Macromol. Symp. ***196***, *301–325 (2003)*

Hybrid Inorganic/Organic Crosslinked Resins Containing Polyhedral Oligomeric Silsesquioxanes

Charles U. Pittman, Jr., Gui-Zhi Li, Hanli Ni*

Department of Chemistry, Mississippi State University, 9573, Mississippi State, MS 35762, USA
E-mail: cpittman@ra.mstate.edu

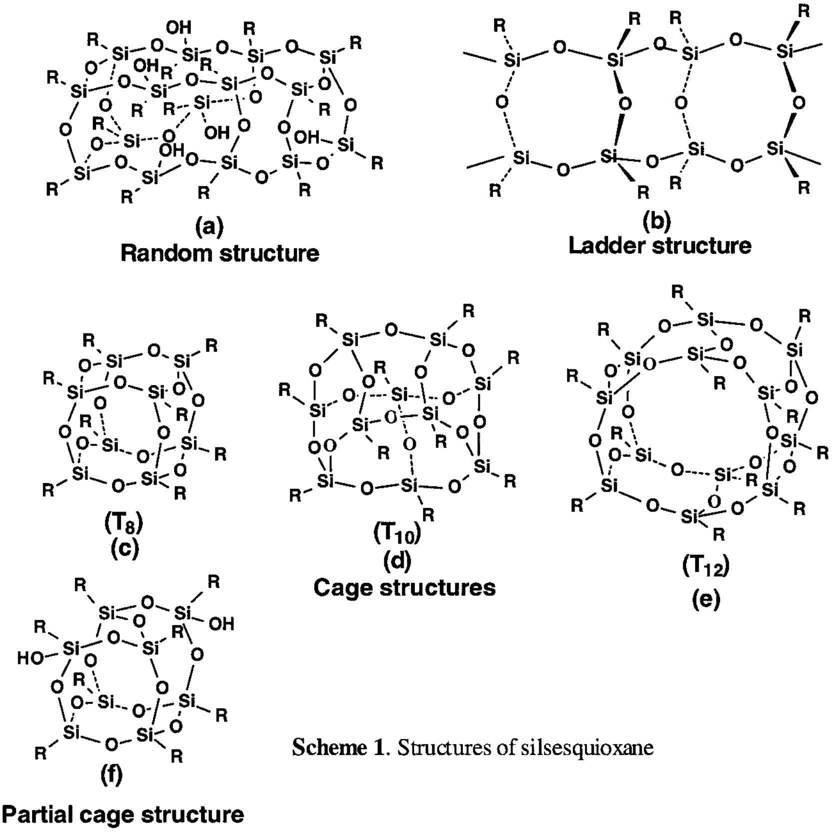
Summary: The incorporation of both monofunctional and multifunctional polyhedral oligomeric silsesquioxane (POSS) derivatives into crosslinked resins has been conducted as a route to synthesize hybrid organic/inorganic nanocomposites. The central cores of POSS molecules contain an inorganic cage with $(SiO_{1.5})_n$ stoichiometry where n=8,10 and 12. Each Si atom is capped with one H or R function giving an organic outer shell surrounding the nanometer-sized inorganic inner cage. By including polymerizable functions on the R groups, a hybrid organic/inorganic macromer is obtained which can be copolymerized with organic monomers to create thermoplastic or thermoset systems. We have focused on incorporating POSS derivatives into crosslinking resins of the following types: (1) dicyclopentadiene (2) epoxies (3) vinyl esters (4) styrene-DVB (5) MMA/1,4-butane dimethacrylate (6) phenolics and (7) cyanate esters. One goal has been to determine if molecular dispersion of the POSS macromers has been achieved or if various degrees of aggregation occur during crosslinked resin formation. As network formation proceeds, a kinetic race between POSS molecular incorporation into the network versus phase separation into POSS-rich regions (which then polymerize) occurs. Ultimately, we hope to determine the effects of such microstructural features on properties. Combustion of these hybrids creates a SiO_2-like surface layer that retards flame spread. Dynamic mechanical properties have been studied.

Keywords: cyanate esters methyl methacrylate resins; epoxy resins; hybrid nanocomposites; phenolic resins; poly(dicyclopentadiene); polyhedral oligomeric silsesquioxanes; styrenedivinylbenzene; vinyl esters

Introduction

The term silsesquioxane refers to all structures with the empirical formulas $RSiO_{1.5}$ where R is hydrogen or any alkyl, alkylene, aryl, arylene, or organofunctional derivative of alkyl, alkylene, aryl, or arylene groups. The silsesquioxanes include random structures, ladder structures, cage structures, and partial cage structures, as illustrated in Scheme 1.[1] The first oligomeric organosilsesquioxanes, $(CH_3SiO_{1.5})_n$, were isolated along with other volatile compounds by Scott in 1946 through thermolysis of the polymeric products obtained from methyltrichlorosilane and dimethylchlorosilane co-hydrolysis.[2] Even though silsequioxane chemistry spans more than half a century, interest in this area continues to increase.

In 1995, Baney et al[1] reviewed the structure, preparation, properties and applications of silsesquioxanes, especially the ladder-like polysilsesquioxanes shown in Scheme 1 (structure b). These include poly(phenyl silsesquioxane) (PPSQ),[3-12] poly(methyl silsesquioxane) (PMSQ)[13-19] and poly(hydridosilsesquioxane) (PHSQ).[20,21] However, in the past few years, much more attention has been paid to the silsesquioxanes with specific cage structures [shown in Scheme 1 (structures c - f)]. These polyhedral oligomeric silsesquioxanes have been designated by the abbreviation POSS.



(a)
Random structure

(b)
Ladder structure

(T_8)
(c)

(T_{10})
(d)
Cage structures

(T_{12})
(e)

(f)
Partial cage structure

Scheme 1. Structures of silsesquioxane

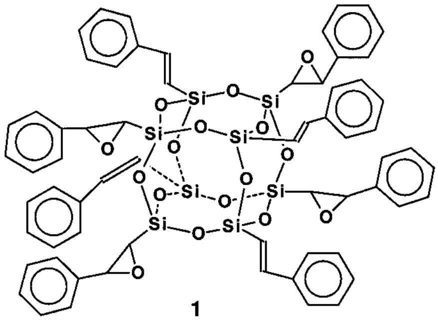
POSS compounds embody a truly hybrid (inorganic-organic) architecture, which contains an inner inorganic framework made up of silicone and oxygen $(SiO_{1.5})_x$, that is externally covered by organic substituents. These substituents can be totally hydrocarbon in nature or they can embody a range of polar structures and functional groups. POSS nanostructured chemicals, with sizes from 1 to 3 nm in diameter, can be thought of as the smallest possible particles of silica. A variety of POSS nanostructured chemicals has been prepared which contain one or more covalently bonded reactive functionalities that are suitable for polymerization, grafting, surface bonding, or other transformations.[22,23] A group at Edwards Air Force Base, CA, has recently developed a large-scale process for POSS monomer synthesis[22,24-27] and a number of POSS reagents. As a result of this success, monomers have recently become commercially available as solids or oils from Hybrid Plastics Company (http://www.hybridplastics.com/), Fountain Valley, CA.

A selection of POSS chemicals now exist that contain various combinations of nonrective substituents and/or reactive functionalities. Thus, POSS nanostructured chemicals may be easily incorporated into common plastics via copolymerization, grafting or blending.[28] The incorporation of POSS derivatives into polymeric materials can lead to dramatic improvements in polymer properties which include, but are not limited to, increases in use temperature, oxidation resistance, surface hardening and improved mechanical properties, as well as reductions in flammability, heat evolution, and viscosity during processing. These enhancements have been shown to apply to a wide range of thermoplastics and a few thermoset systems.[27,28]

In this manuscript we report the incorporation of both monofunctional and polyfunctional POSS derivatives **1-7** into crosslinked organic resin systems to make a series of inorganic/organic hybrid composite materials. As POSS macromers are incorporated, a kinetic race occurs. The solubility of the POSS in the organic monomer mixture of the resin (phenolics, epoxies, vinyl esters, methacrylics, styrene-divinylbenzene, cyanate esters or dicyclopentadiene) decreases during the cure as the number of monomer molecules (hence the entropy of mixing) decreases. Therefore, phase separation of the POSS macromer may occur sometime during the cure. This would occur in competition with the POSS macromer's chemical incorporation into the resin. After such phase separation, the POSS macromer may homopolymerize (or copolymerize with smaller amounts of resin monomers) to form POSS-rich phases within the composite as the resin curing continues. This process can compete against random POSS incorporation into the developing resin network. Random incorporation leads to molecularly dispersed POSS monomer units within a homogeneous resin phase. Phase separation will be increasingly favored if the POSS monomer has a low relative reactivity. This will cause monomer drift during the cure which raises POSS concentration relative to the other monomers, favoring phase separation. Anything that increases the early incorporation of POSS will lower this phase separation.

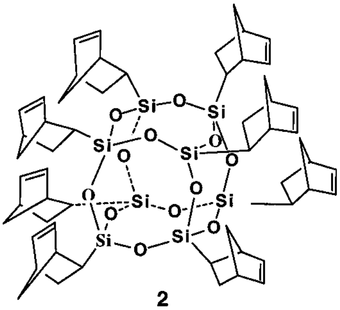
Another type of phase separation process can also operate, even if all the POSS is polymerized randomly into the resin network. POSS macromers bonded into chain segments of the resin may preferentially self-associate with each other, forming POSS aggregates whose structures and sizes are limited by the freedom of motion permitted by the developing resin's chain segmental mobility and the POSS stoichiometry. This process is favored at low crosslink densities where segmental mobility is larger. POSS aggregation has been previously observed in uncrosslinked thermoplastics. Coughlin et al[29-32] have demonstrated that linear copolymers of ethylene with a mono-alpha-olefin-substituted POSS can form POSS nanocrystalline domains due to self-aggregation of pendant POSS moieties. The extent of such aggregation depends on the mole fraction of POSS present and the method of solidifying the polymer (cooling a melt, precipitation from solution etc.) Such aggregation in crosslinked resin matrices will certainly be dependent on (1) the buildup of crosslinked density as a function of the degree of cure, (2) the relative reactivity ratios of the monomers, (3) the solvent used (if any) and (4) other factors (solvent, processing etc.)

We have employed multifunctional POSS macromers **1** – **3** and monofunctional derivatives **4** – **7** in both condensation and addition types of resin-forming polymerization reactions. These monomers and the types of resins they have been polymerized into are listed in Scheme 2. Various resin properties have been studied and POSS aggregation has been studied in a few cases.[33-36]



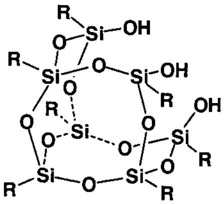
1

Tetraepoxidized octa-b-styryl-POSS
M_w:1305
Vinyl ester, Phenolic, Epoxy
and Dicyclopentadiene (DCPD) resins



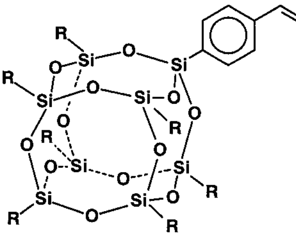
2

Octanorbornyl-POSS
$C_{56}H_{72}O_{12}Si_8$ M_w: 1162
DCPD resin



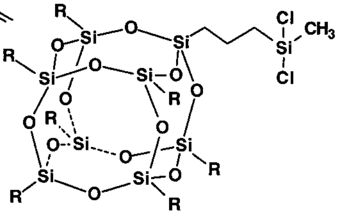
3

Trisilanolphenyl POSS
R = Ph
$C_{42}H_{38}O_{12}Si_7$ M_w: 931.3
Phenolic resins and
Cyanate esters



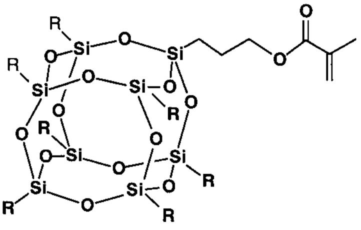
4

Styrylcyclopentyl POSS
R = Cyclopentyl
$C_{43}H_{70}O_{12}Si_8$: M_w 1003.7
Dicyclopentadiene
and Sty/DVB resins



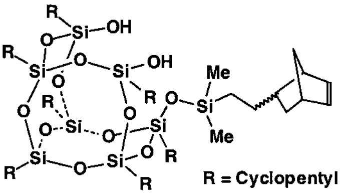
5

Dichlorosilylisobutyl POSS
R = iso-butyl
$C_{32}H_{73}ClO_{12}Si_9$: M_w 938.1
Phenolic resins



6

Methacryl Isobutyl POSS
R = isobutyl
$C_{35}H_{74}O_{14}Si_8$: M_w 943.6
For Acrylic and Vinyl Ester resins



R = Cyclopentyl

7

NorbornenylethylDisilanol
$C_{46}H_{84}O_{12}Si_8$ M_w: 1053.84
For DCPD resins, Siloxane resins
and DCPD/siloxane hybrids

Scheme 2. POSS macromers incorporated in resins in this work and the resin types

Results

Multifunctional POSS monomer incorporation

Multifunctional POSS-1 macromer (prepared for us by R. Blanski at Edwards AFB) has been cured into epoxy[34], phenolic, vinyl ester[35] and dicyclopentadiene[36] (DCPD) resins. For example, **1** in THF was blended into a resole phenolic resin (Borden SC-1008 with 35% isopropanol) and the solvents were removed *in vacuo*. This was cured via 65 °C (50 – 100 psi) 30 min., 105 °C (200 – 500 psi) 90 min., 176 °C (500 psi) 30 min. and then 250 °C post cure for 1h. The same resin was blended with vapor grown carbon fibers (VGCF) (~150nm dia., from Applied Sciences) and cured in the same manner to give a composite with 30 wt% VGCF, 3.5 wt% POSS-**1** and the 66.5 wt% resin. True curing between **1** and the phenolic resin occurs via the epoxy functions. This was confirmed by cryogrinding the resin and extensive extractions. No **1** could be extracted.

This resin (95% phenolic/5% POSS **1**) exhibited higher bending storage moduli, E', both above and below T_g, and a higher T_g than the pure phenolic resin (see Fig. 1). Even after the fibers had been added, both E' and T_g increased with POSS-**1** present.

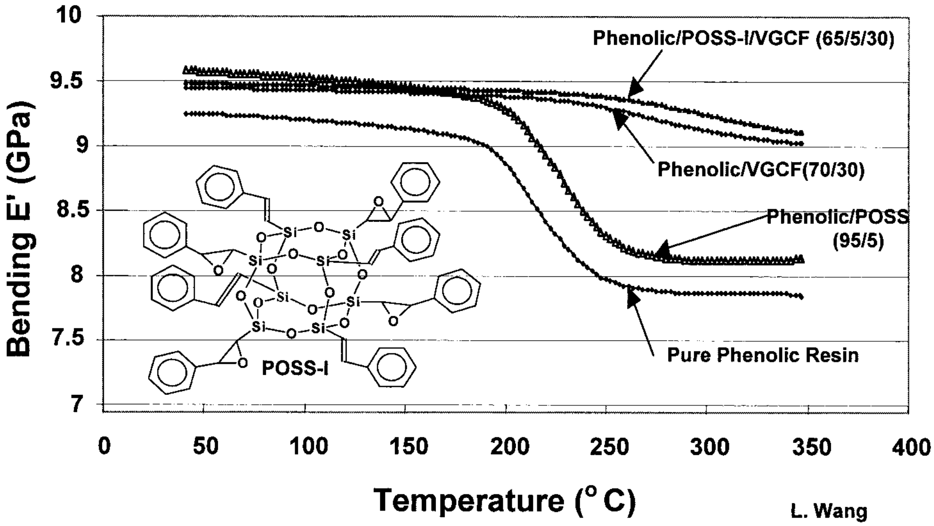
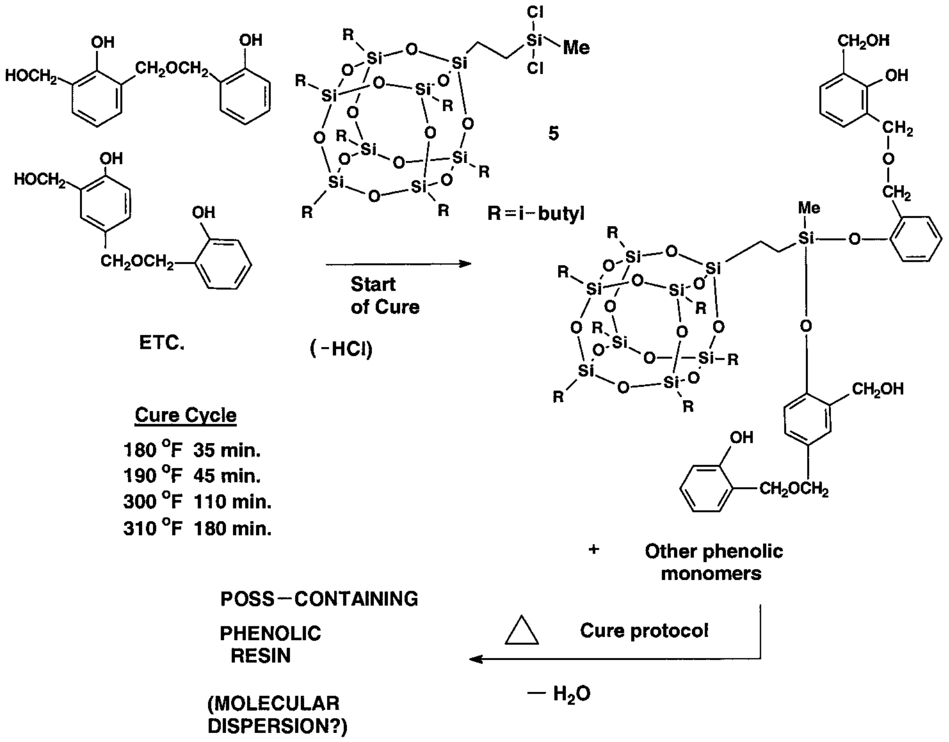


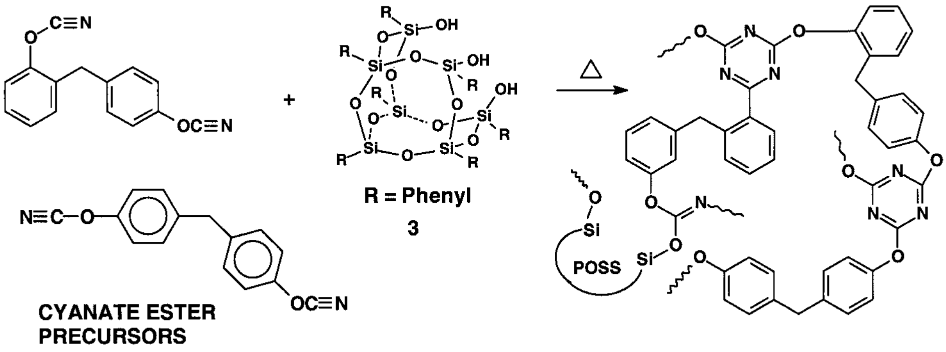
Figure 1. Bending E' (GPA) vs. temperature of different phenolic/VGCF/POSS-1 and related composites at 10 Hz.

Trisilanophenyl POSS, **3**, and dichlorosilylisobutyl-POSS, **5**, have also been cured into resole phenolic resins (Bordon SC 1008 and Hitco 134A). Monomer **3** is soluble in phenolic resins. POSS-**3** is a strongly hydrogen bonding molecule, facilitating its miscibility. This bonds **3** it into the resin during resin curing at higher temperatures. Its phenyl substituents appear to react with methylol functions to form methylene bridges. The states of aggregation of POSS-**3** in these resins is under study. POSS-**5**, in contrast to **3**, reacts very rapidly at low temperature with hydroxyl groups in the resole resin long before curing starts. This occurs due to the presence of the extremely reactive dichlorosilyl moiety. Thus, POSS-**5** is bound to resin molecules prior to cure. After curing it is likely the POSS centers are molecularly dispersed at low mole percents of **5**. This process is shown in Scheme 3 along with the curing protocol for phenolic resin with either **3** or **5**.



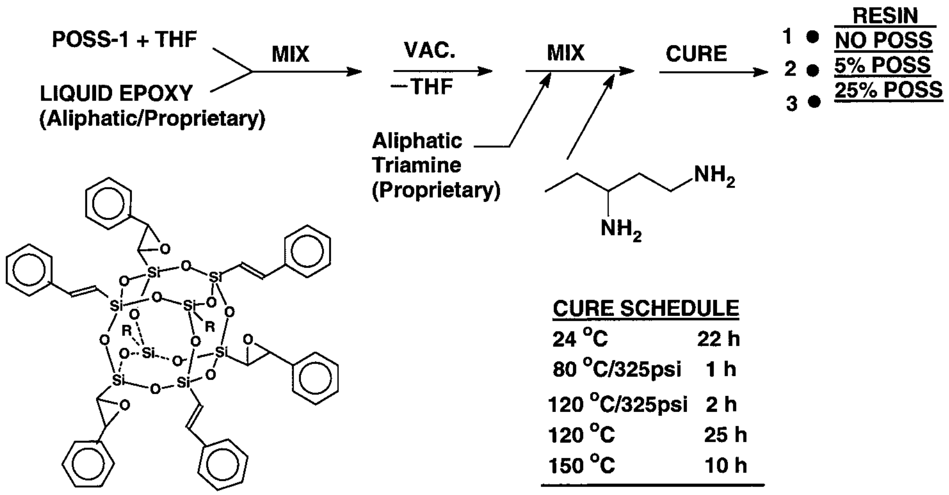
Scheme 3. Phenolic resin/POSS-**5** nanocomposite

Trisilanolphenyl POSS-**3** was dissolved in THF and blended with the liquid cyanate ester resins PT-15 and PT-30 (Lonza Inc.) Then THF was removed *in vacuo* at 80 °C. The temperature was raised to 90 °C for 3h and then to 188 °C (2h), 200 °C (5 min.) and then the temperature was raised 10 °C every 5 min. to 250 °C where it was held 2.5h. Finally, a 300 °C (30 min.) post cure was performed. Direct preblending of **3** with PT-15 resin at 120°C was also successful. In addition to thermal curing, metal acetonylacetate/nonylphenol catalyst mixtures were used. Catalysts must be added after **3** has been blended and the liquid blend is cooled, because curing occurs too rapidly to permit complete dissolution of the POSS at the higher temperatures used for this POSS mixing step. Cyanate esters cure by cyclotrimerization of isocyanate groups to form a trisubstituted triazine (Scheme 4). Therefore, no low molecular weight condensation products are driven off, unlike the curing of phenolic resins where water is extruded. For this reason, we are examining cyanate esters as thermally stable resin precurors for further pyrolysis to carbon-carbon materials. Carbonized cyanate ester resins should be denser than those made from phenolic resins. Therefore, expensive impregnation / repyrolysis / densification steps (required using phenolic resin precursors) may be unnecessary. The purpose of incorporating molecularly dispersed, or nano-sized aggregates of POSS in the cured cyanate ester resins is to use these nanocomposites to generate carbon/carbon materials with silica nanophases. These should stabilize the resulting carbon for use at higher temperatures because the silica-like nuclei should be effective char promoters and oxygen permeation barriers.



Scheme 4. Formation of cyanate ester/POSS-**3** resins

Multifunctional POSS-**1** has been cured into epoxy, vinyl ester and dicyclopentadiene resins. The four epoxy groups in **1** participate in the curing of Clearstream 9000, an aliphatic epoxy resin with its corresponding aliphatic amine curing agent (Clearstream Resins Inc.)[34] It was difficult to dissolve **1** into the resin directly. Therefore, the epoxy resin and **1** were dissolved in THF and the THF was removed to give a clear fluid which was then cured. When cured at an upper temperature of 120 °C (Figure 2) the Tg values dropped as the POSS content increased.[34] The Tg regions became wider (Figure 2) and the bending storage moduli of the resins increased at temperatures above Tg. The Tg value increments in all these systems increased when the cure temperature was raised to 150 °C. TEM studies of a 5 wt% POSS-1/epoxy resin appeared free of any phase separation, suggesting that molecular dispersion of the POSS had occurred.[34] However, EELS and elemental density mapping has not yet been carried out, so some degree of POSS aggregation has not yet been ruled out.



CURE SCHEDULE	
24 °C	22 h
80 °C/325psi	1 h
120 °C/325psi	2 h
120 °C	25 h
150 °C	10 h

POSS 1

Figure 2a. Synthesis and cure of epoxy/POSS-**1** resins.

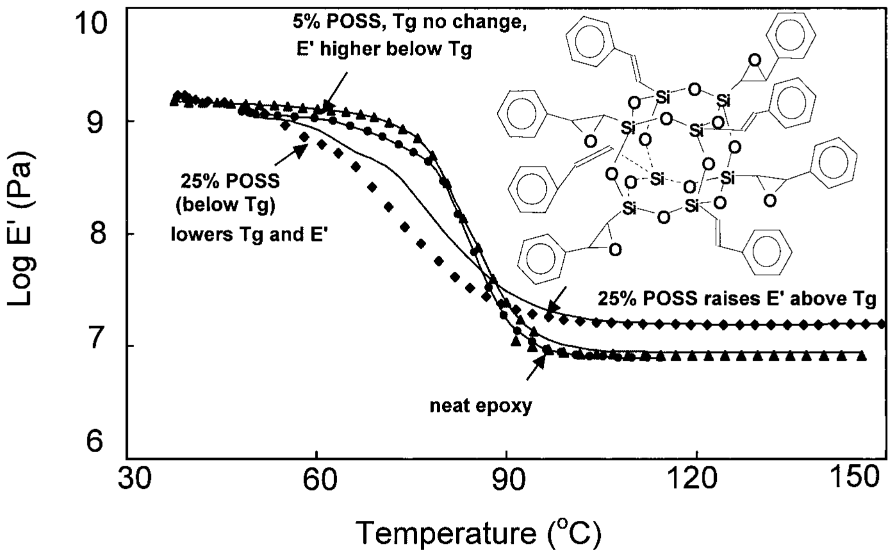
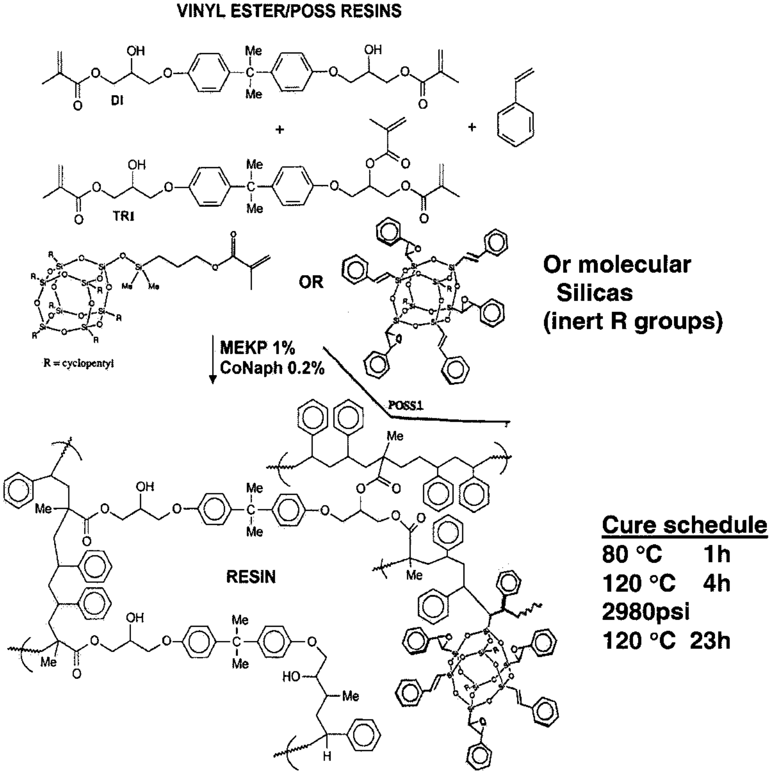


Figure 2b. Bending modulus (E') versus temperature curves at 1Hz (from DMTA) for an aliphatic epoxy resin and its epoxy/POSS 95/5 and 75/25 (wt/wt) composites after final curing at 120 °C/25h.

POSS-**1** was also dissolved in styrene and blended into the commercial vinyl ester, Derakane™ 510C-350 (from Dow Chemical Co.) This compatible liquid system was then cured at room temperature (24h), 90 °C (24h) and 150 °C (5h) using a 1% methyl ethyl ketone peroxide/0.2% cobalt naphthanate catalyst system.[35] This is shown in Scheme 5. Other vinyl ester resins were made with POSS methacrylate, **6**, but these will not be discussed here. All the resins contained 50 wt% styrene. POSS-**1** was incorporated in 5 and 10 wt% into these thermoset resins. The flexural strength dropped from 192 to 175 and 152 MPa with 5 and 10 wt% POSS added into the blends.[35] The extent of strain at failure decreased with increasing levels of POSS. DMTA measurements confirmed that the bending storage moduli of the vinyl ester/POSS-**1** resins were higher than that of vinyl ester resin without POSS at temperatures below T_g. The storage moduli increased greatly with an increase in the POSS-**1** content above T_g. The storage modulus enhancement was larger at temperatures lower than T_g (e.g. in the glassy region). Specifically, at 40 °C the bending storage moduli were 1.24, 1.96 and 1.58 GPa for the pure vinyl ester and the vinyl ester with 5 wt% and 10 wt% POSS, respectively. T_g values also increased with more POSS content.



Scheme 5. Vinyl ester/POSS resins

Swelling studies showed almost no uptake of THF or toluene by the vinyl ester/POSS-**1** composites after 50 days.[35] Furthermore, no POSS-**1** could be recovered on extensive extraction of fragmented samples. TEM micrographs showed no discernable phase separation of POSS at a resolution of 1-2 nm. However, EDAX and EELS studies of Si and Br (from a bromine containing label used) provided evidence of some phase separation of Si–rich regions at a small size scale in the VE/POSS-**1** (10 wt.%) sample (Figure 3).[35] POSS-rich dispersed phases with sizes of 75nm to 1 – 2nm were observed by EELS. All of the epoxy/**1** and vinyl ester/**1** (5 wt.%) composites appeared to largely exhibit molecular level dispersion of chemically-bound POSS-**1**. This illustrates the importance of early chemical bonding of a POSS derivative into the developing crosslinked resin's network structure during the cure. As curing occurs, the entropy of mixing term will contribute less and less to the thermodynamics of POSS monomer solubility. However, before phase separation of the POSS can occur due to a lowering of solubility, the chemical bonds formed between the POSS and the developing resin matrix lock POSS molecules into the resin structure. Thus, migration and phase separation don't occur, or only partial separation takes place. This stands in sharp contrast to the behavior of T_8, T_{10} and T_{12} (Scheme 1) POSS molecules where none of the corner groups have a polymerizable function (e.g. R = *i*-Bu, cyclopentyl, cyclohexyl or phenyl). These molecules regularly phase separate from (or don't dissolve in) and vinyl ester resins. We have observed dispersed POSS particle (phase) sizes from 50nm to 300μm under a variety of conditions with these types of POSS derivatives in cured resins.[36]

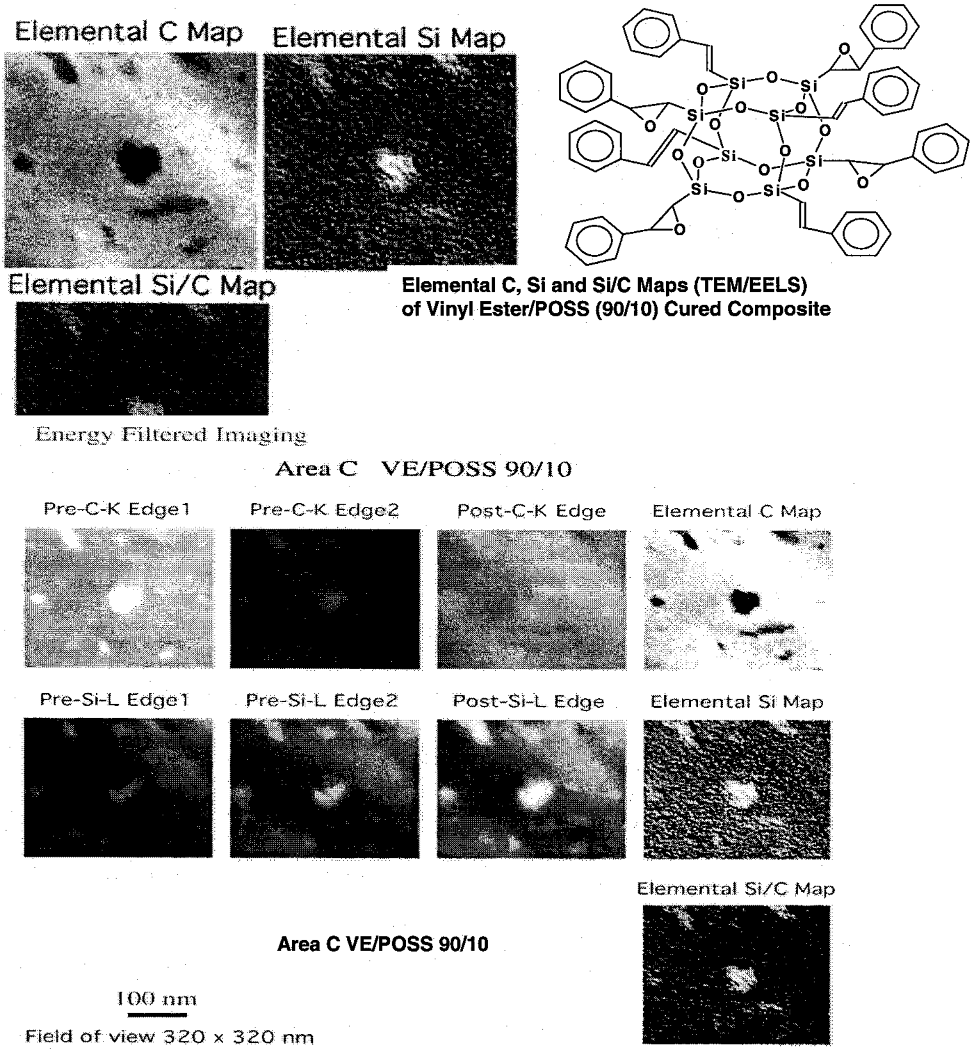
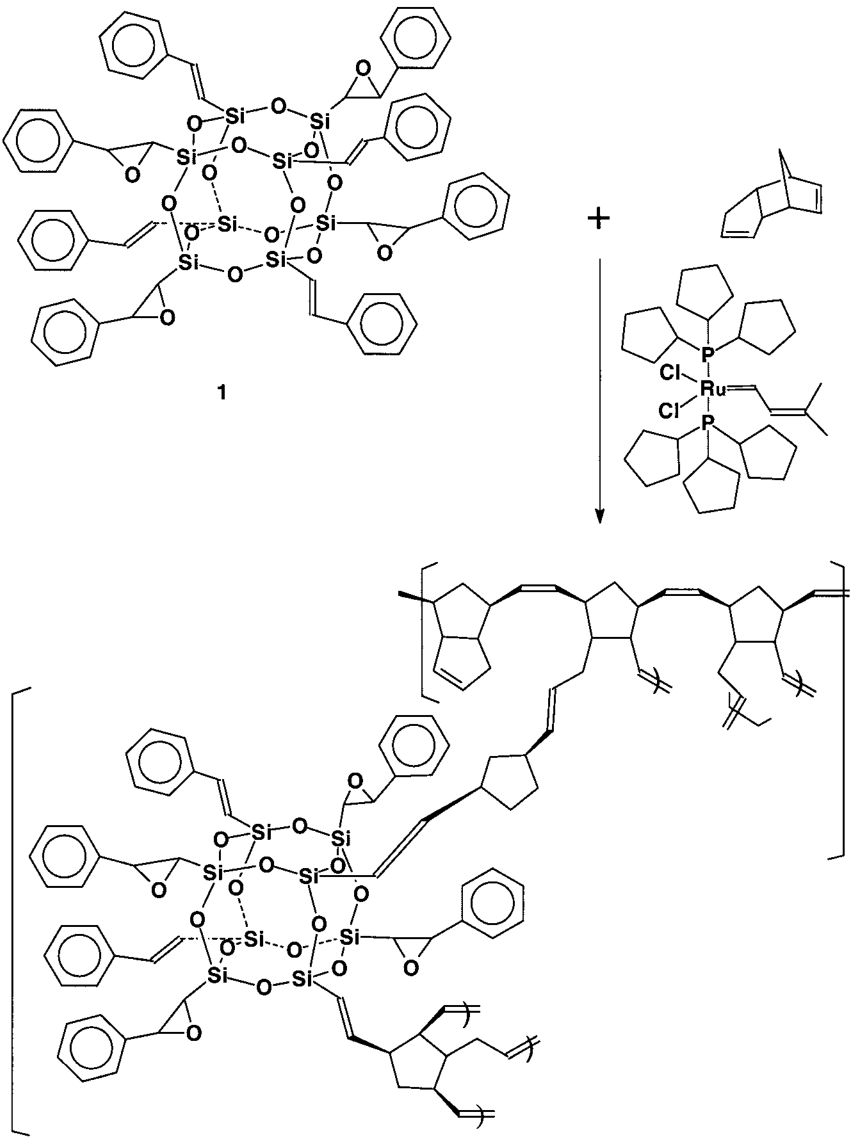


Figure 3. Nanoscale POSS aggregation in cured Derakane 510C-350 (50 wt% styrene) vinyl Ester resins, containing POSS-**1**.

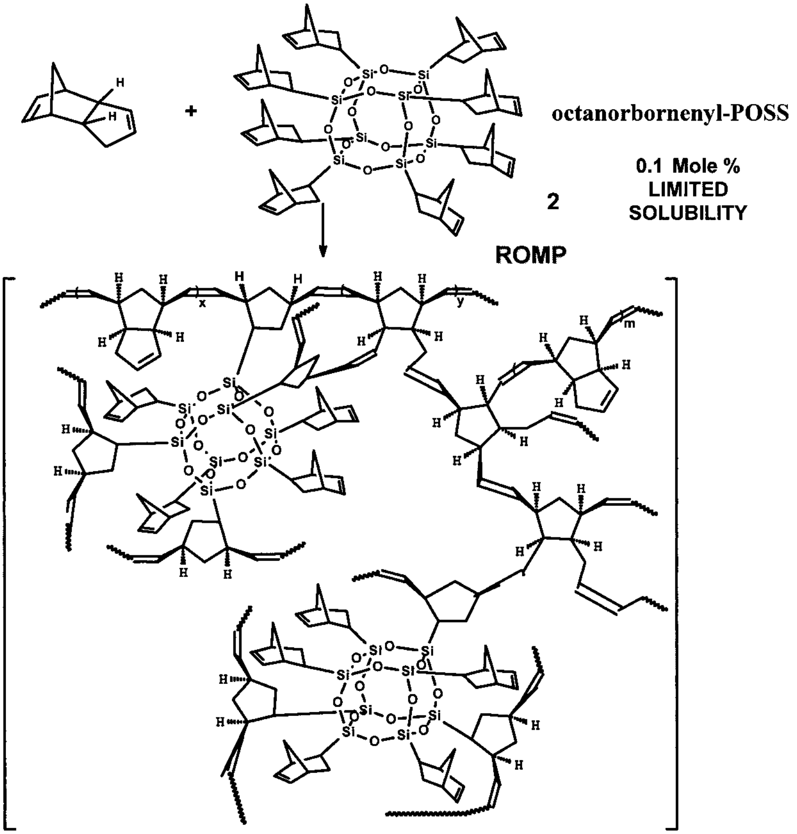
POSS-**1** was dissolved into dicyclopentadiene (DCPD) and this monomer mixture was cured by ring-opening metathesis polymerization (ROMP) using the specific Grubb's catalyst: 3-methyl-2-butenylidene-bis(tricyclopropylphosphine)dichlororuthenium (Scheme 6). The metathesis proceeded on the O_3Si-corner-substituted β-phenyl olefinic moieties of POSS-**1**. Vigorous extractions of finely ground resin did not result in any recovery of **1**, confirming its chemical bonding into the resin via ROMP. Resins were made by the same curing protocol containing as much as 20 wt% POSS. The T_g and E' values of these DCPD resins increased as small amounts of POSS were incorporated but once ~10 wt% POSS-**1** had been added, no further increases occurred.

Specifically, the T_g value of the DCPD resin (182.5 °C) increased by 5.8 °C to 188.3 °C when only 1 wt% of **1** was added. The DCPD/5 wt% **1** resin exhibited a bending storage modulus at 10Hz of 1.54GPa at 40 °C and 0.032GPa at 240 °C which may be compared to those of the pure DCPD resin which were 1.45GPa and 0.027GPa, respectively. Thus, despite the effect that the volume occupied by POSS has on lowering the DCPD resin's crosslink density, the storage modulus increased because POSS-**1** became chemically bound into the resin, probably by forming more than one bond per POSS. These POSS moieties constitute new crosslinks (Scheme 11). All these data confirmed that POSS-**1** actually was, on average, bound into the resin by more than one chemical bond. Thus, ROMP took place readily enough on the β-siloxy-substituted styrene function to multiply bond the cage into the resin. However, the relative rates of the ROMP reaction on **1**, versus the strained norbornene and unstrained cyclopentyl double bonds of DCPD, are unkown. Therefore, one does not know whether or not **1** is, on average, incorporated early or late into the resin. Later average ROMP of **1** would lead to an increased tendency for POSS phase separation or aggregation. TEM/EEL studies have not been done on these resins.

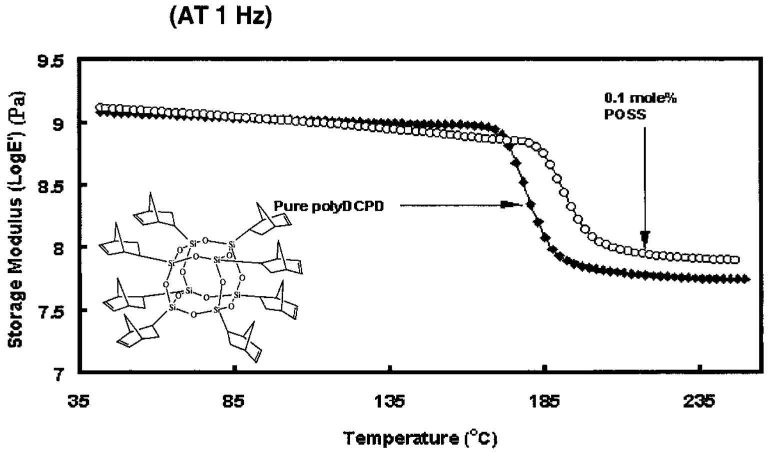


Scheme 6. Copolymerization of polyfunctional POSS-1 with dicyclopentadiene

A second multifunctional POSS macromer, **2**, was ROMPed with DCPD using the same catalyst shown in Scheme 6 during the preparation of DCPD/POSS-**1** resins.[36] Octanorbornenyl POSS, **2**, contains eight reactive norbornene functions. Thus, it should rapidly be incorporated into the developing DCPD resin network and it should be a crosslinking center, itself. However, **2** is extremely insoluble in about 15 solvents ranging from polar to nonpolar, dipolar aprotic to aromatic etc. After high shear stirring in liquid DCPD at 40 and 80 °C, only 1/10 of 1 mole % of **2** could be dissolved! However, after ROMP (Scheme 7), the resulting DCPD resin's T_g was increased by 15 °C! Thus, this tiny amount of POSS uptake into the resin matrix enhanced significantly both the T_g and the storage modulus, E' in the rubbery region (see Figure 4).



Scheme 7. Ring-opening metathesis curing of DCPD with octanorbornenyl POSS-2



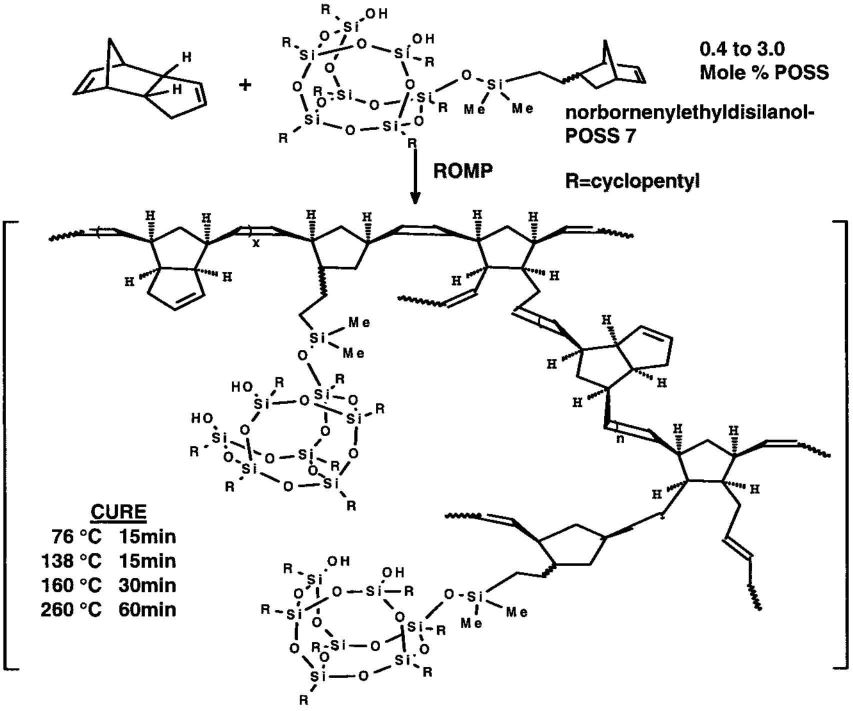
Tg INCREASES ~ 15 °C WITH 0.1 MOLE % POSS ADDITION

Figure 4. Bending storage moduli, E', vs. temperature for poly(DCPD) versus poly(DCPD-co-0.1 mole % octanorbornenyl POSS-**2**).

A likely explanation of the strong effect of **2** on T_g and E' involves early incorporation of the dissolved **2** into the developing matrix, since each macromer contains eight reactive functions. Furthermore, a fairly high crosslink density probably develops around each POSS cage. This may increase the net crosslink density of the overall resin, more than making up for the volume of the POSS moiety which lowers the volume average density of crosslinks, stemming from the original DCPD molecules.

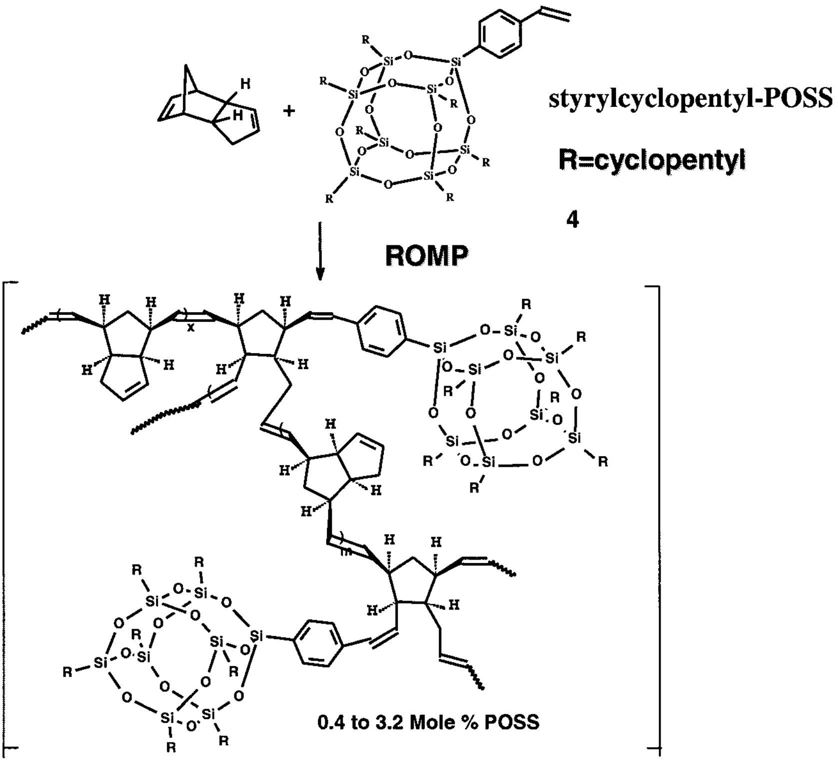
Monofunctional POSS monomer incorporation

Norbornenylethyldisilanol POSS, **7**, and styrylheptacyclopentyl POSS, **4**, are both monofunctional POSS macromers. We have incorporated both of these into DCPD resins via ROMP. The partially opened cage monomer **7** was incorporated in from 0.4 to 3.0 mole % amounts (using the same ruthenium catalyst employed for **1** and **2**) with the final cure stages conducted at either 260 °C or 280 °C for 2hr. (Scheme 8). The POSS-**7** could not be extracted despite vigorous attempts to do so, confirming its chemical bonding into the matrix. However, **7** is monofunctional and cannot serve as a crosslinking site. Due to the large volume of the monomer, its incorporation will lower the cross-link density of the highly cross-linked DCPD resin. Indeed, this interpretation explains the lower T_g values of these POSS-containing resins versus that of the DCPD resin without POSS. The T_g values for resins cured to 260 °C were 182.5 °C for pure DCPD, 172.6 °C for DCPD/5 wt% **7**, and for DCPD/10 wt% **7**. When the final cure temperature was raised to 280 °C, the pure DCPD resin exhibited a higher T_g value and a lower intensity Tanδ peak temperature versus its POSS-containing counterpart. This is in accord with a lower crosslink density per unit volume for the POSS-containing resin.

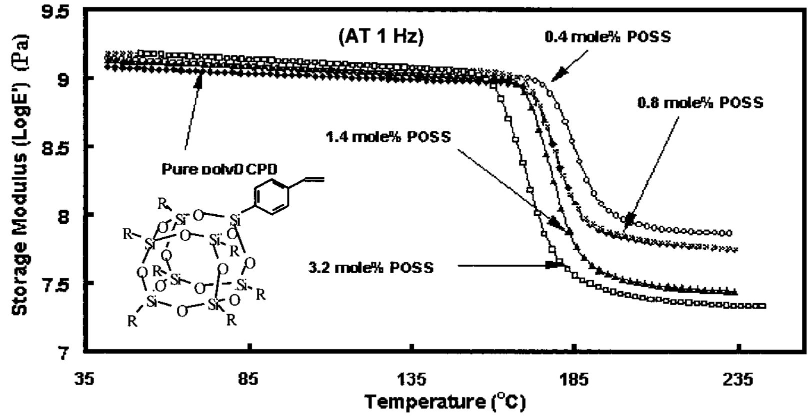


Scheme 8. ROMP of DCPD with POSS-7

Styrylheptacyclopentyl POSS, **4** also was copolymerized with DCPD via ROMP using the same Grubb's catalyst mentioned earlier (Scheme 9). POSS-**4** was incorporated in 0.4, 0.8, 1.4 and 3.2 mole % amounts. Upon the addition of 0.4 mole % of **4**, the T_g increased as did the bending modulus E' both above and below T_g. However, the T_g and E' dropped after 1.4 mole % of **4** had been incorporated and these values dropped even further upon 3.2 mole % **4** addition. These results are shown in Figure 5. Apparently, monofunctional POSS-4 addition lowers the crosslink density and increases free volume.



Scheme 9. ROMP of DCPD with styrylcyclopentyl POSS-4



POLY(DCPD)/STYRYLCYCLOPENTYL-POSS NANOCOMPOSITES

Figure 5. A small amount of POSS: T_g increases, E' increases above and below T_g. Adding more POSS: T_g decreases, E' decreases above T_g, E' increases below T_g.

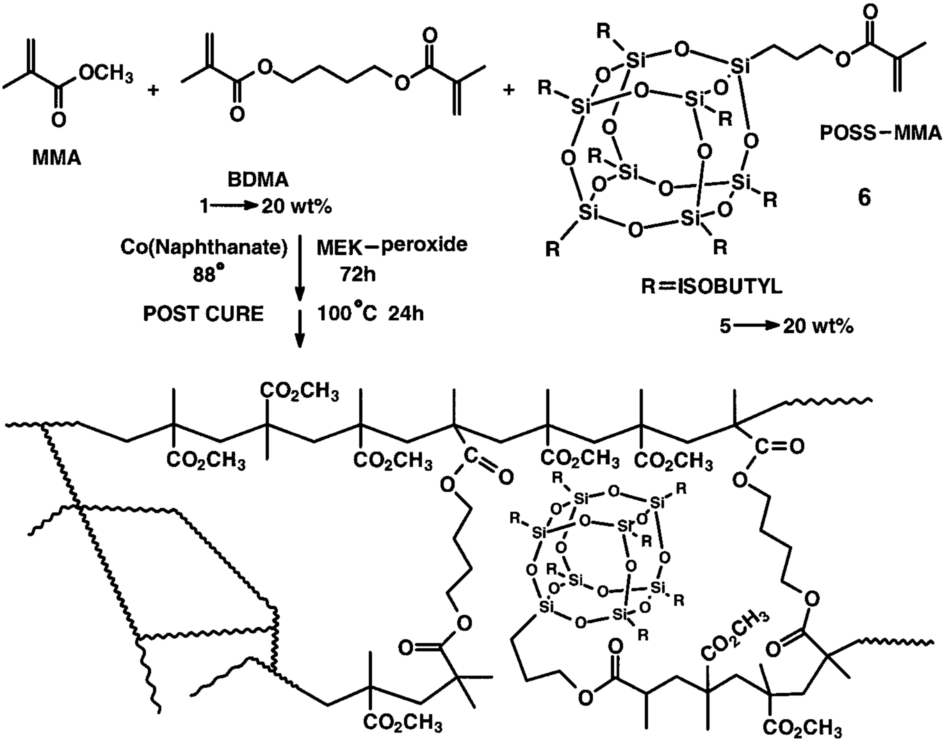
Resin have now been synthesized using POSS-4 with styrene and divinylbenzene (DVB).[37] A matrix of various Sty/DVB/POSS-4 resins was made at several crosslink densities by adjusting the DVB concentrations (0.3, 1.0 and 5.0 wt%). At each crosslink density five different POSS-4 stoichiometries were synthesized (1.0, 5.0, 10.0, 15.0 and 20 wt%) to provide a total of 15 resins. Thus, the effects high POSS-4 contents (e.g. 15 and 20 wt%) could be studied at both low (0.3% DVB) and high (5% DVB) crosslinking densities. These effects could be compared to the effects of low POSS-4 contents (1 and 5 wt%) at both low and high crosslink densities. This series of resins will eventually allow us to examine POSS aggregation as a function of crosslinking and POSS stoichiometry.

The values of the bending storage moduli, Tg and bending tanδ peak intensities are shown in Table 1 for the lightly crosslinked (0.3% DVB) resins as the content of POSS-4 was increased. The E' values increased both above and below T_g. The tanδ curves broadened and their intensities decreased as the POSS-4 content went up. However, these Tanδ intensities were higher than that for the sty/0.3 wt% DVB control resin until the POSS content exceeded 5 wt%. It would appear that lower levels of POSS incorporation induced more free volume into the resin (or lowered the crosslink density per unit volume). A similar trend was observed in the T_g values. Adding 1 wt% POSS-**4**, lowered T_g from 92.5 to 91 °C. Thereafter, the T_g was higher. Unlike the pure sty/0.3% DVB resin and lower POSS-**4** content resins, a large increase in the original T_g was observed upon reheating the 0.3% DVB resins containing 15 and 20 wt% POSS-**4**. For example, the T_g increased from 95 °C to 110 °C for the sample with 15 wt% POSS-**4** on the second heating. We suspect that conformational reorganizations of the loosely crosslinked 0.3% DVB network occurs and this internal structural change allows POSS-**4** moieties to aggregate. Thus, the second heating must overcome these forces of aggregation or clustering to activate segmental motion which had previously been activated at the original T_g.

Table 1. Properties of styrene/0.3 wt%DVB/ POSS-**4** resins as a function of POSS-**4** content.

POSS-4	Bending Storage Moduli		T_g		Bending Tan δ
Content (wt%)	E' (40°C) (Gpa)	E' (125°C) (MPa)	from Tan δ peak (°C)		peak on first heating
			First Heating	Second Heating	
0	1.496	0.375	92.5	92.6	2.35
1	1.481	0.551	91.0	90.6	2.55
5	1.525	0.546	96.5	97.3	2.48
15	1.704	0.825	95.0	110.0	2.06
20	1.705	0.733	97.0	110.0	1.91

A methacrylic resin series was synthesized which incorporated 3-methacrylylpropyl heptaisobutyl POSS-**6**. Methyl methacrylate (MMA), 1,4-butane dimethacrylate (BDMA) and POSS-**6** were cured by radical initiated polymerization using a methyl ethyl ketone peroxide/Cobalt naphthanate catayst system at 88 °C, followed by a 100 °C/24h postcure (Scheme 10). Twenty-five of these resins were made. The crosslink density was varied into five levels, where the wt% BDMA was 1%, 5%, 10%, 15% and 20%. At each of these BDMA wt% levels, four different amounts of POSS-**6** was incorporated (e.g. 0%, 5%, 10%, 15% and 20%). Then dynamic mechanical properties, swelling studies and densities were obtained.



Scheme 10. Formation of MMA/BDMA/POSS-**6** resins via a radical initiated cure

The T_g and E' (above and below T_g) values, swell ratios in THF and density measurements are summarized in Table 2 for MMA/BDMA/POSS-**6** resins with low crosslink densities (e.g. with 1 and 5 wt% BDMA). The T_g values become lower as the amount of POSS-**6** increases from 0 to 20 wt% at both 1 and 5 wt% BDMA crosslink densities. These differences are larger for the less crosslinked (1 wt% BDMA) resins. A drop also occurs in bending moduli, E', (below T_g) as the POSS-**6** content goes up. The changes in E' at 180 °C are irregular and may involve changes in POSS-**6** interactions within the resin matrices. The swelling ratios (volume in THF/dry volume) of the 1 wt% BDMA resins was always higher when POSS-**6** was present. At the higher crosslink density of 5 wt% BDMA, the swelling ratio increased going from 0 to 5 to 10 wt% POSS-**6** before dropping at 15 and 20 wt% POSS-**6**. In all cases the resin densities dropped upon increasing the amount of POSS-**6**. Therefore, it seems clear that the addition of POSS-**6** lowers crosslink density and increases the free volume in these two sets of methacrylic resins.

Table 2. Properties of MMA-co-BDMA-co-POSS-**6** resins with low crosslink densitites.

Composition wt%			Tg (°C)	E' (40 °C) GPa	E' (180 °C) MPa	Swell Ratio (THF)	*p* g/cm^3
MMA	BDMA	POSS					
99	1	0	132.2	1.573	1.599	3.14	1.188
94	1	5	126.9	1.464	0.900	3.97	1.186
89	1	10	127.6	1.416	1.251	3.69	1.183
84	1	15	126.2	1.323	1.192	3.57	1.179
79	1	20	123.7	1.136	0.920	3.66	1.176
95	5	0	133.0	1.298	2.001	2.55	1.188
90	5	5	132.2	1.585	2.141	2.66	1.185
85	5	10	130.2	1.361	2.331	3.34	1.182
80	5	15	129.4	1.117	1.551	2.11	1.180
75	5	20	129.1	1.101	2.199	2.17	1.175

Table 3 summarizes the same properties for a series of MMA/BDMA/POSS-**6** resins with high crosslink densities (10 and 20 wt% BDMA). Again, the values of T_g drop steadily with an increase in POSS-**6** at 10 wt% BDMA but at 20 wt% BDMA this trend no longer exists. As more POSS-**6** is added, the low temperature E' values and the densities steadily decrease in both sets (10 and 20 wt% BDMA) of resins. No clear trends are observed in the swelling ratios or E' (180 °C) values as the POSS-**6** content is increased in the highly crosslinked (10 and 20 wt% BDMA) resins.

Table 3. Poly(MMA-co-BDMA-co-POSS-**6**) networks with high crosslink densities.

Composition wt%			Tg (°C)	E' (40 °C) GPa	E' (180 °C) MPa	Swell Ratio (THF)	*p* g/cm^3
MMA	BDMA	POSS					
90	10	0	140.4	1.256	3.877	1.94	1.188
85	10	5	139.1	1.573	3.756	2.05	1.185
80	10	10	137.7	1.404	4.718	1.98	1.180
75	10	15	133.4 ↓	1.293 ↓	3.701	2.12	1.172 ↓
80	20	0	150.3	1.364	11.992	1.46	1.188
75	20	5	154.4	1.341	11.355	1.59	1.184
70	20	10	151.6	1.206	11.674	1.63	1.182
65	20	15	151.8	1.204 ↓	10.730	1.54	1.177
60	20	20	155.6	1.171	11.097	1.72	1.176 ↓

Conclusions

POSS-containing resin systems can exhibit a range of behaviors depending on (1) the nature of the R-groups on POSS, (2) if multiple or single polymerizable groups are present on POSS, (3) the reactivity of the polymerizable functions versus those of the other monomers, (4) the tendency of the POSS system to aggregate both before and after polymerization, (5) the POSS stoichiometry, (6) the crosslink density and many other features. The studies of crosslinked resins containing these hybrid systems is in its infancy.

Acknowledgements

This work was supported by the Air Force Office of Scientific Research, Grant No. F49620-02-1-0260 (Polymer Organic Matrix Composite Program) and by the Air Force Office of Scientific Research STTR Contract No. F49620-02-C-0086.

[1] R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem.Rev.* **1995**, *95*, 1409.
[2] D. W. Scott, *J. Am. Chem. Soc.* **1946**, *68*, 356.
[3] J. F. Brown Jr., J. H. Vogt Jr., A. Katchman, J. W. Eustance, K. W. Kiser, K. W. Krantz, *J. Am. Chem. Soc.* **1960**, *82*, 6194.
[4] H. Adachi, E. Adachi, O. Hayashi, K. Okahashi, *Rep. Prog. Polym. Phys. Jpn.* **1985**, *28*, 261.
[5] H. Hata, S. Komasaki, *Japanese Patent* Kokai-S-59-108033, **1984**.
[6] X. Zhang, L. Shi, *Chin. J. Polym. Sci.* 1987, *5*, 197.
[7] G. Z. Li, M. L. Ye, L. H. Shi, *Chin. J. Polym. Sci.* **1994**, *12(4)*, 331.
[8] G. Z. Li, M. L. Ye, L. H. Shi, *Chin. J. Polym. Sci.* **1996**, *14(1)*, 41.
[9] G. Z. Li, T. Yamamoto, K. Nozaki, M. Hikosaka, *Polymer* **2000**, *41(8)*, 2827.
[10] G. Z. Li, T. Yamamoto, K. Nozaki, M. Hikosaka, *Macromolecular Chemistry and Physics* **2000**, *201*, 1283.
[11] J. F. Brown, Jr., *J. Polym. Sci., C* **1963**, *1*, 83.
[12] X. Zhang, L. Shi, S. Li, Y. Lin, *Polym. Degrd. Stab.* **1988**, *20*, 157.
[13] *Japanese Patent* Kokoku-S-60-17214 (1985), T. Suminoe, Y. Matsumura, O. Tomomitsu.
[14] *U.S. Patent* 4399266 (1983), Y. Matsumura, I. Nozue, O. Tomomitsu, T. Ukachi, T. Suminoe.
[15] *European Patent* 0406911A1 (1985), S. Fukuyama, Y. Yoneda, M. Miyagawa, K. Nishii, A. Matsuura.
[16] Z. Xie, Z. He, D. Dai, R. Zhang, *Chin. J. Polym. Sci.* **1989**, *7(2)*, 183.
[17] G. E. Maciel, M. J. Sullivan, D. W. Sindorf, *Macromolecules* **1981**, *14*, 1607.
[18] G. Engelhavdt, H. Jancke, E. Lippmaa, A. Samoson, *J. Organomet. Chem.* **1981**, *210*, 295.
[19] H. Adachi, E. Adachi, O. Hayashi, K. Okahashi, *Rep. Prog. Polym. Phys. Jpn.* **1986**, *29*, 257.
[20] C. L. Frye, W. T. Collins, *J. Am. Chem. Soc.* **1970**, **92**, 5586.
[21] V. Belot, R. Corriu, D. Leclerq, P. H. Mutin, A. Vioux, *Chem. Mater.* **1991**, *3*, 127.
[22] *U.S. Patent* 5942638 (1999), J. D. Lichtenhan, J. J. Schwab, F. J. Feher, D. Soulivong.
[23] J. D. Lichtenhan, J. J. Schwab, W. A. Reinerth Sr., *Chemical Innovation*, **2001**, *1*, 3.
[24] J. D. Lichtenhan, *Comments Inorg. Chem.***1995**, *17*, 115.
[25] A. Voigt, *Orgametrallics* **1996**, *15*, 5097.
[26] F. J. Feher, K. J. Weller, *Inor. Chem.* **1991**, *30*, 880.
[27] M. W. Ellsworth, D. L. Gin, *Polymer News* **1999**, *24*, 331.
[28] T. S. Haddad, R. Stapleton, H. G. Jeon, P. T. Mather, J. D. Lichtenhan, S. Phillips, *Polym.Prepr.* **1999**, *40(1)*, 496.
[29] L. Zheng, R. J. Farris, E. B. Coughlin, *J. Polym. Sci. A. Polym. Chem.* **2001**, *39*, 2920.
[30] A. J. Waddon, L. Zheng, R. J. Farris, E. B. Coughlin, *Nanoletters* **2002**, *2(10)*, 1149.
[31] L. Zheng, R. J. Farris, E. B. Coughlin, *Macromolecules* **2001**, *34*, 8034.
[32] L. Zheng, A. J. Waddon, R. J. Farris, E. B. Coughlin, *Macromolecules* **2002**, *35*, 2375.
[33] C. U. Pittman, Jr., L. Wang, H. Ni, G. Z. Li, Air Force Office of Scientific Research Polymer Matrix Composites Contractor Review Meeting, May 11-12, Long Beach, CA, 2001.
[34] G. Z. Li, L. Wang, H. Toghiani, T. L. Daulton, K. Koyama, C. U. Pittman, Jr., *Macromolecules* **2001**, *34(25)*, 8686.
[35] G. Z. Li, L. Wang, L. T. Daulton, C. U. Pittman, Jr. , Polymer **2002**, *43(15)*, 4167.
[36] C. U. Pittman, Jr., POSS^{TM} Nanotechnology Conference, **2002**, Sept. 25-27, Huntington Beach, CA, complete papers based on this conference are available on CD (contact Hybrid Plastics by e-mail at info@hybridplastics.com. Also see H. Ni, MS Thesis **2001**, Mississippi State University.
[37] C. U. Pittman, Jr., G. Z. Li, submitted for publication.