

POSS Oxirane and Oxetane Additives for Energy Cure Coatings and Adhesives

*Joseph D. Lichtenhan and Sukhendu B. Hait
Hybrid Plastics Inc. Hattiesburg, MS. USA*

Abstract

Additives that can be utilized at low percentages to expand the performance of existing polymer systems have become a growth area within the specialty chemicals industry. In response to such demand, families of Polyhedral Oligomeric Silsesquioxane (POSS) chemicals were developed. Each POSS cage melds the desirable thermal stability and modulus of inorganic additives ($\text{SiO}_{1.5}$) with organic (R) groups to render compatibility and reactivity with heritage polymers, monomers, and ingredients.

POSS chemicals range in diameter from 1.5-3.0 nm and differ from traditional chemical additives by providing an envelope of effects. The effects are based on the rigidity, surface area, and volume provided by the cage in addition to the traditional compositional and chemical reactivity of the organic groups attached to each of the silicon vertices.¹

The cationic cure chemistry and resulting physical properties for POSS oxirane and oxetane additives are described in this paper. In general POSS oxiranes provide utility toward improving crosslink density, modulus, hardness, optical transparency, and reduction of dielectric properties.

Introduction

Additives that can be utilized at low percentages to expand the performance envelopes of existing polymer systems, have become a growth area within the specialty chemicals industry. In response to the demand for new additives, families of polyhedral oligomeric silsesquioxane (POSS[®]) chemicals were developed. Each POSS cage melds the desirable thermal stability and modulus of inorganic additives ($\text{SiO}_{1.5}$) with organic (R) chemistry to render compatibility and reactivity with heritage polymers, resins, monomers and ingredients. For cationic coatings, epoxy cyclohexylethyl POSS and glycidylpropyl POSS find increasing use in cationic cured formulations that require high hardness and modulus.

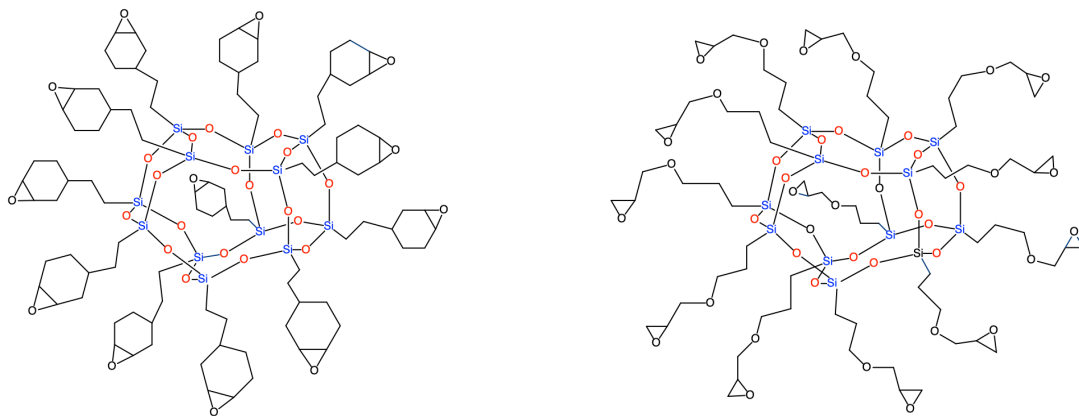


Figure 1. Structural representations of epoxy cyclohexylethyl POSS (CPOSS) and glycidylpropyl POSS (GPOSS).

Representative structures for oxirane POSS are shown in Figure 1. While dodecameric cage sizes are shown, the interior SiO_{1.5} cage sizes vary from octamer, decamer, and dodecamer. The utilization of a cage size distribution renders a melting point depression that allows these additives to exist as clear, low viscosity liquids. Both of these oxirane POSS additive molecules are highly miscible with nearly all conventional coating resins, oligomers and monomers. They are also soluble in solvents, and are routinely characterized by GPC, HPLC, NMR. A summary of their inherent physical properties, toxicology, and regulatory information has been tabulated in Table 1.

Table 1. Physical, Chemical, and Safety Properties of POSS Oxiranes.

	Epoxy cyclohexylethyl POSS	Glycidylpropyl POSS
Appearance	Clear colorless liquid	Clear, pale yellow, liquid
Composition	(C ₈ H ₁₃ O) _n (SiO _{1.5}) _n	(C ₆ H ₁₁ O ₂) _n (SiO _{1.5}) _n
Formula Weight	1418.20	1337.88
Viscosity	500 poise @ 60 °C	48 poise @ 25 °C
Density	1.24 g/ml	1.25 g/ml
Refractive Index	1.52	1.51
UV Sorption	200-300 nm	200-300 nm
EEW	177	167
CASRN	1213770-19-4	68611-45-0
Oral Toxicity	Category IV, LD ₅₀ > 5g/kg	Category IV, LD ₅₀ > 5g/kg
Skin Contact	Non-irritant	Non-irritant
AMES	Non-mutagenic	Non-mutagenic
OEDC 471	Non-mutagenic	Non-mutagenic

POSS chemicals differ from traditional chemical additives by providing an envelope of effects in coatings. The envelope of effects are based on the composition, rigidity, surface area, volume, and chemical reactivity of the POSS additive.

Unique Attributes of Oxirane POSS that Lead to Enhanced Coatings

Attribute 1.

The modulus of the POSS cage is unique and rigid at 11.7 GPa.² The silicon-oxygen core is also mechanically³ and thermally durable⁴. In formulatory work, the addition of POSS additives can impart stiffness (modulus) and hardness. Thus, it is often recommended to formulate POSS with flexible comonomers/oligomers to counter any undesirable modulus build.

Attribute 2.

The crosslinking capability of these additives leads to rapid gelation and increased modulus and hardness. When high degrees of cure-conversion are achieved the glass transition will also increase. However when lower degrees of conversion are reached any nonreacted arms on the POSS cages can serve as internal plasticizers. Local plasticization and depression of glass transition can result from nonreacted arms on the cage. POSS cages do not provide the same level of hardness as wholly inorganic additives. However, they can be utilized synergistically with fillers to impart additional hardness, reinforcement, and durability.⁵

Attribute 3.

The rigid central cage core in combination with the long reactive external arms renders external molecular diameters in the range of 1.5-3.0 nm. These large diameters enable POSS additives to provide surface area control and extensive contact with other ingredients in a formulation. In this respect POSS additives often serve as compatibilizers between ingredients and dissimilar formulation components.⁶

Attribute 4.

The large diameter of POSS enables these additives to provide volume control inside of formulations. When well dispersed into amorphous polymers, POSS additives reside in the amorphous region of the polymer and tend to increase the spacing between polymer chains. The increased volume provides improved rheological properties⁷ (a diluent-like effect) and the volume control also results in modest improvements of toughness and impact properties⁸. Additionally, when associated to filler and ingredient surfaces, POSS cages improve their dispersion and effectiveness.⁹

Attribute 5.

Finally, the hybrid organic-inorganic composition of POSS enables formulations containing it to undergo surface glassification. Surface oxidation is common in many processes as a method to provide enhanced adhesion, bonding, and printability. The methods include: oxygen plasma etching, corona treatment, short wavelength UV, ozone, and flame treatment. For POSS and from a chemistry perspective, the oxidation process involves the removal of organic groups from the cage and subsequent fusing of the cages together (similar to sintering) to form a low density surface glass layer. The resulting surface glass layer is nanoscopically thin and while not abrasion resistant, it does improve harness, scuff and mar resistance. The surface glassification of POSS can also serve as an ideal bondable tie layer between coatings.¹⁰

Experimental

Materials and Methods

All component weights are based on final resin weight. The POSS monomers (epoxycyclohexylethyl POSS EP0408 (A), and glycidylpropyl POSS EP0409 (B)) were provided by Hybrid Plastics Inc. and used as received. The oxetane monomers 3-ethyl-3-oxetanemethanol S-101, and 3-ethyl-3-[[3-ethyloxetane-3-yl)methoxy]methyl]oxetane S-221 and the photoinitiator which was a mixed type triarylsulfonium hexafluoroantimonate salts ((thiodi-4,1-phenylene)-bis-(diphenylbis)(OC-6,11)hexafluoroantimonate, and diphenyl[4-(phenylthio)phenyl]sulfonium hexafluoroantimonate) Syna 6976 were purchased from Synasia and used as received. The 20 nm silica (MEK-ST-U) was purchased from Nissan Chemical Co and used as received.

To prepare a coating solution for UV application, 0.06% (w/w) of the photoinitiator was added to each POSS or POSS oxetane formulation. The mixture was stirred and allowed to stand 12 hours under dark conditions prior to exposure to UV. Cationic cure was carried out by a 3 second exposure at a 5 cm distance from a Fusion D bulb (300 WPI) controlled by a Fusion P300 System. Pencil hardness measurements were carried out according to the ASTM D3363 protocol.

Results

As energy cured oxirane systems continue to undergo development and commercial adoption, formulators are increasingly utilizing oxetanes in combination with oxiranes as a means to tailor properties. Oxetane cure also utilizes a cationic mechanism as they possess ring strain and are

structurally similar to epoxy (oxirane) groups. To facilitate formulation of cationic cure coatings, concentrates of CPOSS and GPOSS were formulated with two common mono-oxetane and bis-oxetane monomers (Figure 2).

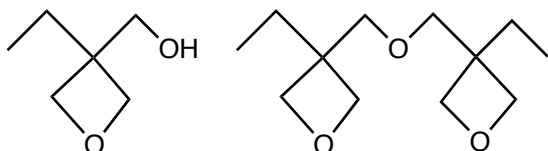


Figure 2. Mono- and bis-oxetanes formulated with POSS oxiranes.

Plaques of 2-3 mm thickness were cured to demonstrate both the depth of cure and optical transparency of each formulation. All the resulting plaques were optically clear. As expected, the speed to reach non-tackiness was fastest for formulations containing the CPOSS. Especially fast cure was observed for the 25% CPOSS + 75% bis-oxetane formulation²⁶ and this was followed closely by the 50% CPOSS + 50% mono-oxetane formulation.²⁷ This finding was not surprising as the cycloaliphatic oxiranes are well known to quickly undergo cationic polymerization. The difunctional nature of the bis-oxetane is also well disposed to crosslinking as is the polyfunctional CPOSS.

The basic physical characteristics of the uncured formulations and postcured plaques are presented in Table 2. Interestingly the incorporation of CPOSS resulted in films with a high hardness level. Formulations using the mono-oxetane coagent also provided increased adhesion and flexibility relative to the bis-oxetane in combination with CPOSS. This finding is not surprising given the presence of a hydroxyl group on the mono-oxetane.

Table 2. Rheological and physical properties of POSS oxirane and oxetane concentrates.

Composition	Viscosity @25 °C	Pencil Hardness	Film Characteristics
50% CPOSS + 50% mono-oxetane	462 mPa-s	7 H	Clear, adhesive, flexible
25% CPOSS + 75% bis-oxetane	51 Pa-s	7H	Clear, reduced flexibility
50% GPOSS + 50% mono-oxetane	166 mPa-s	B	Clear, adhesive, high flexibility
75% GPOSS + 25% bis-oxetane	816 mPa-s	9H	Clear, reduced flexibility
100% CPOSS	*Table 1	9H	Clear, nonadhesive, brittle
100% GPOSS	4.8 Pa-s	9H	Clear, nonadhesive, modest flex

For formulations containing GPOSS, incorporation of the bis-oxetane coagent resulted in faster cure than formulations containing the mono-oxetane. Interestingly, the 50% GPOSS + 50% mono-oxetane²⁸ and 75% GPOSS + 25% bis-oxetane²⁹ films are in stark contrast to each other relative to hardness. The GPOSS + 50% mono-oxetane blend resulted in an adhesive, soft and highly flexible clear plaque, while the 75% GPOSS + 25% bis-oxetane film exhibited 9H level hardness and modest flexibility. A lower degree of network development in the 50% GPOSS + 50% mono-oxetane formulation is a logical explanation for this difference in physical properties.

It is evident from the range of viscosities and cured film properties that oxetane-oxirane POSS concentrates can provide a convenient starting point for use in formulation and design of optical clear hard coatings. Further, inclusion of the oxetane component also provides a convenient means for adjustment of flexural properties.

Nonreactive Blending and Rheological Effects in Nanosilica Dispersion

Having established the propensity of POSS oxiranes toward cationic cure, the ability of the oxirane to associate with the surface of nanosilica was investigated. In all cases formulations of POSS oxirane and oxetane-oxirane POSS were able to render clear dispersions with 20 nm silica at loading levels of 30 wt.% silica (Figure 3). These dispersions also show long 1-yr or longer shelf-life stability against settling. Nanosilica in combination with GPOSS can be viewed as two reinforcing agents in one and can be considered a tool toward the formulation of hard and durable coatings.¹¹ Such formulations are also amenable to surface glassification thereby provide *in situ* hard coatings that are also suitable as bondable tie layers.¹²

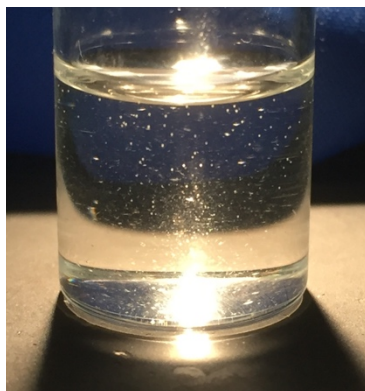


Figure 3. A 30 wt.% nanosilica (20 nm) dispersion in GPOSS.

The dispersion effect of oxirane POSS can also be utilized synergistically with particles and ingredients that have been surface modified with organosilane coupling agents.¹³ The advantage of this synergistic approach is that it does not require changing from heritage coupling agents as surface modifiers on fillers yet offers extension of the performance levels through use of POSS as a dispersion agent and interfacial tie-layer.

Unique rheological synergies were also realized when using the GPOSS as dispersion agent for fumed silica. For example, when equal parts of glycidylpropyl POSS and diglycidylether bisphenol-A (DGEBA) were mixed with 5 wt.% of fumed silica, a rheological synergy resulted (blue trace) (Figure 4). The synergistic combination revealed a drastically reduced viscosity (~ 10x lower) relative to the individual component viscosities also containing 5 wt.% fumed silica, diglycidyl bisphenol-A (red trace), and 5 wt.% silica in GPOSS (gray trace). The synergy observed for the tertiary mixture (blue trace) is believed to arise from the ability of GPOSS to associate to the surface of the silica particles and provide volume around the particles while also rendering it more compatible with the DGEBA resin. Such viscometric enhancements can enable the manufacturability of highly solid-loaded formulations (without the use of a solvent, or oils which degrade physical properties).¹⁴

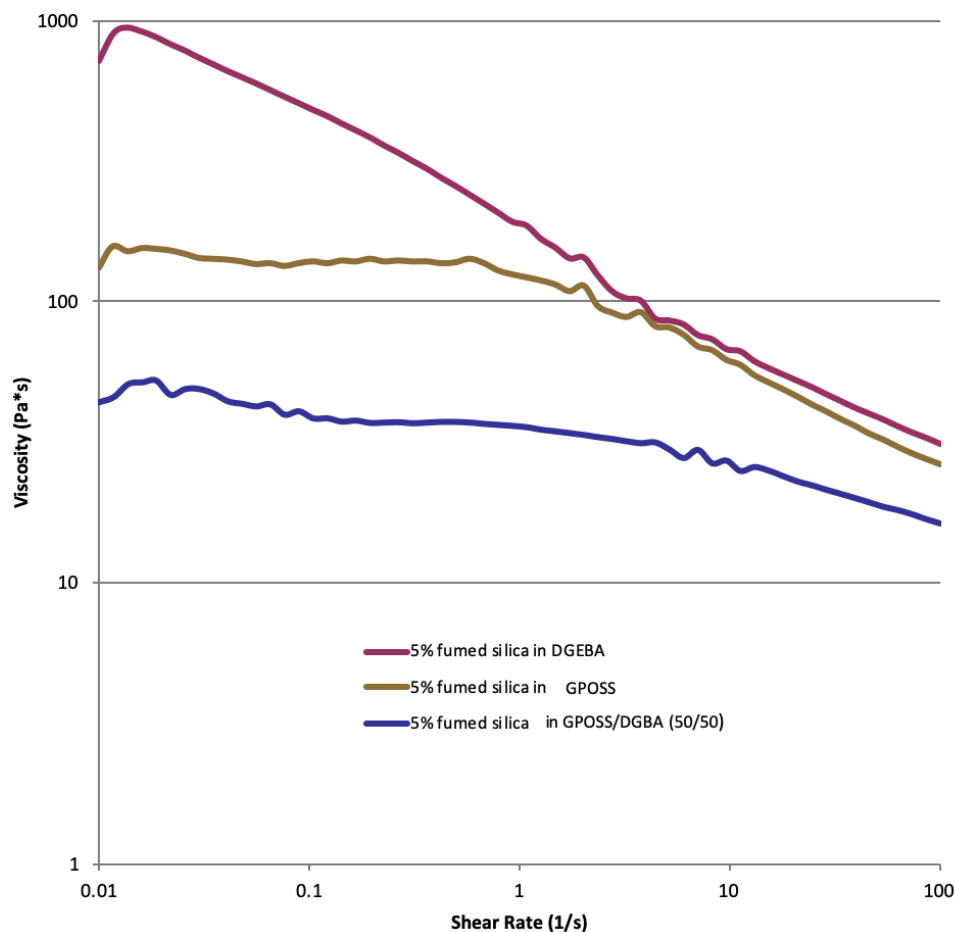


Figure 4. Viscosity vs shear rate of a 5 wt.% fumed silica dispersed in DGEBA resin (red), and in GPOSS (grey), and a 50/50 mixture of DGEBA/GPOSS (blue) trace.

Discussion

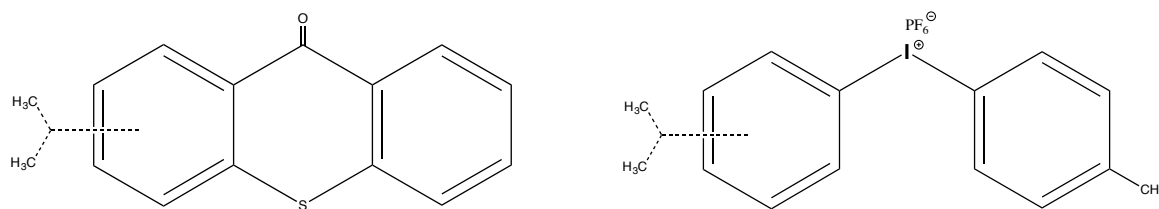
Oxirane POSS and Cationic Cure

UV-curable oxirane coatings are being utilized in an increasing number of commercial applications because of their enhanced solvent resistance and mechanical integrity relative to acrylic chemistry. Oxirane coating chemistry is also expanding into photo-definable polymers which are widely utilized in MEMS, microfluidic devices, imprinting, and microelectronics. Within the oxirane family of resins, cycloaliphatic systems are more reactive than glycidyl chemistries. However, the polyfunctionality of additives like the GPOSS provides a new tool toward fast-cure glycidyl formulations.

As with acrylates, oxirane oligomers have traditionally demonstrated a deficiency in achieving complete cure. Subsequently, the ability to achieve optimal moduli, hardness, and toughness has been somewhat limited. However, the incorporation of polyfunctional oxirane POSS can provide the ability to achieve higher degrees of network formation and enhancements that are not achievable with other additive technologies.

A detailed study regarding the cationic homopolymerization of the GPOSS and CPOSS has been reported in the literature. This earlier work was focused on the development of high temperature low dielectric patternable coatings.²² In that study, each POSS was dissolved in toluene with Darocur® ITX (0.5 mol % relative to epoxy group) and 2 mol % of Irgacure® 250 as photoinitiators (Figure 5). The

formulations were spin coated, imprinted, and cured using a broadband mercury lamp emitting from 350 nm to 410 nm using an EVG770 NIL stepper. The power density of the lamp was 11 mW/ cm² at the coating surface.



Darocur ITX

Irgacure 250

Figure 5. Darocur ITX sensitizer and Irgacure 250 initiator.

The resulting homopolymer coating that utilized CPOSS showed superior imprinting capability presumably because of its inherent adhesive characteristics. Both GPOSS and CPOSS showed 80 % oxirane cure conversion with a 3% degree of shrinkage. The dielectric constant for the CPOSS coating was 3.2 while that with the GPOSS was 3.0. Differences in the dielectric values were attributed to the differences in the alkyl spacer link between the cage and oxirane. It was assumed the longer spacer reduced the dielectric value by increasing the volume between the cages. As might be expected, the resulting homopolymer films did not show a T_g , due to the tightly crosslinked network. Upon heating to 200 °C (post-bake), a 5% maximal weight loss at 393 °C was observed. Therefore a high degree of thermal stability was achieved through the use of the POSS additive.

There is also a desire for development of photo definable epoxy polymers with inorganic characteristics that can provide durability toward chemical etching and mechanical processing such as pattern transfer, pattern filling, and polishing. To demonstrate the ability of CPOSS to meet this need it was dissolved in mesitylene (at 40 % and 60 % concentrations), and an iodonium photo-acid generator (1 wt.%) and sensitizer (0.33 wt.%) relative to POSS were utilized to affect cationic cure. After spin coating and solvent removal, the photosensitive formulations were cured using a 250 mJ/cm² UV source with exposures at (350 - 380 nm) from a 1 kW Hg-Xe lamp. Post-exposure bakes were conducted at 205 °C and 240 °C for 1 hour.²³ The literature findings presented in Table 3 provide the mechanical and contrast properties of the CPOSS homopolymer hard coat in comparison to the commonly used EPON[®] SU8 novalac epoxy photoresist.

Table 3. Mechanical and Contrast Properties of CPOSS Homopolymer and SU8.

	Modulus (GPa)	Hardness (GPa)	Contrast Value
CPOSS post-bake @ 205 °C	5.3	0.64	1.5
CPOSS post-bake @ 240 °C	4.1	0.41	1.5
EPON SU8 (comparative)	4.02	0.294	0.7 - 3.6

After post bake at 205 °C, the CPOSS homopolymer films provided a modulus that was 31% higher than that of the SU-8 film, which was also post-baked. Surprisingly, after a 240 °C post-bake, the CPOSS homopolymer film revealed a decreased modulus, that was attributed to degradation of crosslinks above 205 °C. The properties of SU8 are known to vary with processing conditions,²⁴ therefore, only relative comparisons of data can be made between the CPOSS homopolymer and SU8.

However, the cationically cured CPOSS homopolymer clearly possesses many of the same desirable characteristics including photo-definability.

The same authors report the chemical resistance of cured CPOSS films to be outstanding relative to organic systems. For example, only hydrogen fluoride (HF) exposure caused the CPOSS films to degrade and undergo delamination. The average dissolution rate for CPOSS homopolymer films was measured to be 6.7 nm/min upon submersion in aggressive systems such as isopropanol, acetone, mesitylene, propylene glycol methyl ether acetate, 2-hexanone, hot 3 M sulfuric acid, peroxydisulfuric acid, and phosphoric/acetic/nitric acid. The chemical robustness of the CPOSS homopolymer was attributed to the silicon-oxygen cage core.

Furthermore, oxygen plasma etch rates for the CPOSS homopolymer films are very low relative to wholly organic films. The low etch rate is attributed to the oxidation of organics from the cage core followed by fusion of the Si-O cores into an inert SiO₂ layer.

In a related work, CPOSS was utilized as a negative photoresist hard mask. CPOSS offers the advantage of being a single component resist for which the precise cage structure can aid in pattern resolution and retainment during post-processing steps. To demonstrate this capability, CPOSS was dissolved at 50 - 60 wt.% levels in propylene glycol methyl ether acetate (PGMEA) and 2 - 4 wt.% of the photoacid Irgacure 261 was added as a UV cure catalyst (Figure 6).²⁵

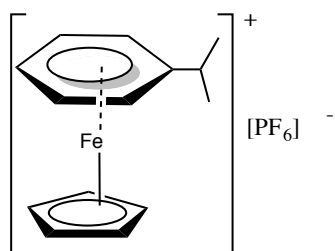


Figure 6. Irgacure 261.

After deposition, the coating was soft baked at 65 °C, and the film was patterned and cured using interfering (532 nm, Nd:YVO₄) laser beams to fabricate 2D and 3D patterns. The SEM images of 2D and 3D films suggested that CPOSS had a photosensitivity similar to SU8. The structural integrity of the 2D patterned cylinders from CPOSS were examined relative to their volume, weight, and structural changes after calcining (glassification) in air. The high thermal stability of the cured CPOSS resist was exemplified by the less than 10 wt.% change in density between the 25 °C and 400 °C processing temperatures (Table 4).

Table 4. Effects of Calcining Temperature on CPOSS Homopolymer.

Calcining Temperature	Residual Weight %	Relative Volume %	Relative Density (g/mL)
25 °C	100	100	1.0
400 °C	72	63 - 67	1.1
500 °C	51	30 - 35	1.5 - 1.7
600 °C	32	16 - 18	1.8 - 2.0

Finally, the authors reported that the 2D and 3D printed patterns were maintained after calcining for 1 hour at 400 °C. They also reported that structural integrity was sufficiently high to enable back-filling of the printed patterns using silanes deposited by CVD at 325 °C. This opens the prospect of

CPOSS resists to provide multifunctionality and pattern transformation. When calcined at 500 °C, the features and film underwent densification to a more SiO₂ rich network which is thermodynamically favorable.

Conclusions

Oxirane POSS can be considered as crosslinkable additives for cationically cured coatings and resin systems. However, their unique hybrid (organic-inorganic) compositions, high density of reactive groups, in combination with their surface area, volume contributions, enable these additives to provide an envelope of physical property enhancements to coatings. In particular, these systems are capable of providing, dispersion, rheological control, modulus and glassification in addition to the traditional crosslinking function. These desirable effects arise from their unique and topological features that are able to favorably alter network formation and connectivity at low loading levels.

Acknowledgements

The authors express gratitude to Dr. Joseph Schwab for useful technical discussions and to Dr. Charles Grayson for careful reading of the manuscript.

References

- ¹ "POSS Additives in Energy Cure Coatings: A Technical Review", *Curr Trends Nanotechnol* 1: 101. DOI: 10.29011/CTNT-101.100001
- ² "The mechanical properties of crystalline cyclopentyl polyhedral oligomeric silsesquioxane", DOI: 10.1063/1.2208355
- ³ "Evaluation of Force Fields for Molecular Simulation of Polyhedral Oligomeric Silsesquioxanes", DOI 10.1021/jp052707j
- ⁴ "Thermolysis of Polyhedral Oligomeric Silsesquioxane (POSS) Macromers and POSS-Siloxane Copolymers" DOI: 10.1021/cm950536x
- ⁵ "Evaluation of dental restorative composites containing polyhedral oligomeric silsesquioxane methacrylate". DOI: 10.1016/j.dental.2004.08.003
- ⁶ "Multimethacryloxy-POSS as a crosslinker for hydrogel materials". <https://doi.org/10.1016/j.eurpolymj.2015.09.007>
- ⁷ Diluent Properties Ref (a) "POSS Driven Chain Disentanglements, Decreased the Melt Viscosity and Reduced O₂ Transmission in Polyethylene". <https://doi.org/10.1016/j.polymer.2019.01.024> (b) "Small Particle Driven Chain Disentanglements in Polymer Nanocomposites". DOI: 10.1103/PhysRevLett.118.147801. (c) ref 6.
- ⁸ (a) "Dynamic Mechanical Characterization of Epoxy/Epoxyhexyl-POSS Nanocomposites". DOI: 10.1016/j.msea.2011.10.100 (b) "Preparation and Properties of UV-Cured Epoxy Acrylate/Glycidyl-POSS Coatings". DOI: 10.1007/s11998-016-9886-1. (c) Epoxidized Pine Oil-Siloxane: Crosslinking Kinetic Study and Thermomechanical Properties". DOI: 10.1002/app.42451
- ⁹ "Toughening of Epoxy Adhesives by Combined Interaction of Carbon Nanotubes and Silsesquioxanes". doi:10.3390/ma10101131
- ¹⁰ Photocurable Silsesquioxane-Based Formulations as Versatile Resins for Nanoimprint Lithography. DOI: 10.1021/la1025119
- ¹¹ (a) <https://hybridplastics.com/product/ma4135-01-nanosilica-dispersion-methacrylate-poss/> (b) <https://hybridplastics.com/product/ep4f09-01-nanosilica-dispersion-epoxy-poss/>
- ¹² Engardio, T. J., Hu, G. Y., Kang, D. K., Rorye, E. R. US. Patent 8,163,357.
- ¹³ Hybrid SiO₂@POSS nanofiller: a promising reinforcing system for rubber nanocomposites. DOI: 10.1039/c7qm00045f
- ¹⁴ (a) Polyhedral Oligosilsesquioxane-Modified Boron Nitride Nanotube Based Epoxy Nanocomposites: An Ideal Dielectric Material with High Thermal Conductivity". DOI: 10.1002/adfm.201201824 (b) "On the Key Role of SiO₂@POSS Hybrid Filler in Tailoring Networking Interfaces in Rubber Nanocomposites". <https://doi.org/10.1016/j.polymertesting.2017.12.022>