

Incorporation of Metallic POSS, POSS Copolymers, and New Functionalized POSS Compounds into Commercial Dental Resins

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ABSTRACT: An array of polyhedral oligomeric silsesquioxane (POSS) compounds, including metal, methacrylate, and amine functional POSS, and POSS copolymers were incorporated into aromatic and aliphatic dental resins. Heptaphenyl-propylamine POSS and methacrylate derivatives were synthesized by corner-capping and Michael addition reactions, respectively. The POSS compounds were tested for solubility in commercial resins at concentrations of 1, 5, 10, and 15 wt %, followed by UV polymerization of all soluble combinations. The POSS compounds generally increased

modulus and had an unpredictable effect on T_g . The modulus of the aliphatic resin increased 83% by incorporation of 15 wt % aluminum-phenyl POSS, while aromatic resins saw a maximum modulus improvement of 18% at 30°C and 72% at 160°C by incorporating 1 wt % of heptaphenyl-methacrylate POSS. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2856–2862, 2006

Key words: nanotechnology; dental polymers; modulus; POSS; methylmethacrylate; methacrylic acid

INTRODUCTION

Polymeric dental composites were introduced over forty years ago and are continuing to expand in use and properties. Areas for improvement include decreased polymerization shrinkage, increased wear resistance, biocompatibility, esthetics, and modulus of elasticity.¹ Nanotechnology in the form of inorganic-organic hybrid materials including sol-gel and nanofillers incorporation can be used to improve some or all of these properties.¹

One potential solution only recently available is the family of polyhedral oligomeric silsesquioxane (POSS) nanomaterials. POSS is a well-defined 3-dimensional silicate cage that can contain one or more functional group, allowing incorporation into diverse polymeric systems. Its uses range from unreactive fillers to covalently bound reactants. POSS is unique in that it is small (1.5 nm in core diameter) compared to other “nano” fillers, and that it is functionally tailorable to incorporate a wide range of reactive groups.² POSS derivatives have been shown to increase glass transition temperature, modulus, and decomposition temperature, reduce flammability, and increase oxygen permeability when incorporated into polymer matrices.^{2,3}

There are a few published studies on the effects of POSS on the properties of dental composites. Fong et al., studied the effect of an 8, 10, and 12 methacrylate-substituted POSS cage in popular dental resin formulations.⁴ Methacrylate POSS was substituted at varying percentages for bisGMA in a bisGMA/TEGDMA system.⁴ It was found that polymerization shrinkage remained unchanged, double-bond conversion decreased slightly as the mass fraction of POSS was increased, and mechanical properties improved with 2–10% POSS incorporation. At best, a 20% increase in flexural strength and a 35% increase in modulus were observed for the complete dental composite with 78% filler. At higher levels of POSS incorporation, from 10 to 50%, flexural strength, modulus, and tensile strength progressively decreased, presumably due to “over-crosslinking” and excessive inorganic content, both of which can cause brittleness.

Culbertson and coworkers, evaluated three different ways of incorporating a mono-methacrylate POSS into dental composites: one-pot polymerization of POSS and monomers, synthesizing a POSS-containing macromonomer and copolymerizing that with dental composite monomers, and synthesizing a POSS-containing copolymer followed by *in situ* polymerization with dental monomers.⁵ Simply mixing methacrylate-POSS into the dental formulation significantly reduced polymerization shrinkage but tended to decrease mechanical properties, especially at loadings

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greater than 10%. Synthesizing a POSS-containing macromonomer allowed the POSS to disperse better when mixed with the dental monomers, resulting in decreased shrinkage while increasing compressive strength by 23%, flexural strength by 60%, and tensile strength by 48%. Synthesizing a nonreactive POSS-containing copolymer followed by *in situ* polymerization with dental formulations yielded similar results. This work indicates that properly dispersing the POSS is critical to mechanical property enhancement.

The present work explores the effect on thermo-mechanical properties of incorporating a wide range of POSS compounds into two different commercial dental resins. POSS materials include methacrylate-containing species that can copolymerize with the resin, metal-containing POSS cages that may coordinate with the resin's carbonate groups, and POSS copolymers.

EXPERIMENTAL

Materials

The following materials were obtained from Hybrid Plastics, Hattiesburg, MS: aluminum-isobutyl POSS, aluminum-phenyl POSS, yttrium-isobutyl POSS, boron-isobutyl POSS, titanium-isobutyl POSS, trisilanol-phenyl POSS, aminoethylaminopropyl-isobutyl POSS, phenyl POSS/methacrylic acid copolymer, and phenyl POSS/methacrylic acid/methyl methacrylate copolymer. The following solvents were purchased from Fisher Scientific: methylene chloride, acetonitrile, toluene, acetone, and THF. 3-(Acryloyloxy)-2-hydroxypropyl methacrylate (AHM) and aminopropyltrimethoxysilane were purchased from Aldrich. Irgacure 651 was purchased from Ciba. An aliphatic and an aromatic dental resin were donated by Pentron Clinical Technologies, LLC, Wallingford, CT.

Characterization

^{13}C and ^1H solution NMR spectra were obtained on a Varian Mercury 300 MHz spectrometer, and ^{29}Si spectra were obtained on a Varian Mercury 500 MHz spectrometer. DMA was performed on a Rheometric Scientific DMTA V in tensile mode at a frequency of 1 Hz, a strain rate of 0.05%, and a ramp rate of $2^\circ\text{C}/\text{min}$ from 25°C up to 160°C . One sample from each formulation was analyzed.

POSS synthesis

Heptaisobutyl methacrylate POSS

To a 100 mL round bottom flask were added aminoethylaminopropyl isobutyl POSS (10 g, 11 mmol), AHM (5.8 g, 27.5 mmol), methylene chloride (25 mL), and a magnetic stir bar. This mixture was stirred and

refluxed for 2 days, followed by solvent removal with a rotary evaporator. The remaining white powder was stirred with acetonitrile for 1 h to remove residual AHM, filtered, and dried under vacuum at room temperature for 5 h. $^1\text{H-NMR}$ shows ~ 2.1 methacrylate groups per POSS cage. Total yield was 11.1 g (76%).

Heptaphenyl propylamine POSS

To a 100 mL round bottom flask were added trisilanol phenyl POSS (24.8 g, 26.6 mmol), toluene (40 mL), and a stir bar. The flask was placed in a dry ice/acetone bath and stirred for 5 min. Aminopropyltrimethoxysilane (6 g, 33.5 mmol) was added to the viscous, nearly frozen, solution. This mixture was allowed to stir and heated up to room temperature overnight. The resulting solution and the white precipitate were poured into an Erlenmeyer flask containing 100 mL of acetonitrile and the mixture was stirred for 10 min. The white precipitate was then collected by vacuum filtration on a Buchner funnel and dried under vacuum at room temperature for 16 h, yielding 18.1 g (68%) of white product. $^1\text{H-NMR}$ (300 MHz, ppm, CDCl_3): ~ 7.80 – 7.75 (m, 14H, ArH), ~ 7.49 – 7.36 (m, 21H, ArH), 2.69 (t, 2H, $-\text{CH}_2-\text{NH}_2$), 1.65 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{NH}_2$), 0.88 (t, 2H, $-\text{Si}-\text{CH}_2-\text{CH}_2-$). $^{13}\text{C-NMR}$ (75 MHz, ppm, CDCl_3): 134.45 (s, 14C, Ar), 131.05 (s, 7C, Ar), 130.46 (s, 7C, Ar), 128.16 (s, 14C, Ar), 44.85 (s, 1C, $-\text{CH}_2-\text{NH}_2$), 27.14 (s, 1C, $-\text{CH}_2-\text{CH}_2-\text{NH}_2$), 9.24 ($-\text{Si}-\text{CH}_2-\text{CH}_2-$). ^{29}Si (99.3 MHz, ppm, CDCl_3): -64.76 (s, 1Si), -78.30 (s, 4Si), -78.78 (s, 3Si).

Heptaphenyl methacrylate POSS

To a scintillation vial was added heptaphenyl propylamine POSS (1.07 g, 1.1 mmol), AHM (0.206 g, 0.96 mmol), methylene chloride (6 mL), and a magnetic stir bar. The vial was stirred and heated to 40°C for 16 h. The methylene chloride was removed on a rotary evaporator, leaving a white powder, which was placed in a vacuum oven at room temperature for 16 h. Yields were quantitative. $^1\text{H-NMR}$ (300 MHz, ppm, CDCl_3): ~ 7.78 – 7.75 (m, 14H, ArH), ~ 7.43 – 7.37 (m, 21H, ArH), 6.15 (s, 1H, $-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$), 5.59 (s, 1H, $-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$), 4.35–4.03 (m, 5H, $-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-$), 2.73 (t, 2H, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CO}-$), 2.62 (t, 2H, $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-$), 2.43 (t, 2H, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CO}-$), 1.96 (s, 3H, $-\text{O}-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$), 1.70 (m, 2H, $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-$), 0.87 (t, 2H, $-\text{Si}-\text{CH}_2-\text{CH}_2-$).

Preparation of solubility test samples

Both aliphatic and aromatic dental resins were dissolved in an equal weight of THF to create a low-

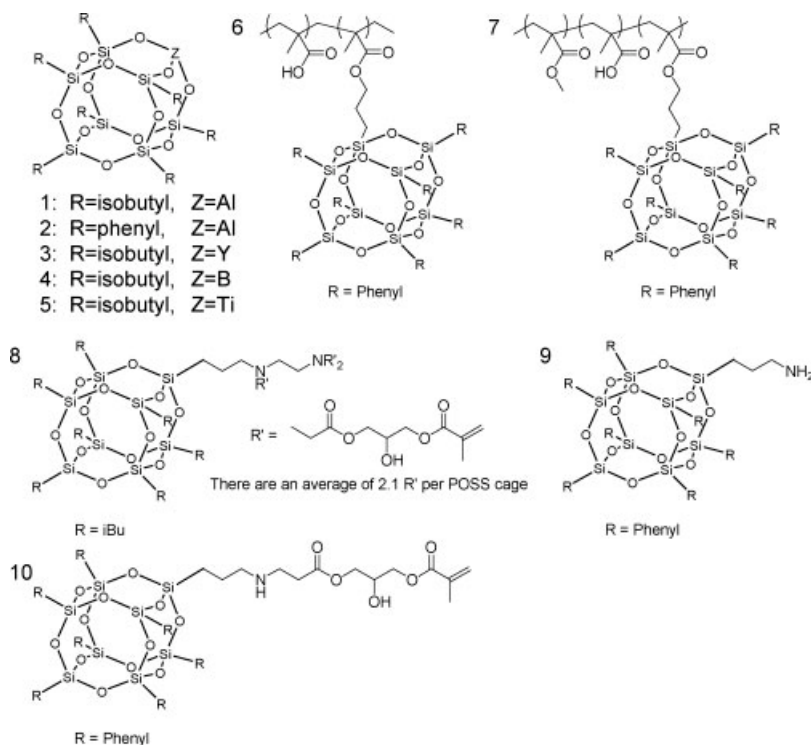


Figure 1 Chemical structures of POSS and POSS copolymers used in solubility screening.

viscosity 50 wt % resin solution. POSS samples were dissolved in THF to create a 5 wt % solution. Resin solution (1 g) and the appropriate amount of POSS solution were placed in a scintillation vial and shaken

by hand until homogeneous. The open vials were then placed in a fume hood and the THF allowed to evaporate for 24 h. The solubility of the POSS/resin mixture was determined by the clarity of the dried sample.

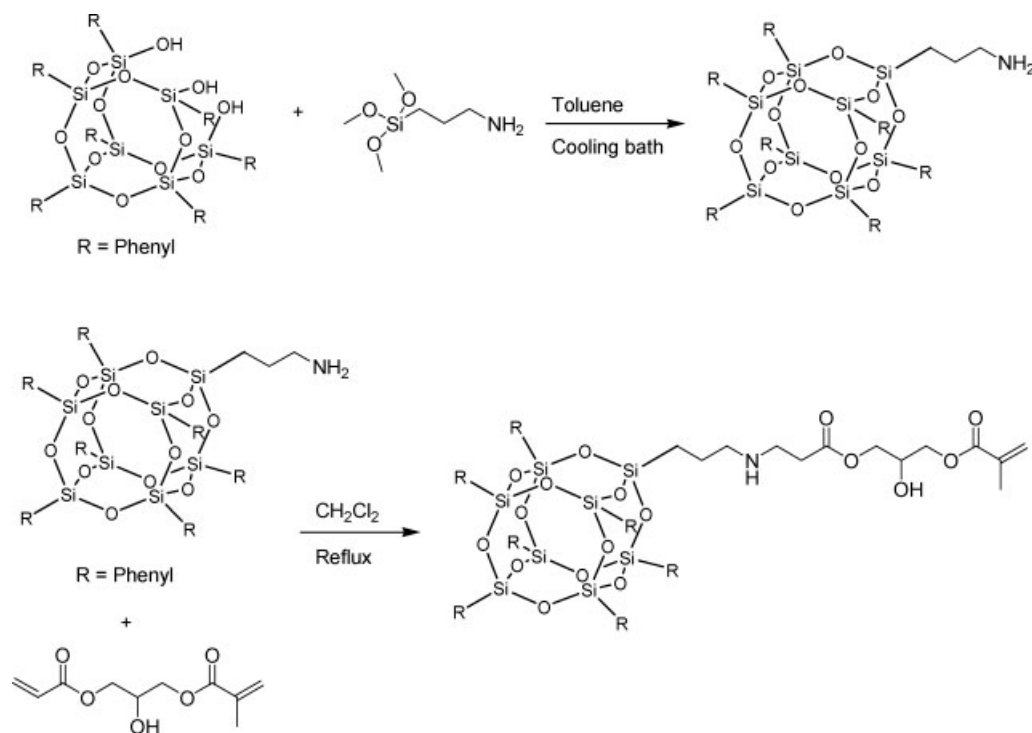


Figure 2 Synthesis of heptaphenyl propylamine POSS and heptaphenyl methacrylate POSS.

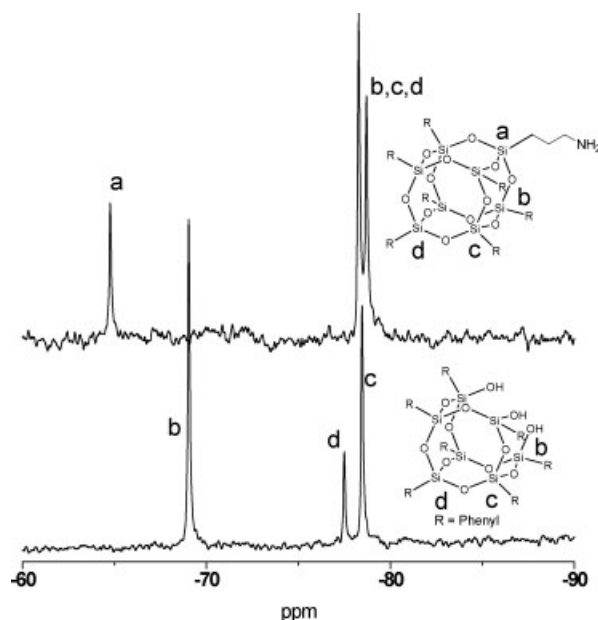


Figure 3 ^{29}Si -NMR of aminopropyl-phenyl POSS and the trisilanol starting material in CDCl_3 .

Preparation of films

Both aliphatic and aromatic dental resins were dissolved in an equal weight of THF to create a low-viscosity 50 wt % resin solution. POSS samples were dissolved in THF to create a 5 wt % solution. Irgacure 651 was dissolved in THF to form a 5 wt % solution. To a scintillation vial were added 4 g of resin solution, the appropriate amount of POSS solution, and the appropriate amount of photoinitiator solution (1 mol %, 11 mg for aromatic and 24 mg for aliphatic resins). The vials were shaken by hand until homogeneous and then poured into aluminum weigh pans. The pans were placed in a fume hood overnight to allow most of the THF to evaporate, then transferred to a vacuum oven with an acetone/dry ice trap for 4 h at room temperature. The pans, with a liquid monomer mixture, were removed from the vacuum oven and placed in a glass dish, covered with plastic wrap, purged with argon for 5 min, then irradiated with UV for 30 min (Blak-Ray Longwave Ultraviolet Lamp with a 100 W longwave mercury spot lamp). DMA samples were cut from the cured films with a razor blade.

RESULTS AND DISCUSSION

Synthesis of POSS derivatives

The structures of the POSS compounds used in this study are shown in Figure 1. Compounds 1 through 7 were obtained from Hybrid Plastics, whereas 8 through 10 were synthesized from POSS starting materials from Hybrid Plastics. Compound 8 was synthesized through a Michael addition reaction of the acry-

late of AHM with the primary and secondary amines of aminoethylaminopropyl-isobutyl POSS, similar to the reaction shown in Figure 2. The amount of substitution was calculated from proton NMR integration.

Compound 9 was synthesized through a condensation reaction of aminopropyltrimethoxy silane (APS) with an open-caged phenyl-substituted POSS shown in Figure 2. Various reaction conditions including temperature and solvent were tested, and it was found that the cold temperatures in toluene maximized yields, with the side product being an oligomeric POSS resin. Toluene was the only solvent which produced this product, seemingly due to the limited solubility of the starting materials and the product. The POSS trisilanol does not dissolve to any appreciable amount in toluene. Upon the addition of APS, everything dissolves after a few minutes of stirring. After an hour at room temperature, the product begins to precipitate. The same reaction in THF, in which both starting materials and products are readily soluble, produces only resin. This is the first report of synthesis of this POSS derivative.

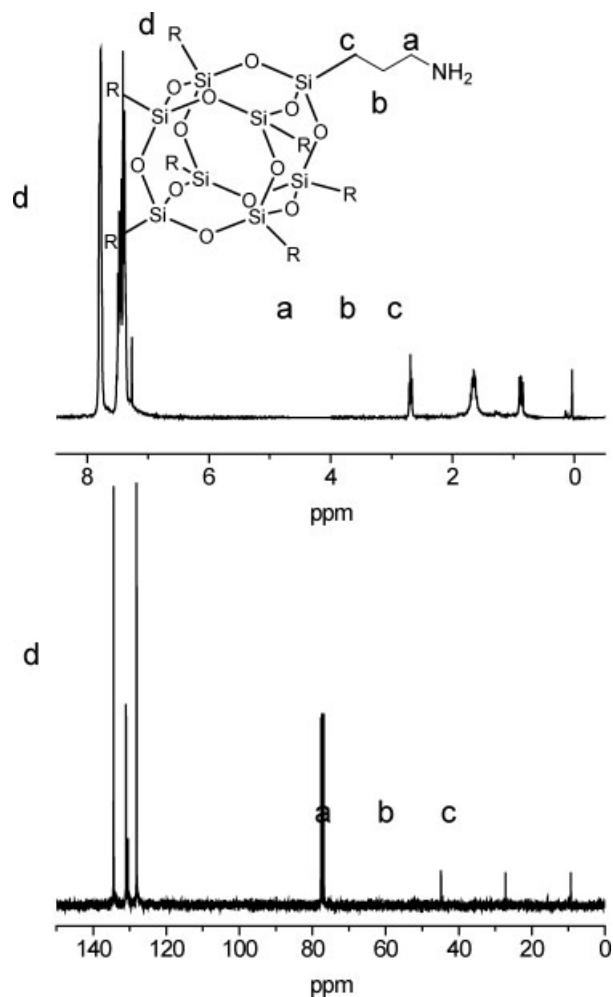


Figure 4 ^1H and ^{13}C -NMR of aminopropyl-phenyl POSS in CDCl_3 .

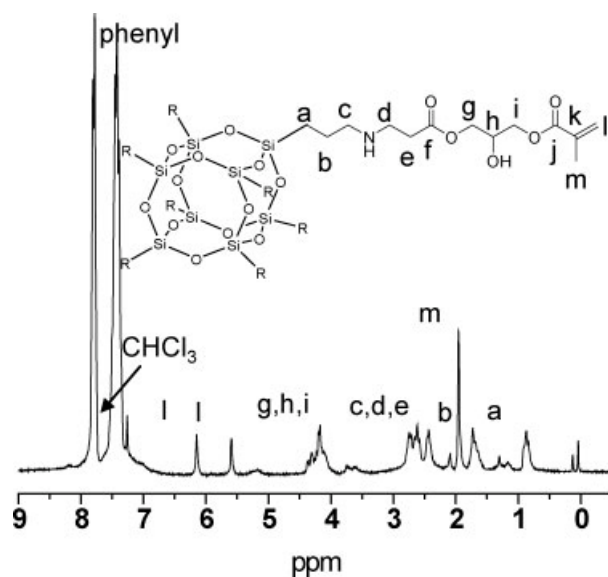


Figure 5 ^1H -NMR of methacrylate-phenyl POSS in CDCl_3 .

Figures 3 and 4 show the ^{29}Si , ^{13}C , and ^1H -NMR characterization of the product. Figure 3 shows both the starting material and the product for comparison. The starting material exhibits three peaks at -69.1 , -77.4 , and -78.5 ppm corresponding to the silanol, the silicon farthest away from the silanol, and the silicons next to the silanol, respectively. After the corner capping reaction, the product shows three peaks at -64.8 , -78.3 , and -78.7 ppm corresponding to the new corner silicon and the remaining silicons bonded to phenyl rings. ^{13}C and ^1H spectra show disappearance of the methoxy peaks of APS (50.6 ppm in CDCl_3), evidence of complete reaction.

Once this product was obtained and purified, compound 10 was synthesized through a Michael addition reaction with AHM, depicted in Figure 2. The addi-

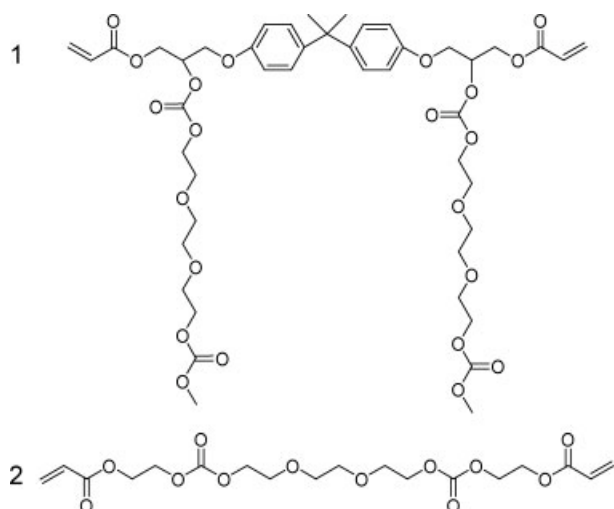


Figure 6 Chemical structures of dental resins, referred to as (1) aromatic and (2) aliphatic.

TABLE I
Solubility of Various POSS Compounds in Aromatic and Aliphatic Dental Resins

POSS type	Dental resin	Weight % POSS			
		1%	5%	10%	15%
1. Al-Isobutyl	Aromatic	I	I	I	I
	Aliphatic	I	I	I	I
2. Al-Phenyl	Aromatic	S	I	I	I
	Aliphatic	S	S	S	S
3. Y-Isobutyl	Aromatic	I	I	I	I
	Aliphatic	I	I	I	I
4. 6-Isobutyl	Aromatic	I	I	I	I
	Aliphatic	I	I	I	I
5. Ti-Isobutyl	Aromatic	I	I	I	I
	Aliphatic	I	I	I	I
6. MNMMJ734 (1 : 1)	Aromatic	I	I	I	I
	Aliphatic	I	I	I	I
7. MNMMAIMAO734	Aromatic	S	S	S	S
	Aliphatic	I	I	I	I
8. Methacrylateisobutyl	Aromatic	S	I	I	I
	Aliphatic	S	I	I	I
9. Amino propylPhenyl	Aromatic	S	S	S	I
	Aliphatic	S	I	I	I
10. MethacrylatePhenyl	Aromatic	S	I	I	I
	Aliphatic	S	I	I	I

I, insoluble; S, soluble.

tion of amines to the acrylate of AHM is well-understood.⁶ The proton NMR spectrum of the product is shown in Figure 5. Evidence of Michael addition is seen by the disappearance of acrylate proton peaks and the appearance of peaks d and e in the aliphatic region. It is possible for the resulting secondary amine to undergo Michael addition to another AHM molecule, although this reaction typically occurs at higher temperatures. In this case, the reactants were added at a 1 to 1 stoichiometric ratio and no evidence of disubstituted species is seen.

Solubility testing of POSS in dental resins

The structure of the dental resins are shown in Figure 6 and Table I outlines the results of the solubility study. Each compound was tested at 1, 5, 10, and 15 wt % concentration in the dental resins by dissolving the individual components in THF, combining them, and then allowing the solvent to evaporate. Solubility was determined by the appearance of the evaporated mixture. If the mixture was clear and homogeneous, it was considered miscible. If it was nonhomogeneous or cloudy, it was considered immiscible. Aluminum-phenyl POSS was the only metallized POSS that was soluble in the dental resins, and it was soluble in the aliphatic resin up to 15 wt %. It is expected that the aluminum on the corner of the POSS cage associates with the carbonate groups in the resins, thus increasing its solubility.^{7,8} It is surprising, however, that the aluminum phenyl POSS is only soluble in the aromatic resin up to 1 wt %.

TABLE II
Mechanical Properties from DMA of Dental Resin Nanocomposites

Dental resin	POSS type	wt %	T_g (°C)	Modulus at 30°C (GPa)	Modulus at 160°C (MPa)
Aromatic	None	N/A	90	1.47	93.6
Aromatic	2	1%	109	1.67	75.9
Aromatic	7	1%		Sample broken during prep	
Aromatic	7	5%		Sample broken during prep	
Aromatic	7	10%	108	1.49	69.7
Aromatic	7	15%	97	1.61	63.2
Aromatic	8	1%	85	1.57	76.3
Aromatic	9	1%	103	1.60	137.0
Aromatic	10	1%	100	1.73	161.0
Aromatic	10	5%	85	1.44	114.0
Aromatic	10	10%	86	1.44	89.3
Aliphatic	None	N/A	79	0.98	34.5
Aliphatic	2	1%	76	1.55	56.4
Aliphatic	2	5%	83	1.63	56.4
Aliphatic	2	10%	78	1.23	46.6
Aliphatic	2	15%	79	1.79	63.2
Aliphatic	8	1%	73	1.45	57.9
Aliphatic	9	1%	68	1.45	59.7
Aliphatic	10	1%	68	1.49	54.8

Isobutyl-methacrylate POSS was the only isobutyl-substituted cage that showed solubility, and only at 1 wt % in both resins. Overall, phenyl substituted POSS cages exhibited the greatest solubility.

Film polymerization and mechanical testing

Once soluble mixtures were obtained, liquid films were cured via UV polymerization with Irgacure 651 as a photoinitiator and then evaluated with DMA. The mechanical data obtained is summarized in Table II. The incorporation of POSS had a wide range of effects but did not induce general trends. For the aromatic resin, none of the POSS compounds had a profound

effect on storage modulus at 30°C. A representative set of DMA curves are shown in Figure 7. The highest increase was seen with methacrylate-phenyl POSS at 1 wt %, increasing modulus by 20% and T_g by 10°C. However, modulus at 160°C increased dramatically by 70%. This effect diminished as the amount of POSS was further increased. At 5 wt %, the high-temperature modulus was only 20% higher than the control, and at 10% incorporation, it was nearly equal to the control. Also, the T_g of the 5 and 10 wt % samples were about 15°C less than the 1% sample. At low concentrations, the POSS, which is presumably chemically incorporated into the film through the methacrylate group, clearly acts as a reinforcing agent, increasing storage

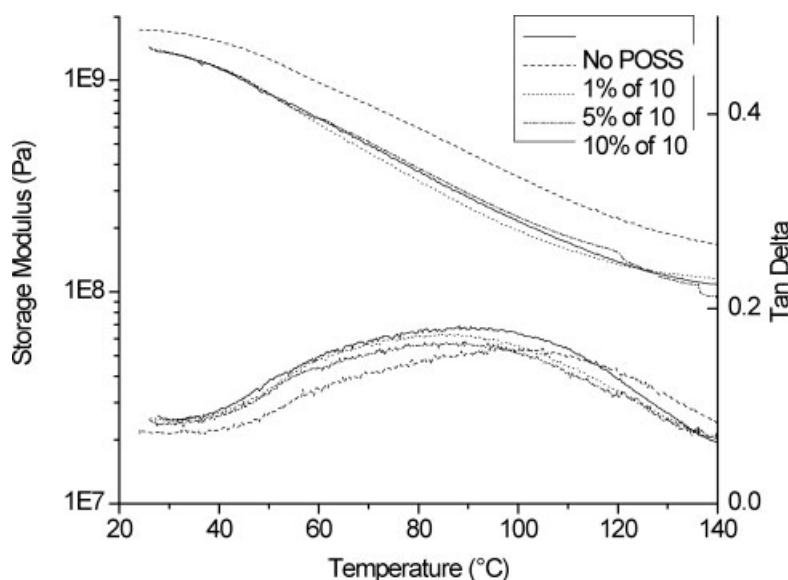


Figure 7 DMA data of phenyl-methacrylate POSS (10) incorporated into the aromatic dental resin at 1, 5, and 10 wt %.

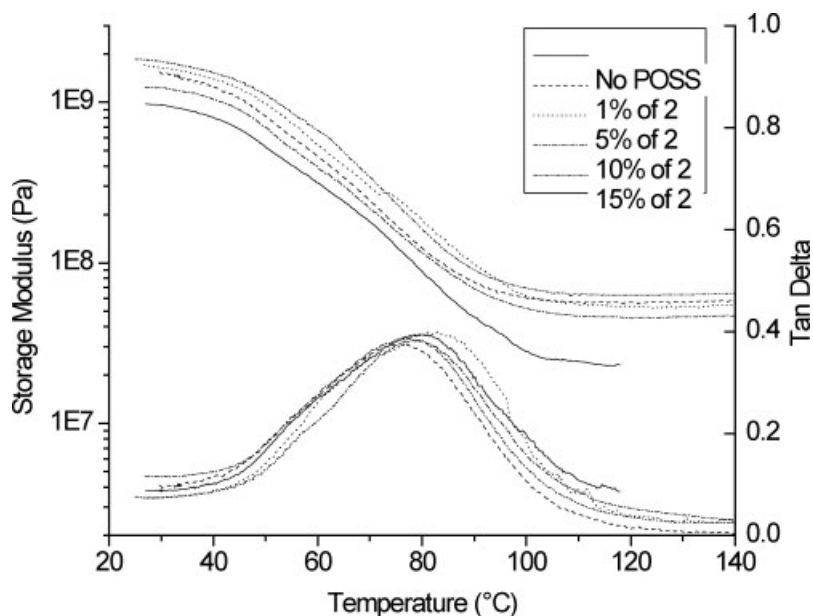


Figure 8 DMA data of aluminum-phenyl POSS (2) incorporated into the aliphatic dental resin at 1, 5, 10, and 15 wt %.

modulus across a wide temperature range. At higher concentrations, however, it seems to act as a plasticizer, leading to a decrease in T_g and having little effect on the modulus.

In the aliphatic resin, large increases of storage modulus of up to 80% were observed. Referring to Table II, it is observed that the addition of any of the soluble POSS molecules increased the modulus of the aliphatic resin by at least 25%. DMA data for the aluminum-phenyl POSS materials is shown in Figure 8. The aluminum-phenyl POSS was very soluble in the resin and increased modulus by 83% at 30°C and 160°C at a 15 wt % concentration. In general, low concentrations of POSS decreased T_g in this series although at 5–15% incorporation, T_g was similar to that of the unfilled resin.

CONCLUSIONS

Incorporating POSS compounds into dental resins generally increased modulus and had an unpredictable effect on T_g . The modulus of the aliphatic resin was affected the most, with all POSS compounds increasing the modulus from 25 to 83% between 30 and 160°C. Aromatic resins saw a maximum modulus improvement

of 18% at 30°C and 72% at 160°C. Significant improvements in mechanical properties were achieved, although it is important to note that dental formulations contain only 20–30% resin. Thus, the entire formulation series described here needs to be further tested to see if the improvements are maintained with commercial amounts of added inorganic filler.

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