cage mixture) - liquid	1.20
AM0281 (N-phenylaminopropyl cage mixture) - liquid	1.20
AM0275 (aminoethylaminopropyl i-butyl) - solid	1.17
EP0402 (epoxycyclohexyl i-butyl) - solid	1.17
MS0813 (phenyl i-butyl) - solid	1.17
AM0265 (aminopropyl i-butyl) - solid	1.16

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

Table 2 POSS® Densities (all value measured by Hybrid Plastics using a pycnometer except, * measured by H. W. Oviatt SwRI)

Refractive Indices

POSS® Type	Refractive Index
SH1311 (octahydrido) - solid	1.51
MS0830 (octamethyl) - solid	1.51
SO1458 (trisilanolphenyl) - solid	1.65
OL1160 (octavinyl) - solid	1.47
MS0840 (octaphenyl) - solid	1.61
MS0822 (octaethyl) - solid	1.50
SO1444 (trisilanolethyl) - solid	1.50
AM0273 (aminopropylphenyl) - solid	1.58
SO1460 (tetrasilanolphenyl) - solid	1.60
MS0802 (dodecaphenyl) - solid	1.56
EP0417 (glycidylethyl) - solid	1.47
EP0409 (glycidyl cage mixture) - liquid	1.51
EP0408 (epoxycyclohexyl cage mixture) - semi-solid	1.52
SH1310 (octasilane) - solid	1.43
MA0736 (acrylo cage mixture) - liquid	1.45
MA0735 (methacryl cage mixture) - liquid	1.46
AM0281 (N-phenylaminopropyl cage mixture) - liquid	1.57
AM0275 (aminoethylaminopropyl i-butyl) - solid	1.50
EP0402 (epoxycyclohexyl i-butyl) - solid	1.50
MS0813 (phenyl i-butyl) - solid	1.50
AM0265 (aminopropyl i-butyl) - solid	1.49

POSS® Type	Refractive Index
MS0865 (octatrimethylsiloxy) - solid	**1.43**
TH1550 (mercaptopropyl i-butyl) - solid	**1.48**
EP0418 (glycidyl i-butyl) - solid	**1.47**
OL1118 (allyl i-butyl) - solid	**1.48**
SO1450 (trisilanol i-butyl) - solid	**1.48**
AL0130 (1,2-propanediol i-butyl) - solid	**1.47**
MA0701 (acrylo i-butyl) - solid	**1.47**
MA0702 (methacryl i-butyl) - solid	**1.47**
SO1450 (trisilanol i-butyl) - solid	**1.48**
OL1123 (monovinyl i-butyl) - solid	**1.46**
OL1163 (octavinyldimethylsilyl) - solid	**1.41**
PG1190 (PEG POSS® cage mixture) - liquid	**1.45**
EP0423 (trisglycidyl i-butyl) - liquid	**1.47**
TH1555 (mercaptopropyl i-octyl) - liquid	**1.47**
MA0719 (methacryl i-octyl) - liquid	**1.45**
AM0270 (aminopropyl i-octyl) - liquid	**1.46**
EP0419 (glycidyl i-octyl) - liquid	**1.45**
MS0805 (i-octyl cage mixture) - liquid	**1.45**
SO1455 (trisilanol i-octyl) - liquid	**1.45**

Table 3 Refractive index for POSS®

Homogeneous materials are transparent. When a material is inhomogeneous it may be transparent or opaque depending upon certain factors. If there are two phases with the same refractive index then the material will still be transparent because the light does not “see” the phases. If there are domains with a different refractive index than the matrix and those domains are smaller than the wavelength of light (~400-800nm in the case of visible light), then the material will still be transparent. If the domains are similar in size to the wavelength of light and have different refractive index to the matrix then light scattering will occur and the material will become opaque. These effects are used to pigment polymers to make them white for example and the opposite is also used commercially, namely that the refractive index of the particles and the matrix are matched on purpose. Examples of the latter are transparent ABS (MABS) and antiblock particles for polymer films.

Properly chosen POSS® will dissolve in the polymer or coating and so the product will be homogeneous with no opacity even if the refractive index of the POSS® is different to that of the continuous phase (matrix polymer or coating). Similarly, if the POSS® chosen is not quite soluble then the domains of POSS® will still be too small to scatter visible light so the material will be transparent. If the POSS® is rather incompatible with the matrix then the domains of POSS® will be large enough to scatter light. The result will be a cloudy, or opaque material. This phenomenon can be used as an easy indication of POSS® compatibility. If the selected POSS® gives opacity then another, more compatible POSS® type should be considered.

Refractive indices give here are calculated based on elemental contribution values from the work of Vogel, published in the Journal of the Chemical Society in 1949. H.W. Oviatt of the Southwest Research Institute proved this method to be effective for POSS as calculated RI values agreed well with measured values for POSS liquids. In most cases we find that the calculated RI and measured values agree within 0.5% and in all cases they agreed within ~1%. Atom contributions were taken from values in the CRC Handbook 68th Edition except for * taken from examining the original Vogel work and the value for Si determined by fitting experimental and calculated RI values. C = 2.591, Cl = 5.844, =S = 7.921, H = 1.028, Br = 8.741, CΞN = 5.459, =O = 2.122, I = 13.954, N primary = 2.376, N secondary = 2.582, -O- = 1.764*, Phenyl = 25.463, Naphthyl = 43.00, -OH = 2.553, -S- = 7.729, Si = 5.10. Those are used to calculate the molar refractivity and from there the refractive index.

For example, for C_2H_5COOH: R_{calc} = 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.

Specific heat capacity

Specific heat capacities for several POSS® were determined by oscillating / modulated DSC. Values were typically in the range 1.8-2.0 $Jg^{-1}K^{-1}$.