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Review Article

POSS Additives in Energy Cure Coatings: A Technical Review

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Abstract

Polyhedral oligomeric silsesquioxane (POSS®) additives provide a simple-to-use chemical tool kit that that requires only small loading levels to improve traditional formulations. At 1.5-3.0 nm in diameter, POSS cages provide a tremendous amount of surface area and volume control when incorporated into formulations. POSS additives impart adhesion, hardness, and scratch resistance properties in optical coatings. They also improve the degree and rate of ultraviolet light cure due in part to their surface area and high degree of functionalization. The fundamental attributes of acrylic and epoxy POSS will be discussed as well as the related material science models that explain the observed effects in energy-cure coating formulations.

Introduction

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 $(SiO_{1.5})$ with organic (R) groups to render compatibility and reactivity with heritage polymers, monomers, and ingredients. Representative structures for Methacrylic POSS (MA0735), Acrylic POSS (MA0736), Epoxy cyclohexyl POSS (EP0408), and Glycidyl POSS (EP0409) are shown in (Figure 1). For coatings, Methacrylic POSS and Glycidyl POSS find significant use as additives in new and emerging formulations. While octameric cage sizes are shown, the $SiO_{1.5}$ silsesquioxane cage core sizes are a mixture of octamer, decamer, and dodecamer with the dodecamer as the predominant cage size (~65%). A cage size distribution is favorable as it results in a melting point depression, and allows these additives to exist as clear, low viscosity liquids. As liquids, they are readily miscible with nearly all conventional coating resins and monomers.
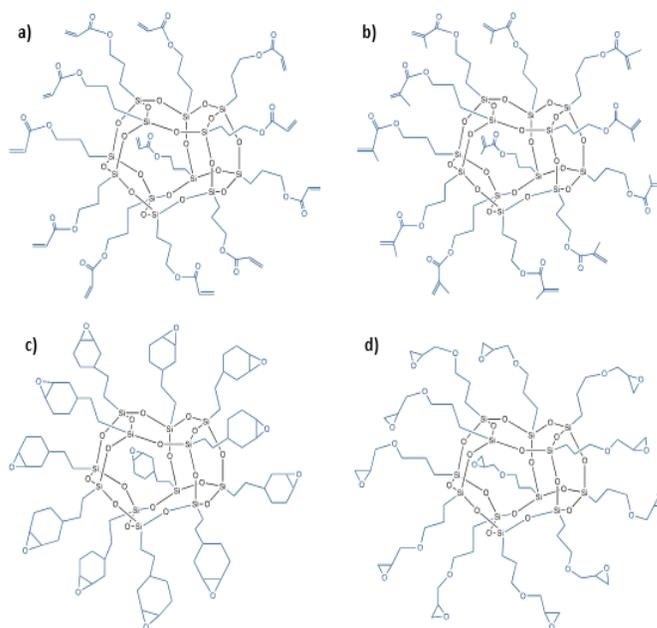
Figure 1: a) Methacryl POSS (MA0735), b) Acrylic POSS (MA0736), c) Epoxy cyclohexyl POSS (EP0408), and d) Glycidyl POSS (EP0409).

These POSS cage mixtures are also soluble in common solvents, and are characterized by GPC, HPLC, and NMR. A summary of their physical properties is provided in Table 1.

	Methacrylic POSS	**Acrylic POSS**	**Epoxycyclohexyl POSS**	**Glycidyl POSS**
Appearance	Clear colorless liquid	Clear straw liquid	Clear straw wax	Clear straw liquid
Composition	$(C_7H_{11}O_2)_n(SiO_{1.5})_n$	$(C_6H_9O_2)_n(SiO_{1.5})_n$	$(C_8H_{13}O)_n(SiO_{1.5})_n$	$(C_6H_{11}O_2)_n(SiO_{1.5})_n$
Mol. Wt. (n = 12)	2150.96	1982.63	2127.29	2006.83
Viscosity @ 25 °C	30 Poise	22 Poise	500 Poise @ 60 °C	43 Poise
Density	1.20 g/mL	1.23 g/mL	1.24 g/mL	1.25 g/mL
Refractive index	1.46	1.45	1.52	1.51
UV absorption	200-300 nm	200-300 nm	200-300 nm	200-300 nm
EEW	N/A	N/A	177	167
ENE EW	179	165	N/A	N/A
CASRN	160185-24-0	1620202-27-8	1213770-19-4	68611-45-0
Oral toxicity	Category IV, $LD_{50} > 5$ g/kg			
Skin contact	Non-irritant			
AMES	Non-mutagenic			
OEDC 471	Non-mutagenic		-	-
EEW – epoxy equivalent weight				

Table 1: Physical Characteristics for Methacrylic POSS, Acrylic POSS, Epoxycyclohexyl POSS, and Glycidyl POSS.

POSS chemicals 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 traditional composition and chemical reactivity of the organic groups attached to each of the silicon vertices.

Five Unique Attributes of POSS Additives

Attribute 1

The modulus of the POSS cage is unique and rigid at 11.7 GPa. Capaldi FM, et al. [1] The silicon-oxygen core is also mechanically and thermally durable. Ionescu TC, et al., Mantz RA, et al. [2,3] In formulary work, 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 networks with increased modulus and hardness properties. When high degrees of conversion are achieved, the glass transition temperature (T_g) also increases. However, at lower degrees of conversion, any non-reacted arms of the POSS cage can serve as internal plasticizers. POSS cages do not provide the same level of hardness as wholly inorganic additives. However, they can be used synergistically with fillers to impart additional hardness, reinforcement, and durability [4].

Attribute 3

The rigid core, in combination with the reactive external arms, result in 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 [5].

Attribute 4

The large diameters of POSS enable them to provide volume control inside of formulations. When well-dispersed into polymers, POSS additives tend to increase the spacing between polymer chains. The increased volume provides improved rheological properties (a diluent-like effect) and also results in modest improvements in toughness and impact properties. Additionally, when associated with filler and ingredient surfaces, POSS cages improve their dispersion and effectiveness [6].

Attribute 5

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. These processes include oxygen plasma etching, corona treatment, short wavelength UV, ozone, and flame treatment. From a chemistry perspective, the oxidation process involves the removal of organic groups from the POSS cage and a subsequent oxidative-fusing of the cores together (similar to sintering) to form a surface glass layer (SiO_2). The resulting surface glass layer is nanoscopically thin and while not completely abrasion resistant, it does improve hardness, scuff, and mar resistance. The surface glassification of POSS can also serve as an ideal bondable tie-layer between coatings [7].

Extent of Cure for POSS

The extent of cure for MA0735 POSS has been extensively investigated. The free radical cure of MA0735 POSS using peroxide initiators has been detailed by Lungu and coworkers [8]. This group studied the reaction of binary and ternary mixtures of MA0735 POSS. While all formulations reached conversions approaching 90%, the incorporation of MA0735 POSS slightly decreased the polymerization rate due to hindrance from the cage volume. Yet, the resulting crosslink density achieved was higher due to the high concentration of methacrylate groups associated with POSS MA0735. Any remaining nonreactive methacrylate groups on the POSS cage were reported to provide local plasticization. In ternary mixtures, MA0735 resulted in an overall increase of methacrylic conversion and at a rate that was essentially equivalent to that of wholly organic methacrylic reagents. Similar findings have been observed for the Ultraviolet (UV) light cure of MA0735 POSS in binary mixtures with bisphenol-A ethoxylated dimethacrylate. In this system, > 95% conversions of POSS were realized along with an increased rate of polymerization, higher T_g, and enhanced scratch resistance [9].

The extent of cure in photo-induced free radical polymerization of more complex ternary mixtures containing MA0735 POSS and 77.5 wt% barium glass filler have also been investigated. Fong H, et al. [10] The POSS methacrylic groups were polymerized immediately after photo initiation, and formulations containing 2% and 10% mass fractions of POSS achieved ~75% double bond conversion. Residual nonrelated methacrylate groups on the POSS cage served to locally plasticize the formulation. As might be expected, the higher crosslink density resulting from POSS incorporation could be expected to impact the degree of shrinkage for resins. While non-filled methacrylates typically express a volumetric shrinkage of 6-10%, filled methacrylate systems shrink from 3-7% [11]. Incorporation of POSS into filled methacrylic formulations has not been found to statistically change the volume shrinkage. The cationic cure of EP0408 POSS and epoxides structurally related to EP0409 have been extensively studied. Crivello JV, et al. [12]. High conversion and crosslink density

are dependent upon the type and concentration of photo initiator as well as the type of UV source. With 1-2 mol% of the initiator p-(decylphenyl) phenyliodonium hexafluoroantimonate, irradiation from a UVEXS 16 mW/cm^2 UV source for 20-30 sec resulted in conversions of 78 - 90%. The high degree of conversion for the highly functionalized POSS molecules is attributable to the high surface area and volume provided by the cages. While intramolecular reactions cannot be ruled out, the resulting colorless, transparent, hard films support the occurrence of significant levels of intermolecular polymerization. Polymerization is also supported by the disappearance of a DSC detectable T_g. As expected, the cycloaliphatic EP0408 POSS polymerized faster than the glycidyl EP0409 POSS under cationic conditions.

The following case studies are intended to illustrate the trend of effects obtained from incorporation of POSS into a diverse number of formulations cured under UV conditions. The impact on cure and properties are attributed to one or more of the five unique attributes of POSS in addition to conventional compositional dependencies.

POSS in Hydrophilic Systems

Polyethylene Glycol (PEG) diacrylates and dimethacrylates are ideal ingredients to improve the hydrophilicity of coatings, particularly in high value medical and biomedical coatings. While they are often deficient in robustness due to the flexibility and mobility of the PEG linkage, the Young's modulus of cross-linked PEG monomers is known to decrease as the molecular weight of PEG increases. In lithographic printing and microfluidic applications, lower modulus can result in degradation of desired fine surface features. This deficiency can be corrected by utilizing the modulus building and crosslinking attributes of MA0735 POSS. A combination of formulations incorporating 50% MA0735 POSS with three different molecular weight dimethacrylate PEG oligomers (330 amu, 550 amu, and 750 amu, (Figure 2)) resulted in optically clear, homogeneous blends. The systems were cured using 2 wt% of the photo initiator (2,2-dimethoxy-2-phenylacetophenone, DMPA) for 30 min under vacuum and 365 nm (1000 mJ/cm^2) UV radiation. All ratios of components showed > 90% transmittance across the visible spectrum.
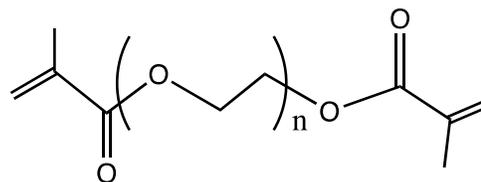
Figure 2: Dimethacrylate PEG oligomers: a) n = 4, 330 amu, b) n = 9, 550 amu and c) n = ~14, 750 amu.

In contrast to conventional PEG acrylics, the incorporation of MA0735 POSS resulted in enhanced stability of nanoimprinted patterns. The increased stability was attributed to significant increases in Young's modulus and reduced swelling of features while

in contact with aqueous fluids. In particular, incorporation of MA0735 POSS at 50 wt% resulted in negligible swelling despite being fully wetted (contact angle) and hydrated (swelling) with phosphate buffered saline. The cage modulus, crosslink density, and volume provided by MA0735 POSS resulted in PEG-methacrylic networks that were durable under nanoimprinting conditions, and even after exposure for one month at the fully swelled state. Lee BK, et al. [13] A tabulation of physical properties relative to composition is provided in (Table 2).

Composition (Weight%)	Young's Modulus	Equilibrium Water Contact Angle	Saline Swell Weight %
100% PEGDMA, 330 MW	1 GPa	56°	7.6
50% MA0735 / 50% PEGDMA 330	2.815 GPa	51°	1.3
100% PEGDMA, 550 MW	40.3 MPa	41°	25.8
50% MA0735 / 50% PEGDMA 550	2.038 GPa	48°	2.6
100% PEGDMA, 750 MW	16.5 MPa	38°	50.3
50% MA0735 / 50% PEGDMA 750	1.898 GPa	42°	5.1

Table 2: Modulus, Contact Angle, and Swelling Trend of PEGDMA Formulated with MA0735 POSS.

MA0735 POSS has been reported to be an ideal additive in UV curable nanoimprint lithographic resins. Lee BK, et al. (2010) [14] In these formulations, 2 wt% of DMPA was utilized as a photo initiator under 365 nm (200 mJ/cm² UV dose) with 30-35 second UV exposures while maintaining the imprinting pressure. The dilutive effect of MA0735 POSS with formulatory ingredients was utilized to effect a minimal increase of viscosity upon addition of MA0735 POSS up to the 20% level relative to methyl methacrylate (MMA), tert-butyl methacrylate (*t*-buMA), ethylglycidyl dimethacrylate (EGDMA), and tetraethyleneglycol dimethacrylate (TEGDMA) (Figure 3).
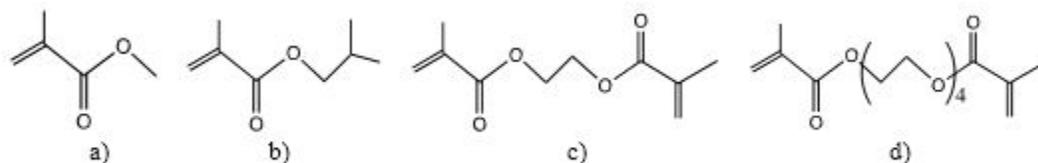
Figure 3. Comonomers a) MMA, b) t-buMA, c) EGDMA and d) TEGDMA.

At POSS concentrations below this critical loading level, the cages provide a diluent effect that can be attributed to increased free volume between chains/components. At MA0735 POSS concentration of 50% and higher, its concentration effect on increasing viscosity are attributed to steric crowding effects due to POSS cages in close contact with each other, and the viscometric parameter approaches that of the pure MA0735 POSS system (Table 3).

MA0735/Comonomer Weight%	MMA/MA0735 POSS Viscosity (cP)	t-BMA/ MA0735 POSS Viscosity (cP)	EGDMA/MA0735 POSS Viscosity (cP)	TEGDMA/ MA0735 POSS Viscosity (cP)
50/50	3.9	7.1	22.1	50
20/80	0.8	1.4	4.3	14.5
0/100	0.56	0.93	3.2	9
*viscosities include 2 wt% DMPA initiator and measurements were made at 25 °C				

Table 3: Viscosity Trends of MA0735 POSS Addition to Comonomers.

Aside from the diluent effect of POSS cages at low concentrations, the formulations indicated that incorporation of MA0735 POSS provided a baseline pencil scratch hardness of 2H (140 MPa). By way of comparison, a human nail provides a hardness of 120 MPa.

Thus, the inherent hardness imparted by POSS additives provides scratch and mar resistance that is sufficient to thwart damage from human interaction with display coatings. The durability of coatings with fine imprinted features was demonstrated through measurements of Young's modulus, which relates to the propensity of features to collapse or remain under stress (Table 4). For low modulus comonomers such as TEGDMA, the incorporation of MA0735 POSS at 50% loading greatly increased the observed modulus of the formulations. For comonomers with inherently higher moduli, the incorporation of MA0735 POSS resulted in smaller increases in modulus. In the case of EGDMA, a synergy was observed at 20 weight% of MA0735 POSS but not at 50 weight% of MA0735 POSS.

| MA0735/Comonomer Weight%	Young's Modulus (GPa)
100 % MA0735 (homopolymer)	3.413
50% MA0735 / 50 % MMA	4.015
100% MMA (homopolymer)	1.8 - 3.0
50% MA0735 / 50 % t-buMA	4.002
50% MA0735 / 50 % EGDMA	3.991
20% MA0735 / 80 % EGDMA	4.272
100% EGDMA (homopolymer)	4.421
50% MA0735 / 50 % TEGDMA	2.922
20% MA0735 / 20% TEGDMA	2.445
100% TEGDMA (homopolymer)	2.036

Table 4: Young's Modulus Relative to Composition.

The durability of the fine features of these nanoimprinted coating was further improved through glassification of the coating via oxygen plasma and tetrafluoromethane etching. As described previously, the ability to convert POSS *in situ* into a glass surface layer without degradation of fine features is a special advantage provided by POSS that is not available with traditional organic systems. In this work, the glassification of the nanoimprintable formulations enabled the usefulness and durability of multiple generations of imprint stamping replications.

Bisphenol-A Glycidyl Dimethacrylate and MA0735 POSS

Bisphenol-A glycidyl dimethacrylate (Bis-GMA, (Figure 4)) is commonly utilized in UV formulations. Its high viscosity, low degree of double bond conversion, and 6 - 10% volumetric shrinkage often render it deficient in providing desirable property improvements, prompting the use of fillers and additives with Bis-GMA. The deficiencies of Bis-GMA speak directly to those qualities imparted by the high modulus, high volume, crosslinkability, and rheological diluent effects of the MA0735 POSS additive.
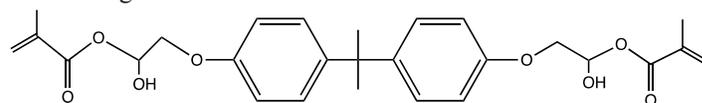
Figure 4: Bis-GMA.

Formulations based on MA0735 POSS, Bis-GMA, and TEGDMA were cured with a visible light photo initiator (camphor quinone) and co-initiator (ethyl-4 (N, N-dimethylamino) benzoate). Fong H, et al. [15]. At 2% and 10 wt% of MA0735 POSS and 300 seconds of UV exposure, the extent and rate of cure were nearly identical to the control system of 50% Bis-GMA and 50% TEGDMA. With increasing amounts of MA0735 POSS, lower degrees of photopolymeric conversion was observed, however, there was no negative effect on shrinkage or mechanicals. At 2 wt% of MA0735 POSS, the Young's modulus increased by 35% relative to the control system. At 10 wt% of MA0735 POSS, the flexural strength was improved by 20% relative to the control (Table 5).

Weight% Composition	Conversion	Young's Modulus (GPa)	Flexural Strength (MPa)	% Volume Shrinkage
50% BGMA / 50% TEGDMA	81%	7.7 ± 0.6	112 ± 22	3.67 ± 0.18
2% MA0735 / 48% BGMA / 50% TEGDMA	> 75 %	10.4 ± 0.9	120 ± 10*	3.55 ± 0.27
10% MA0735 / 40% BGMA / 50% TEGDMA	75%	7.6	140 ± 12	3.86 ± 0.32
*Data taken from published graph in cited reference				

Table 5: Composition, Conversion, Mechanicals and Shrinkage Trends.

The incorporation, at the additive level, of MA0735 POSS into this complex UV formulation resulted in a highly homogenous system with enhanced physical properties. Typically loading levels above 10 wt% POSS require the use of flexible comonomers to retain desirable engineering properties.

Acrylic and Methacrylic POSS Cage Mixtures with Cyanoacrylates

Cyanoacrylates are an outstanding family of adhesives with extensive consumer, medical, and industrial utility. A deficiency of these adhesives is their low mechanical properties, shrinkage, and hydrolytic instability. To demonstrate that these deficiencies can be overcome, MA0736 POSS was incorporated into octylcyanoacrylate (Figure 5). Fadaie P, et al. [16].
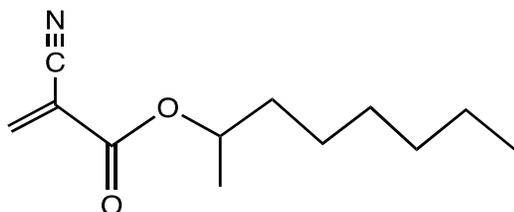
Formulations were prepared with MA0736 POSS concentrations ranging from 10-60 wt% and two photo initiators (1-phenyl-1,2-propanedione and 2,3-butanedione). The photoinitiator 2,3-butanedione at 3 wt% provided superior polymerization efficiency under a 550 mW/cm^2 visible light source. The mechanical and adhesive properties for a series of loading ranges of MA0736 are provided in Table 6. As expected, the flexural modulus of the formulations improved in a linear fashion with increasing concentrations of MA0736 POSS with a maximum being reached at the 80 wt% level. The increase in flexural modulus is attributed to contributions from both the rigidity of the POSS cage and the increased crosslink density. Incorporation of MA0736 POSS improved the overall physical properties at concentration ranges from 10-30 wt%.

Figure 5: 2-Octylcyanoacrylate.

Composition Wt % Cyanoacrylate/POSS	Flexural Modulus (MPa)	Flexural Strength (MPa)	Dentin Bond Strength (MPa)	30 Day Water Uptake (%)	% Shrinkage Strain (100 sec irradiation)
100/0 POSS	180	8.5	12.5	2.6	1.0
90/10 POSS	210	15.7	17.0	1.3	2.0
80/20 POSS	290	14.0	9.0	1.0	3.5
70/30 POSS	300	11.0		0.9	4.0
60/40 POSS	310	9.0			5.5
50/50 POSS	350	6.0			5.6
40/60 POSS	410	8.5			5.5
20/80 POSS	550	14.0	5.0		
0/100 POSS	375	12.0			

Table 6: Mechanical, Adhesive and Shrinkage Properties Relative to Composition.

The reduction in saturated moisture and improved hydrolytic stability of the adhesives improved with increasing concentration of MA0736. However, it should be noted that methacrylics are less prone to hydrolysis than acrylics and such is the case for POSS systems. POSS incorporation dramatically improved resistance to water uptake (75% improvement at 10 wt% loading level of POSS) and prevented moisture absorption during aging. The increased crosslink density and comparative hydrophobicity

of MA0736 POSS relative to octylcyanoacrylate likely accounts for this enhancement. The shrinkage strain in the coating at 100 seconds exposure increased with POSS concentration, possibly due to rapid gelation of the system. Despite this, the increases in shrinkage strain can also be indicative of incomplete consumption of the acrylic functionality. In a follow-up work, the same authors concluded that the strain was attributed to a high degree of crosslinks and increased double bond conversion. This finding was fur-

ther supported by the observation by DMA of significantly higher rubbery-state modulus (past T_g), which is indicative of restricted chain motion caused by crosslinks, and the molecular weight and volume of the POSS cage. Ghasaban S, et al. [17] As has been reported for other (meth)acrylic formulations containing MA0735/MA0736, the analysis of storage modulus (E') versus temperature plot by DMA often reveals enhanced retainment of storage modulus past T_g. Similarly, the tan ∂ transition is observed to broaden significantly and decrease enthalpically. These observations reflect retention of high mechanical properties and increased dimensional stability past the T_g. Mechanistically, the enhanced rubbery state phenomena can be understood as an increase of crosslink density and/or increase of entanglements and molecular interactions at or near the POSS additive. Bizet S, et al. [18] Consequently, molecular motion is restricted thereby allowing retainment of glassy state physical properties at higher temperatures. Qin Y, et al. [19] (Figure 6) shows a DMA data plot illustrating the ability of POSS to enhance the rubbery plateau relative to loading level.
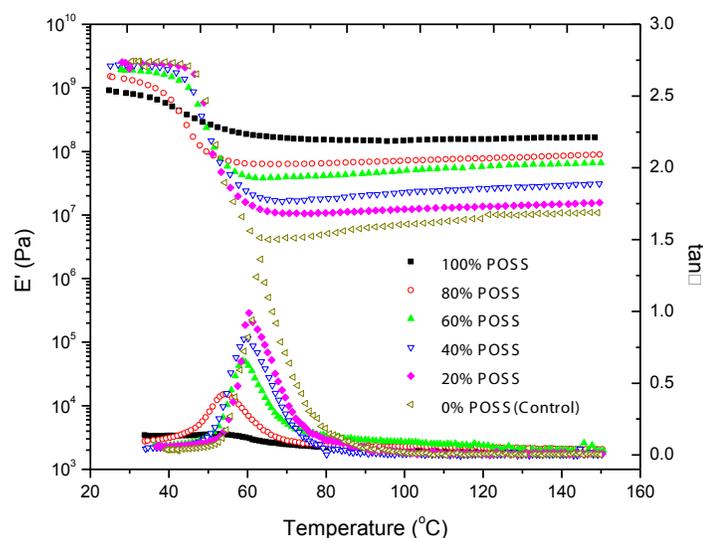

Figure 6: DMA data plot of storage modulus (E') and tan ∂ (T_g) versus temperature relative to loading level of POSS as a cross linker.

Methacryl POSS Cage Mixture and Epoxyacrylates

Epoxy acrylate (EA, Figure 7) blend the desirable physical properties of epoxy with the desirable cure characteristics of acrylics, and are widely utilized in UV curing systems to provide enhanced chemical resistance, adhesion, and mechanical strength. However, they do not reach complete cure (olefin conversion) partly due to the low ratio of curable olefin relative to molecular weight. The incorporation of methacryl POSS can be viewed as a logical solution.
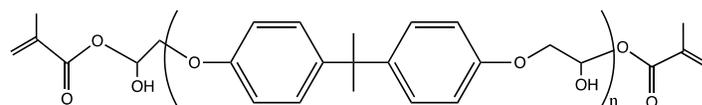
**Figure 7**: Representative structure of epoxy acrylate resin.

A study was conducted using Sartomer CN120 (EA) in combination with methacryl POSS. Wang Y, et al. [20]. Photoinitiators benzophenone (2.8 wt%) and triethanolamine (0.96 wt%) were used to effect cure using 15 sec exposures from a 5 kW high pressure mercury lamp. The addition of Methacryl POSS (MA0735) at 3 wt% and 10 wt% levels increased the double bond conversion. The EA alone reached a plateau conversion level of 80% while its blend with 10 wt% MA0735 achieved conversions approaching 95%. The enhanced conversion was attributed to the miscibility of MA0735 POSS with EA, and the high volume and surface area of methacrylic groups provide by the methacryl POSS relative to its molecular weight. The thermal and mechanical properties for the various loading levels of MA0735 into EA is provided in (Table 7).

Weight% Composition	T_g (°C)	Pencil Hardness	Impact (cm)	Flexibility (mm)
100% EA	83.2	6H	20	5
1% MA0735/99% EA	--	6H	25	5
3% MA0735/97% EA	94.8	6H	30	6
5% MA0735/95% EA	99.7	6H	40	10
10% MA0735/90% EA	99.4	4H	40	12

Table 7: Dependencies of MA0735 POSS Loading on EA Thermal and Mechanical Properties.

A consistent increase in T_g was noted with increasing levels of MA0735 POSS. Addition of 10 wt% MA0735 POSS resulted in a 20-25 °C increase in T_g (measured via DMA), and the tan ∂ transition was significantly broadened with significantly reduced enthalpy. These observations are consistent with POSS cage cross-linking and restricted local chain-network motion at temperatures above the T_g, thereby retaining glassier state characteristics at elevated temperatures. The impact and flexural properties of the blends were remarkably enhanced by the presence of MA0735. For example, a 5 wt% loading of methacryl POSS doubled the impact and flexural values relative to the EA control, and also maintained a pencil hardness of 6H. The enhancement of impact and flexural properties while simultaneously increasing crosslink density can seem counterintuitive. However, the contributions of volume and surface area provide by POSS may enable these additives to provide such effects in addition to its role as a cross linker. The authors of the cited work also attribute the improvement of impact resistance to the ability of POSS additives to absorb and dissipate energy through a plastic deformation mechanism as opposed to undergoing brittle fracture. The ability of nanostructures such as silica to control free volume in formulations and their ability to absorb and dissipate energy is well known. Zhenga Y, et al. [21]. It appears that MA0735 POSS behaves in a similar manner with the additional advantages of being a miscible, cross linkable, transparent, and dilutive comonomer.

Epoxy POSS and Cationic Cure

Epoxy acrylates are being adopted into an increasing number of commercial applications because of their enhanced mechanical integrity, and so are UV-curable oxiranes. Within the oxirane family of resins, cycloaliphatic systems are more reactive than glycidyl chemistries. Photo definable polymers are also widely utilized in MEMS, microfluidic devices, imprinting, and microelectronics. Epoxy-based resins, are often utilized as overcoats for devices but are deficient in mechanical stability and lack durability during the etching processes required to form features and patterns. UV initiated cationic cure of oxiranes is an expanding area for epoxy resin systems, and is driven by the thermal and mechanical deficiencies of olefin (acrylic, methacrylic) chemistry to meet the demands of microelectronic and macro-printing, nano-imprinting requirements. As with epoxy acrylates, oxirane oligomers are deficient in achieving complete cure and therefore present reduced moduli, reduced hardness, and toughness relative to acrylic systems. In this capacity, the incorporation of polyfunctional oxirane POSS can provide enhancements that are not achievable with other additive technologies. A detailed study regarding the cationic homopolymerization of the glycidyl epoxy POSS and epoxy cyclohexyl POSS (EP0408) has been conducted for the purpose of developing high temperature low dielectric patternable coatings. De Girolamo J, et al. [22]. Each POSS was dissolved in toluene with Darocur® ITX (0.5 mol % relative to epoxy group) and 2 mol % of Irgacure® 250 until visual homogeneity was observed (Figure 8). The formulations were then 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.
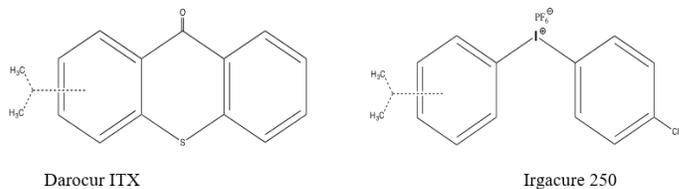
Figure 8: Darocur ITX sensitizer and Irgacure 250 initiator.

The coating with EP0408 POSS showed superior imprinting capability presumably because of its inherent adhesive characteristics. Both POSS products showed 80% oxirane conversion with 3% degree of shrinkage. The dielectric constant for the coating with EP0408 was 3.2 while that with the glycidyl POSS was 3.0. Differences in the dielectric values are associated with the differences in alkyl spacer link between the cage and oxirane. It is assumed the longer spacer reduces the dielectric value by increasing the volume between the cages. As might be expected, the resulting homopolymer films did not show a T_g and upon heating to 200 °C (post-bake), a 5% maximal weight loss at 393 °C was observed. There is a need for photo definable epoxy polymers with inorganic characteristics that provide durability toward chemical etching and mechanical processing such as pattern transfer, pattern filling, and polishing. This need has been met in part through the use of EP0408 POSS.

The EP0408 POSS 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. Fritz N, et al. [23] (Table 8) provides the mechanical and contrast properties of the EP0408 homopolymer hard coating in comparison to the commonly used EPON® SU8 novalac epoxy photoresist.

	Modulus (GPa)	Hardness (GPa)	Contrast Value
EP0408 POSS post-bake @ 205 °C	5.3	0.64	1.5
EP0408 POSS post-bake @ 240 °C	4.1	0.41	1.5
EPON SU8 (comparative)	4.02	0.294	0.7-3.6

Table 8: Mechanical and Contrast Properties of EP0408 Homopolymer and SU8.

The EP0408 POSS films that were post-baked at 205 °C yielded a modulus 31% higher than that of the SU-8 film, which is also commonly post-baked. Surprisingly, the 240 °C post-baked EP0408 film revealed a decreased modulus, which 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 EP0408 and SU8. However, the EP0408 homopolymer clearly possesses many of the same desirable characteristics including photo-definability. The same authors report the chemical resistance of EP0408 POSS films to be outstanding relative to organic systems. For example, only Hydrogen Fluoride (HF) exposure caused the EP0408 films to degrade and undergo delamination. The average dissolution rate for EP0408 POSS 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 EP0408 homopolymer was attributed to the silicon-oxygen cage core, which is normally susceptible to degradation only by HF or certain ammonium hydroxide bases. Oxygen plasma etch rates for the EP0408 POSS films were also very low and was attributed to the oxidation of organics from the cage core followed by their fusion into an inert SiO_2 layer. Such durability is not possible with wholly organic films. In a related work, EP0408 POSS was utilized as a negative photoresist hard mask. EP0408 POSS 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. The EP0408 was dissolved at 50-60 wt% levels in Propylene Glycol Methyl Ether Acetate (PGMEA) and 2-4 wt% of the photo acid Irgacure 261 was added as a UV cure catalyst (Figure 9) [25].
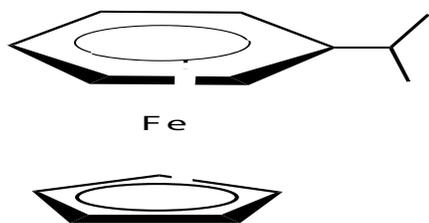

Figure 9: Irgacure 261.

After deposition, the coating was soft baked at 65 °C, and the film was patterned and cured using interfering (532 nm, Nd:YVO$_4$) laser beams to fabricate 2D and 3D patterns. The SEM images of 2D and 3D films suggested that EP0408 had a photosensitivity similar to SU8. The structural integrity of the 2D patterned cylinders from EP0408 were examined relative to their volume, weight, and structural changes after calcining (glassification) in air. The high thermal stability of the cured EP0408 resist was exemplified by the less than 10 wt% change in density between the 25 °C and 400 °C processing temperatures (Table 9).

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

Table 9: Effects of Calcining Temperature on EP0408 Homopolymer.

Favorably, both 2D and 3D printed patterns were maintained after calcining for 1 hour at 400 °C. The authors 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 EP0408 resists to provide multifunctionality and pattern transformation. When calcined at 500 °C, the features and film underwent densification to a more SiO_2 rich network. It is thermodynamically favorable to oxidize the $SiO_{1.5}$ core of POSS into SiO_2. Therefore, densification during conversion into silica resulted in some cracking of the printed patterns. Finally, as energy cured epoxy 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 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 EP0409 and EP0408 POSS have been prepared with common mono-oxetane and bis-oxetane monomers (Figure 10).
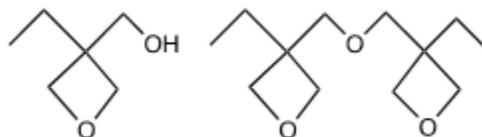

Figure 10: Mono- and bis-oxetanes formulated with EP0409 and EP0408.

To demonstrate their cure characteristics, a 2 wt% solution of 4-thiophenyl phenyl diphenyl sulfonium hexafluoroantimonate was added to each of these POSS oxetane masterbatches. Films were drawn onto a glass substrate at a thickness of 100 μ and exposed to sunlight for 30 min. All the resulting coatings were optically clear. As expected, the speed to reach non-tackiness was fastest for the 25% EP0408 +75% bis-oxetane formulation [26] and was followed closely by the 50% EP0408 +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. The characteristics of the resulting films are presented in (Table 10). Interestingly the incorporation of EP0408 resulted in films with a high hardness level. The mono-oxetane provided increased adhesion and flexibility relative to

the bis-oxetane in combination with EP0408. This finding is not surprising given the presence of a hydroxyl group on the mono-oxetane.

Composition	Viscosity @25 °C	Hard-ness	Film Characteristics
50% EP0408 +50% mono-oxetane	462 mPa-s	7 H	Clear, adhesive, flexible
25% EP0408 +75% bis-oxetane	51 Pa-s	7H	Clear, reduced flexibility
50% EP0409 +50% mono-oxetane	166 mPa-s	B	Clear, adhesive, high flexibility
75% EP0409 +25% bis-oxetane	816 mPa-s	9H	Clear, reduced flexibility

Table 10: POSS Epoxy and Oxetane Concentrate Properties and Film Characteristics.

For the concentrates containing EP0409, incorporation of bis-oxetane resulted in faster cure than the film containing mono-oxetane. The 50% EP0409 +50% mono-oxetane [28] and 75% EP0409 +25% bis-oxetane [29] films are in stark contrast to each other. The EP0409 +50% mono-oxetane blend resulted in an adhesive, soft and highly flexible clear coating, while the 75% EP0409 +25% bis-oxetane film exhibited 9H level hardness and modest flexibility.

It is evident from the range of uncured viscosity and film properties that oxetane-POSS concentrates provide a convenient starting point for use in formulation and design of optical clear coatings.

Conclusions

At first glance, polyfunctional epoxy and acrylic POSS can be considered as cross linkable additives for coatings and resin systems. Their unique hybrid (organic-inorganic) compositions and high density of reactive groups, in combination with their surface area and volume contributions, enable these additives to provide an envelope of physical property enhancements to coatings. In addition to the traditional crosslinking function, these systems are effective at providing dispersion, rheological control and modulus and impact enhancement. These desirable effects arise from POSS's unique features that are able to alter network formation and connectivity at low loading levels. The examples presented are intended to provide general guidelines for formulation with these types of POSS. An all-encompassing generic guideline for POSS additives is not possible because the compositions and specific application requirements must always be finely tweaked to meet user requirements. However, because of their high modu-lus, surface area and crosslinking capability, POSS are easiest to formulate with flexible comonomers and resins. Typically, POSS loading levels within the range 3-5 wt% are suggested as an initial starting point for existing formulations.

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