Synthesis and characterization of vinyl-polyhedral oligomeric silsesquioxanes-reinforced silicone resin with three-dimensional cross-linking structure

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ABSTRACT: A novel thermal stability and highly transparent silicone resin-type material was prepared via hydrosilylation of vinyl-polyhedral oligomeric silsesquioxanes (POSS)-grafted methylhydrosilicone oil and vinylmethylsilicone oil in the presence of Karstedt catalyst. The morphology, mechanical property, thermal stability, optical transmittance, thermal-oxidation resistance of the vinyl-POSS-reinforced silicone resins were systematically investigated. Scanning electron microscopy showed that the vinyl-POSS-reinforced silicone resins had good compatibility with polydimethylsiloxane (PDMS) systems. The mechanical analysis and thermo gravimetric analysis indicated that the mechanical properties and thermal stability increased with increasing quantity of vinyl-POSS. However, the optical transmittance increased with the increasing amount of vinyl-POSS rather than decreased. In addition, the incorporation of vinyl-POSS did not improve the thermal resistance of the PDMS polymers. The product has the potential application for LED packaging. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42187.

INTRODUCTION

Silicone-based materials have gained considerable attentions for use as LED encapsulants. Compared to epoxy resins or modified epoxy resins, silicone-based materials have some excellent properties (such as higher thermal stability, ultralow temperature toughness, UV resistance, and high optical transparency) which make it perfect substituent for LED packaging materials.[1–5] Polydimethylsiloxane (PDMS), a typical polysiloxane which has been widely used as LED encapsulants, has some serious weaknesses (such as low refractive index, bad mechanical properties, poor thermal stability) that hinder its further application in high-power light emitting diodes. Hence, the improvement of thermal and mechanical properties of LED encapsulation materials is very essential.[6–9]

Among the two regular ways of reinforcing PDMS, physical blending of PDMS with other reinforcing fillers is easier and more effective than chemical synthesis of PDMS-based copolymers.[10–13] Inorganic and metal oxides are routinely incorporated into silicone polymer to improve its thermal properties; however, poor compatibility significantly affects the improve-

ment of mechanical property. Polyhedral oligomeric silsesquioxanes (POSS) with their combined organic–inorganic characteristics have raised lots of interest. POSS molecule with a generic empirical formula $(RSiO_{1.5})_n$ is an inorganic core that cladded with some organic alkyl groups or other reactive groups, which ensure their good compatibility with the matrix resin and effective reinforcements of polymer systems (such as used temperatures, decomposition temperatures, oxidation resistance, surface hardening, mechanical properties, and so on).[14] However, due to the insurmountable drawbacks of aggregation of POSS monomers, a slight increase of them will cause viscosity increment and segregation unevenly. Therefore, as aforementioned, properties enhancement cannot be easily achieved merely by physically blending. The incorporation of POSS into polymer chain by chemical bonding seems to be a better alternative. Chen et al.[15] reported a novel room temperature vulcanized silicone rubbers using vinyl-POSS derivatives as cross-linking agents which has greatly improved the thermal stabilities, mechanical properties, and hardness of silicone rubbers. Baumann[16] also reported the synthesis and characteristics of silicone nanocomposites that involved POSS-derivatives as

modifier to get higher mechanical properties of the polydimethylsilicone matrix. Although such work used POSS to modify silicone matrix, the study in which vinyl-POSS was directly grafted on the main chain of hydropolysilicone oil by means of hydrosilylation reaction and further used as curing agent to get vulcanized silicone rubbers is rare.

In this article, we used octavinyl-POSS as both cross-linking agents and fillers in PDMS systems to get highly cross-linked silicone rubber with improved thermal properties and mechanical properties. First, we incorporated octavinyl-POSS into hydropolysilicone systems by hydrosilylation reaction to form some localized three-dimensional cross-linked networks which set as prepolymer. Then further hydrosilylation cross-link was performed by an addition reaction between the prepolymer and vinyl end-capped silicone polymer (E-Vi) and multivinyl functional (Si—CH$_2$=CH$_2$) silicone polymers (M-Vi) in the presence of Karstedt catalyst via heating process. The effects of the different contents of POSS on thermal properties, mechanical properties, hardness, optical transparency, and thermal aging of such systems were systematically investigated.

EXPERIMENTAL

Materials
Vinyl-terminated polydimethylsiloxane (E-Vi) (viscosity of 200 pa s) and multivinyl functional (Si—CH$_2$=CH$_2$) silicone polymers (M-Vi) (viscosity of 500 pa s) were obtained from Dongguan Hongyi Chemical Co. Ltd. Hydrogen-siloxane fluid was purchased from Guangzhou Xinhou Chemical Co. Ltd. Octavinyl-POSS was prepared in the laboratory via hydrolytic condensation between vinyltriethoxysilane monomers. Toluene was obtained from Akzo Nobel Peroxide (Tianjin, China). Karstedt catalyst was obtained from Aladdin reagent. All above reagents were used as received.

Preparation of Octavinyl-POSS
Octavinyl-POSS was synthesized by hydrolytic condensation of vinyltriethoxysilane according to the previous report.[17] Briefly, vinyltriethoxysilane (50 mL) and distilled water (17 mL) were dissolved in 80 mL of anhydrous alcohol with stirring and then some amount of hydrochloric acid was added to adjust the solution to pH = 3. The reaction was conducted at 60°C for 3 days. A white crystalline product was yielded during the reaction. The product was washed with methanol for three times, and then it was dried in vacuum oven at 60°C for 24 h.

Preparation of Octavinyl-POSS-Grafted Hydropolysilicone
The procedure for octavinyl-POSS-grafted hydropolysilicone (HPDMS) was prepared by hydrosilylation method between hydropolysilicone (20 g) and certain amount of octavinyl-POSS in a toluene solvent (60 mL) catalyzed by Karstedt catalyst (5 ppm of the total mass) at 70°C for 6 h under dry nitrogen. Then the solvent was removed on a rotary evaporator. The obtained products were colorless transparent viscous liquids. The formulations of reactants were tabulated in Table I.

Preparation of Vinyl-POSS-Reinforced Silicone Resin
The octavinyl-POSS-grafted hydropolysilicone and vinyl end-capped silicone polymer (E-Vi) multivinyl functional (Si—CH$_2$=CH$_2$) silicone polymers (M-Vi) were mixed according to the desired Si—H/

Table I. Formulations of the Vinyl-POSS-Reinforced Silicone Resins

Samples	Vinyl-POSS (g)	HPDMS (g)	E-Vi (g)	M-Vi (g)	Pt (ppm)
POSS-0 wt %	0	20	32	4.7	5
POSS-2 wt %	0.4	20	32	4.7	5
POSS-4 wt %	0.8	20	32	4.7	5
POSS-6 wt %	1.2	20	32	4.7	5
POSS-8 wt %	1.6	20	32	4.7	5

Si—Vi ratio with 5 ppm of Karstedt catalyst of the total amount of the mixed resin. The mixtures were degassed *in vacuo* and then poured into a Teflon mold subsequently, and cured at 80°C for 1 h, 100°C for 2 h, and 150°C for 1 h, respectively. Finally a 2-mm-thick sheet of silicone resin was obtained.

Characterizations and Measurements
^{1}H-NMR spectra of the reaction products were recorded on a Bruker AVANCE AV400 (400 Hz) spectrometer in CDCl$_3$ at room temperature with tetramethylsilane as the internal reference. Fourier-transform infrared (FT-IR) spectroscopic analysis of cured silicone resin was carried out using Analects RFX-65 spectrometer over the frequency range of 4000–400 cm^{-1} using KBr pellets. Optical transmittance of the cured resin was tested on a Unico UV2550 UV/vis spectrophotometer in a wavelength range of 300–800 nm. Dynamical mechanical analysis (DMA) tests were carried out using a dynamic mechanical analyzer (NETZSCH DMA 242), in tensile mode at a fixed frequency of 1 Hz and amplitude of 10 μm. The specimen dimensions were $\sim$8.5 × 2.0 × 6.5 mm^3 with a heating rate of 5 K/min from −165 to −40°C. The thermal stability of fully cured silicone samples were measured on a Perkin–Elmer Pyris-1 TG analyzer with a heating rate of 10°C/min from 40 to 800°C in nitrogen atmosphere. The tensile strength and elongation at break of the samples were measured with a RGM-3030 universal testing machine based on ASTM D638-08 at 25 ± 2°C under a testing rate of 2 mm/min. The hardness of the samples was measured with a Shore A meter following ASTM D 2240. The morphology of the fracture surface of the cured resin was observed with a Quanta 400 FEI XL-30 scanning electron microscope (SEM) after coated with a thin gold layer.

RESULTS AND DISCUSSION

In this work, vinyl-POSS-reinforced materials were prepared though hydrosilylation reaction in the presence of Pt catalyst. The grafting process between vinyl-POSS and HPDMS was very sensitive to changes in several factors such as the amount of catalyst, the volume of solvent, reaction temperature, and time. Hence, we had done lots of exploring experiments to ensure the most suitable reaction conditions in order to get the most excellent product, and all experimental samples were prepared under the same conditions. When conducting curing process, we found that cured silicone resin prepared by vinyl end-capped silicone oil (E-Vi) and multivinyl functional (Si—CH$_2$=CH$_2$) silicone polymers (M-Vi) and POSS-grafting HPDMS had better thermal and
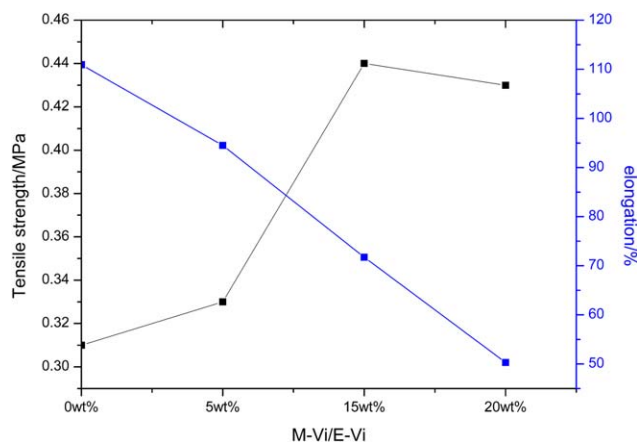
Figure 1. Mechanical properties of M-Vi involved silicone resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. Maldi-TOF MS of vinyl-POSS.

mechanical properties, compared with those only using vinyl end-capped silicone oil (E-Vi) as base silicone. Besides, among these cured products, the sample with 15 wt % M-Vi content had satisfying properties: relative higher tensile strength and suitable elongation. The exploring results are showed in Figure 1. Hence, we designed the following experiments according to the ratio (15 wt % M-Vi relative to the amount of E-Vi).

The structures of the cured silicone were confirmed by FT-IR and XRD analysis. Optical transmittance, morphology, thermal stabilities, mechanical stabilities, and hardness of the final products were investigated by UV–vis spectrophotometer, SEM, thermal gravimetric analysis experiments, universal tensile testing experiment, and shore A durometer, respectively. The relevant results would be discussed in the following sections in detail.

Characterization of POSS-Grafted HPDMS and POSS-Reinforced Silicone Resin

The ^{1}H-NMR spectrum of vinyl-POSS and Maldi-TOF MS is separately showed in Figures 2 and 3. It is clear that there is only one multipeak with the chemical shift of about 6.0 ppm in the spectrum, which is the typical chemical shift of vinyl group and indicates that the chemical environment of H atoms are quite the same and unique, and the results from TOF show that
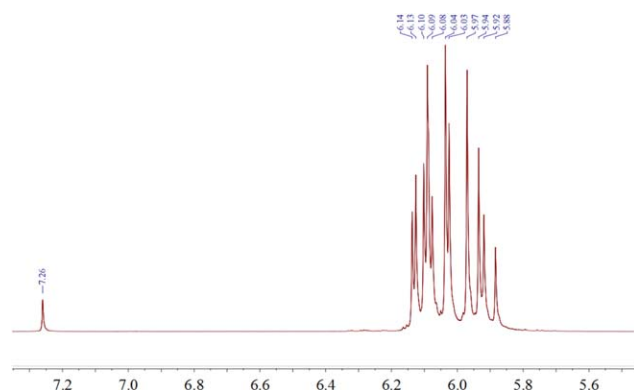
the molecular weight is about 506 and 632, which proves that we have got the desired T6 and T8 cage-like products.

Figure 4 shows the FT-IR spectra of vinyl-POSS, HPDMS, POSS-grafted HPDMS (POSS-HPDMS), and POSS-4 wt %-reinforced silicone resin (POSS-4 wt %). From the four curves, the peaks at 1010–1120 cm^{-1} represent the stretching vibration of the siloxane network (Si—O—Si). Compared with Figure 4 (a,b), CH_2=CH_2 (peaks at 3010–3070 cm^{-1}, 1600 cm^{-1}) from Figure 4(c) are disappeared, which means vinyl-POSS was basically completely grafted on the main chain of HPDMS. From Figure 4(d), it can be seen that the peak at 2100 cm^{-1} that represents the stretching vibration of Si—H, the peaks at 3010–3070 cm^{-1} that represent the stretching vibration of =C—H, and the peak at 1600 cm^{-1} that represent the stretching vibration of C=C are almost disappeared, which indicate that the curing process was conducted completely in some degree.

Figure 2. ^{1}H-NMR spectrum of vinyl-POSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

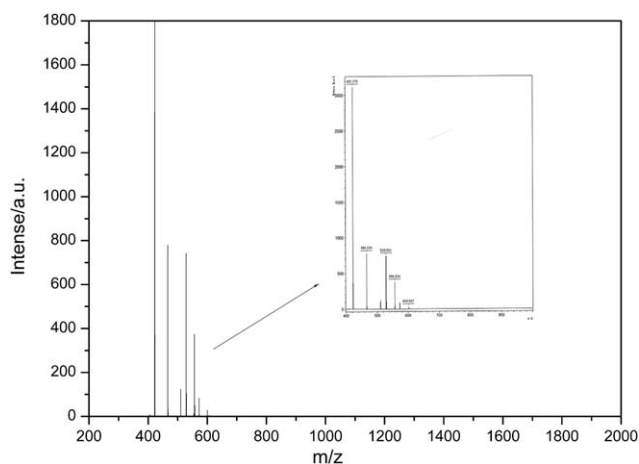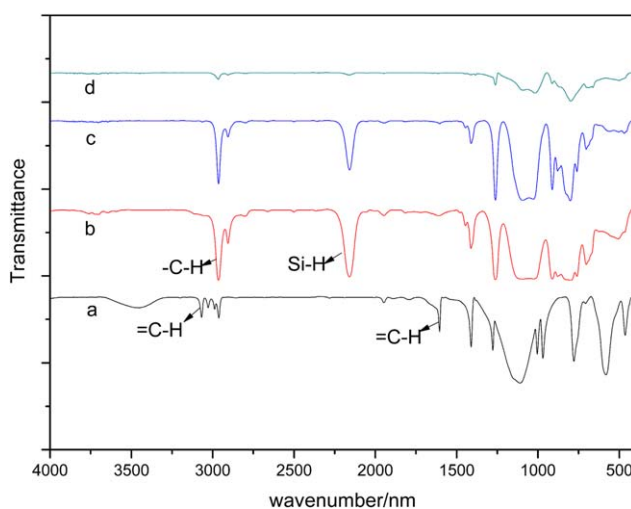**Figure 4.** FTIR spectra of vinyl-POSS, HPDMS, POSS-grafted HPDMS, and POSS-reinforced silicone resin. (a) vinyl-POSS, (b) HPDMS, (c) POSS-HPDMS, and (d) POSS-4 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
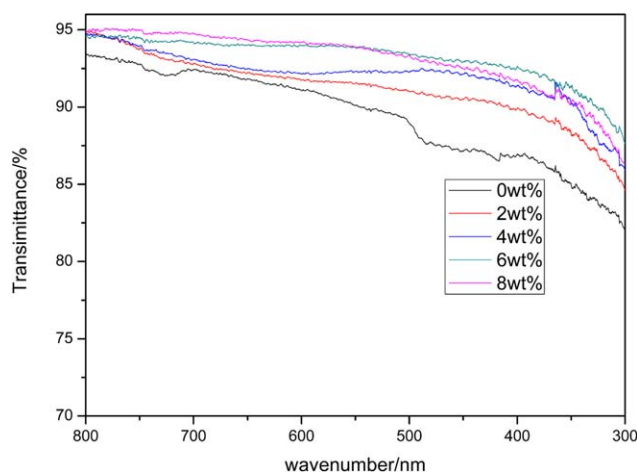
Figure 5. Optical transmittance of the vinyl-POSS-reinforced silicone resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
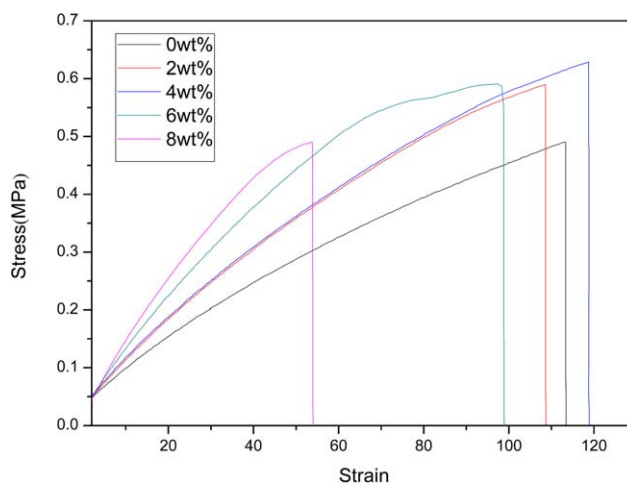

Figure 6. Stress–strain curves of the vinyl-POSS-reinforced silicone resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Optical Transmittance of the Vinyl-POSS-Reinforced Silicone Resin

No matter incorporated with vinyl-POSS or not, the appearance of these cured samples is transparent. The transmittance of different content of vinyl-POSS-reinforced silicone resins is shown in Figure 5. As can be seen, with the increase of vinyl-POSS content, the optical transmittance of final cured products is increasing. Besides, from 800 to 300 nm, the transmittance of cured silicone resins with the addition of vinyl-POSS decreases <10% while the one without vinyl-POSS decreases 11.3%. However, a different trend can be seen in sample POSS-8 wt % that from 650 to 300 nm, it decreases heavier than sample POSS-6 wt %. All these phenomena indicate that the incorporation of vinyl-POSS contributes to the slight increase of the transmittance of cured silicone resin rather than lowering them; on the other hand, it also helps to keep higher transmittance in the whole UV–vis scale, which is completely different from the phenomenon that when added other kinds of fillers such as SiO_2, TiO_2, and so on. The results can be explained by the nano cage-like structure of POSS which is less than visible

wavelength, thus it has no influence on the transmission of visible light. Besides, the hollow cage-like structure of POSS helps reduce the light absorption of the PDMS polymers, thus the optical transmittance increases with the increasing of POSS content. Furthermore, the incorporation of vinyl-POSS improved the ultraviolet shielding resistance, so within low wavelength we can see the slight decrease of transmittance.[18,19]

Dynamical Mechanical Analysis

Table II is the summary of DMA results of the vinyl-POSS-reinforced silicone resins. The relative change in G' of the different vinyl-POSS amount reinforced silicone resins compared to the respective unmodified silicone resin at $-100°C$, are presented in the table. Apparently, there is an increase of G' with the addition of vinyl-POSS. The T_g can be defined as the temperature corresponding to the peak maximum of the loss modulus or of the tan δ.[20] The glass transition temperature increases first and then decreases with the increasing of vinyl-POSS, and the tendency is similar based on the two definitions. And the results are consistent with the variation of cross-linking density.
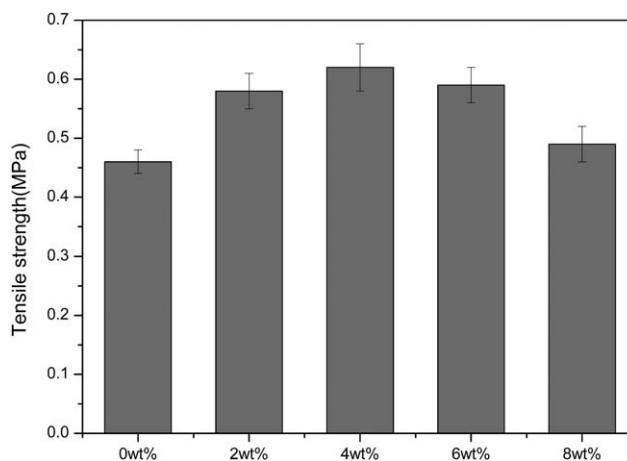
Table II. Summary of DMA Results of the Vinyl-POSS-Reinforced Silicone Resins

Samples	$\Delta G'^a$ (%)	T^b at G''^{peak}_{DMA} (°C)	$T^c\ \delta^{peak}_{DMA}$ (°C)	ρ^d (mol cm^{-3})
POSS-0 wt %	–	−142.2	−130.5	2.4×10^{-3}
POSS-2 wt %	3.02	−143.8	−133.1	4.7×10^{-3}
POSS-4 wt %	29.03	−133.7	−121.7	7.9×10^{-3}
POSS-6 wt %	2.83	−141.7	−131.5	4.0×10^{-3}
POSS-8 wt %	3.81	−150.1	−134.7	1.7×10^{-3}

[a] $\Delta G'$ is the relative change of storage modulus at $-100°C$.
[b] T at G''^{peak}_{DMA} is the temperature at the loss modulus maximum, associated to the apparent T_g.
[c] T at δ^{peak}_{DMA} is the temperature corresponding to the tan δ peak maximum, defining the apparent T_g.
[d] ρ refers to the cross-linking density of the network.

Figure 7. The tensile strength of vinyl-POSS-reinforced silicone resins.
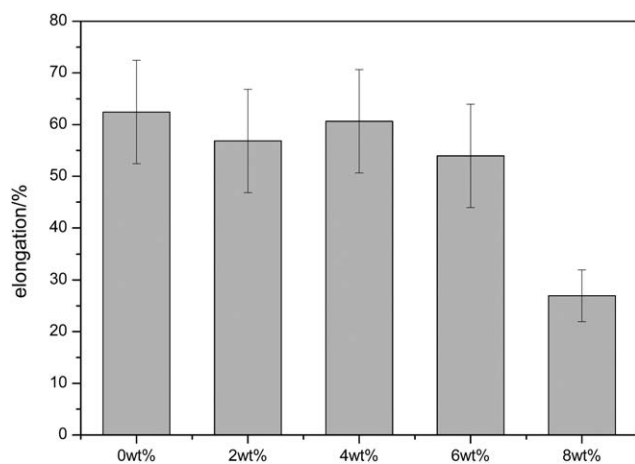
Figure 8. Elongation of vinyl-POSS-reinforced silicone resins.

Figure 10. TG curves of the vinyl-POSS-reinforced silicone resins in nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to the polymer elasticity theory, the cross-linking density (ρ) can be calculated according to[21]

$$\rho = \frac{G'}{3RT}$$

where ρ is the cross-linking density of the silicon resins, G' and T are the storage modulus at $T_g + 50$ K and the absolute temperature of $T_g + 50$ K, respectively. R is the gas constant, 8.314 J mol^{-1} K^{-1}.

From Table II, we can see that the cross-linking density of modified silicon resins increase first and then decrease with the increasing of vinyl-POSS. It can be explained as follows: vinyl-POSS works as cross-linking agent first; when added moderate amount of vinyl-POSS, it helps to increase the cross-linking density. However, when keep increasing the amount of vinyl-POSS, aggregations occur between vinyl-POSS molecules and the vinyl-POSS cannot disperse evenly in the silicone matrix,
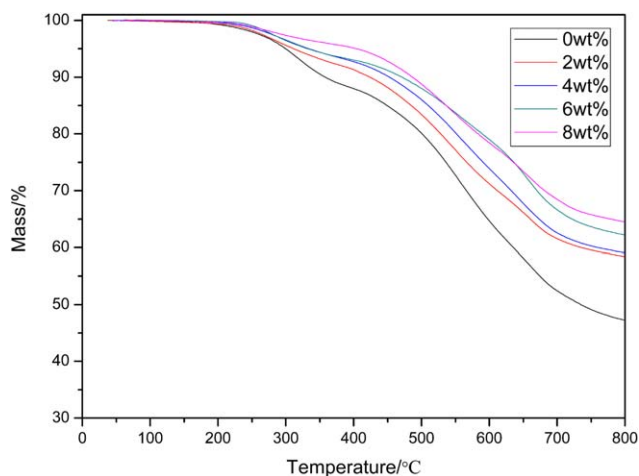
thus it lowers effective cross-linking, and so the cross-linking density decreases.

Mechanical Properties Analysis

The mechanical properties of vinyl-POSS-reinforced resins are presented in Figures 6–8. The tensile strength increases first and then decreases to some point with the increasing content of vinyl-POSS. However, the tensile strength of vinyl-POSS-reinforced silicone resins is higher than the one that had no vinyl-POSS, which proves that the incorporation of vinyl-POSS contributes to the increase of the tensile strength of silicone matrix. While the elongation decreases sharply when the additive amount of vinyl-POSS increased. The results can be explained as follows: vinyl-POSS is one kind of multifunctional cross-linking agent that can help to build a complete and fine
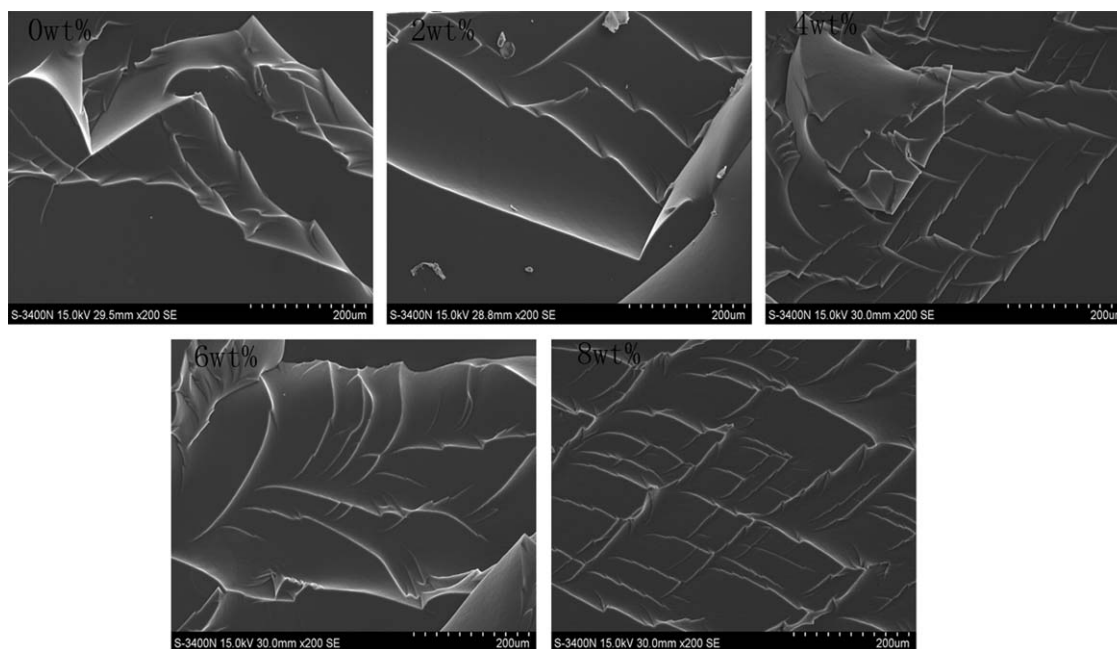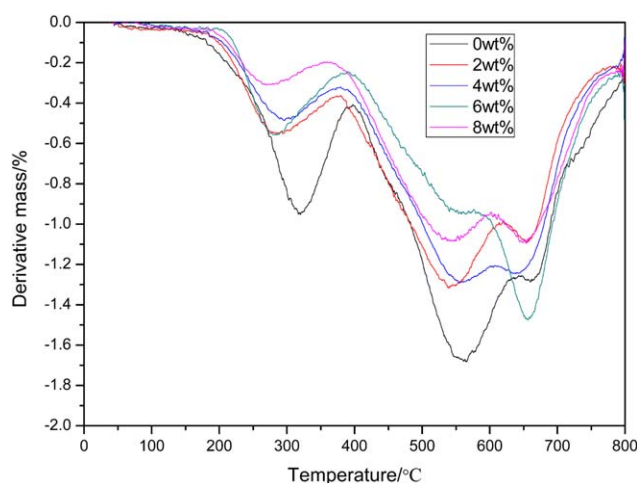

Figure 9. SEM micrographs of the vinyl-POSS-reinforced silicone resins.

Table III. TGA Results of the Vinyl-POSS-Reinforced Silicone Resins in Nitrogen Atmosphere

Sample	T_{onset} (°C)[a]	T_{max} (°C)[b]	Residual yield (%)
POSS-0 wt %	313	560	55.23
POSS-2 wt %	311	540	58.42
POSS-4 wt %	334	557	59.12
POSS-6 wt %	331	543	62.17
POSS-8 wt %	406	654	64.54

[a] Temperature for 5% weight loss.
[b] Temperature for the maximum rate of degradation.

network which can improve the mechanical properties of the system.[22] When added moderate amount of vinyl-POSS, it helps to increase the cross-linking density and then the mechanical strength of silicone matrix is improved. However, while keep

Figure 11. DTG curves of the vinyl-POSS-reinforced silicone resins in nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
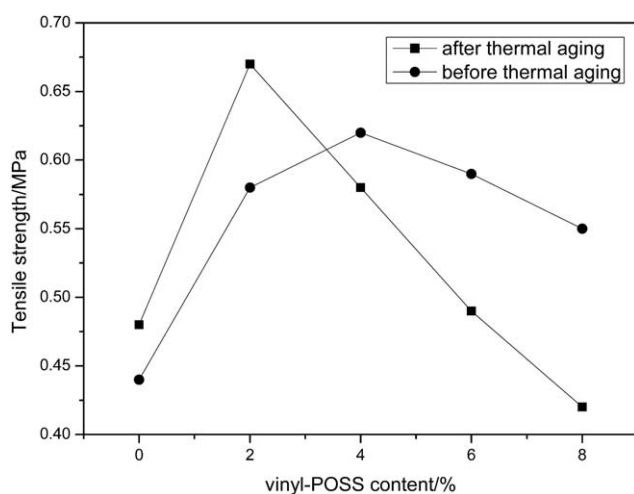
Figure 12. Tensile strength of the vinyl-POSS-reinforced silicone resins before and after thermal aging.
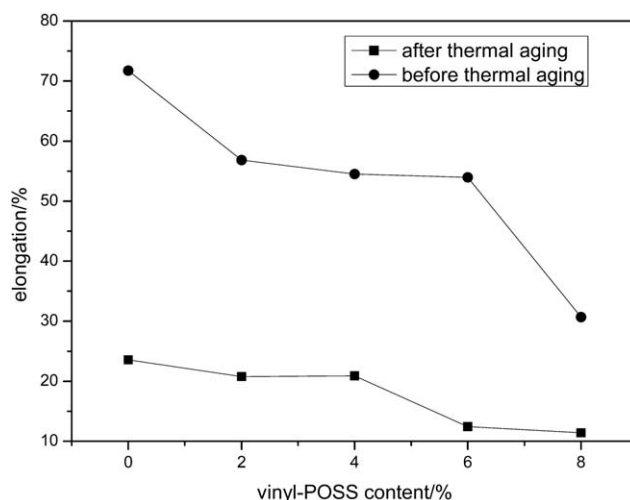
Figure 13. Elongation of the vinyl-POSS-reinforced silicone resins before and after thermal aging.

increasing the amount of vinyl-POSS to 6 wt %, aggregations occur between vinyl-POSS molecules and the vinyl-POSS cannot disperse evenly in the silicone matrix, thus it lowers effective cross-linking and work as flaws to cause cracks in the matrix when subjected to stress.[23] Nevertheless, when the cross-linking density increases, the distance of two molecular chains between two junction points decrease which hinder the motion of molecular chain, furthermore the cracks in the matrix when subjected to stress also reduce mechanical properties of the silicone matrix; in this way, the elongation of the cured silicone resins decreases when the addition of vinyl-POSS increases.[24,25]

Morphologies of the Vinyl-POSS-Reinforced Polysiloxane: SEM Characterization

In this study, vinyl-POSS was chemically incorporated into PDMS system, and ultimately transparent cured samples were obtained, which indicate that vinyl-POSS has good compatible with the silicone matrix. To further prove that, subsequent morphologies of these cured samples were investigated by means of
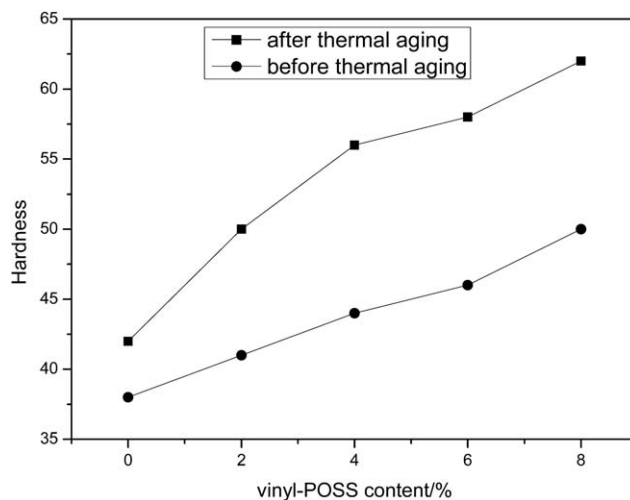

Figure 14. Hardness of the vinyl-POSS-reinforced silicone resins before and after thermal aging.

Table IV. Mechanical Properties of Vinyl-POSS-Reinforced Silicone Resin Before and After Thermal Aging

Samples	Tensile strength (MPa)		Elongation (%)		Hardness	
	Before	After	Before	After	Before	After
POSS-0 wt %	0.44	0.48	71.73	23.58	38	42
POSS-2 wt %	0.58	0.67	56.84	20.76	41	50
POSS-4 wt %	0.62	0.58	54.53	20.90	44	56
POSS-6 wt %	0.59	0.49	53.95	12.42	46	58
POSS-8 wt %	0.55	0.42	30.68	11.43	50	62

SEM. From Figure 9, all these five samples have no visible phase separation and the fractured surfaces are homogeneous without any particles which suggest that vinyl-POSS was successfully grafted into PDMS system and it has great compatible with the PDMS polymers. Besides, with the increase of the content of vinyl-POSS, more and more lamellar cracks appear and the edge of these cracks is stress whitening which represents vinyl-POSS in the junction under stress.[23] Moreover, from 0 to 8 wt %, the scale of the lamellar cracks decreases because vinyl-POSS works as hard spot to end the crack when sustained stress, so the more vinyl-POSS added, the more and smaller lamellar cracks.

Thermal Stability
The TGA results of the vinyl-POSS-reinforced silicone resins in nitrogen are shown in Figure 10 and Table III. As is shown in Figure 10, all these PDMS polymers exhibits a similar trend of degradation and the important characteristic data are tabulated in Table III. For instance, the temperature of 5% mass loss of the cured samples is 313, 311, 334, 331, and 406°C, respectively. The initial thermal degradation temperature of the PDMS polymers maximally increases by 93°C when incorporated with 8 wt % of vinyl-POSS. Besides, the degradation remaining residues of the tested samples also increases with the increasing content of vinyl-POSS from 55.2 to 64.54%. Some small humps at around 243°C (0 wt %), 282°C (2 wt %, 4 wt %), 268°C (6 wt %), 290°C (8 wt %) are observed in Figure 8. The peak decomposition temperature (T_{max}) of the tested samples also shifted to higher temperature with increasing vinyl-POSS content. The results indicate that the thermal stability of the PDMS polymers that added vinyl-POSS is improved. This is due to the formation of the three-dimensional networks of PDMS systems when added vinyl-POSS, which decreases the flexibility of the PDMS chain, hinders the formation of cyclic oligomers, and delays the temperatures of the thermal degradation.[26] The small humps in Figure 11 represent the chain exchange of Si—O—Si when degradation occurred. And when the temperature kept rising, alkyl groups in polymer chain were oxidized to further cross-link with other polymer chain.[27,28] In one word, the higher amount of vinyl-POSS can increase the cross-linking density of the PDMS system, thus the temperature of thermal degradation increases.

Thermal-Oxidative Stability
To investigate the thermal-oxidative stability of the vinyl-POSS-reinforced silicone resins, the treatment at 200°C for 48 h in the air was conducted and corresponding mechanical properties were studied, which were presented in Figures 12–14. The results show that the hardness increases after thermal aging compared to that of

before thermal aging, whereas the tensile strength and elongation at break decrease sharply after thermal aging. The increased hardness implies that cross-linking occurred during thermal aging because of the oxidation of alkyl groups in polymer chain.[28] And the reduction in tensile strength and elongation indicates that chain scission, additional cross-linking and degradation occurred in the PDMS systems during thermal aging. This effect could have been due to the chain exchange of Si—O—Si and the oxidation of alkyl groups in silicone framework during thermal aging. However, compared with the sample that has no vinyl-POSS, the ones added with vinyl-POSS have a worse thermal aging resistance, and with the increasing of the content of vinyl-POSS, the thermal aging resistance of the corresponding samples becomes weaker. It can be explained by the increasing cross-linking density of the PDMS system when added more vinyl-POSS, when the chain exchange between Si—O—Si occurred easier. And the data of the mechanical properties before and after thermal aging were presented in Table IV.

CONCLUSIONS

In this study, high-performance vinyl-POSS-reinforced silicone resins were synthesized. The morphology, mechanical properties, thermal stability, optical transmittance, and thermal-oxidation resistance of the vinyl-POSS-reinforced silicone resins were systematically investigated. The structure of the vinyl-POSS-reinforced silicone resins were confirmed by FTIR. The SEM micrographs showed that vinyl-POSS had good compatibility with the PDMS matrix. The cured resins exhibited good thermal stability and high optical transmittance which can be lasted in a long UV–vis area. And the mechanical properties were also improved compared to the one without any vinyl-POSS. The vinyl-POSS-reinforced silicone resins did not turn yellow during thermal aging at 200°C for 48 h. However, the incorporation of vinyl-POSS did not improve the thermal resistance of the PDMS polymers, which was decreased heavily after thermal aging due to the occurrence of cross-linking and degradation.

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