

Influence of Methacryl Polyhedral Oligomeric Silsesquioxane on the Thermal and Mechanical Properties of Methylsilicone Resin

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ABSTRACT: A methacryl polyhedral oligomeric silsesquioxane (POSS)-reinforced methylsilicone resin was prepared in this work. The structures of the obtained products were confirmed with Fourier transform infrared and atomic force microscopy. The influence of methacryl-POSS on the thermal behavior of the methylsilicone resin was studied by thermogravimetric analysis and isothermal thermogravimetric analysis. The results showed that the thermal stability of the methylsilicone resin was improved, and the degree of thermooxidative degradation was lowered; this was due to the retardation of polymer chain motion and the formation of a protective layer of SiO₂.

The interlaminar shear strength and flexural strength of quartz fiber/methylsilicone resin composites were tested to determine the effects of methacryl-POSS on the mechanical properties of methylsilicone resin. The results revealed that the mechanical properties of the methylsilicone composites also increased obviously after the incorporation of methacryl-POSS because of the increase in the cure degree and rigidity of the resin. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2989–2995, 2008

Key words: mechanical properties; silicones; thermal properties; thermogravimetric analysis (TGA)

INTRODUCTION

Polyhedral oligomeric silsesquioxane (POSS) molecules are hybrid inorganic/organic structures synthesized through the self-condensation reactions of alkyl trichlorosilanes.¹ Typical POSS cages have the empirical formula (RSiO_{1.5})₈, (RSiO_{1.5})₁₀, or (RSiO_{1.5})₁₂. Incompletely closed cage structures are also possible.² POSS has two features: (1) POSS is a structurally well-defined compound composed of a silicon–oxygen framework having the general formula (RSiO_{1.5}), and (2) POSS molecules are physically large, ranging from approximately 1 to 3 nm. The cage-shaped POSS molecules represent a novel class of nanofillers. In contrast to conventional fillers, most chemically grafted POSS molecules can be dispersed in a polymer matrix at the molecular level, being much smaller in size than the average conventional filler.^{3,4} The uniqueness of POSS molecules arises from the thermally stable silicon–oxygen framework and the flexible chemical composition, by

which a variety of organic substituents can be attached to each corner silicon atom to give different functionality. This route creates an opportunity for fine-tuning the interactions between POSS molecules and polymer chains and therefore provides ways of controlling the thermal and mechanical properties.⁵

Studies have shown that the addition of POSS monomers via copolymerization, grafting, or blending results in numerous property enhancements, including, but not limited to, increases in the use temperature, oxidation resistance, surface hardening, and mechanical properties, as well as reductions in flammability. To date, these enhancements have been shown to apply to a wide range of thermoplastic and thermoset systems, that is, methacrylate,^{6,7} styrene,^{8–10} norbornene,¹¹ polyethylene,^{12,13} polypropylene,^{14,15} polyimide,^{16,17} epoxy resin,^{18–21} phenolic resin,²² cyanate ester,²³ polyurethane,^{24–26} benzoxazine,^{27–29} and siloxanes.^{30–34} These property enhancements are attributed to the incorporation of bulky structures along the polymer chain and the nanoreinforcement effects of POSS on the polymer matrix.

It has been noted in the aforementioned studies that general property enhancements result from chemically and structurally well-defined POSS macromers. Therefore, chemical modification is the most studied method in the field of POSS nanocomposite. However, the study of physically mixed POSS–polymer nanocomposites is very limited. Compared with

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chemically reinforced POSS–polymer nanocomposites, physically mixed POSS–polymer nanocomposites have better potential for industrial applications because their cost will be low. In other words, no extensive modification of the existing industry setup is needed. In this study, we investigated POSS–polymer nanocomposites prepared by the melt mixing of a methylsilicone resin with methacryl-POSS cage structures. Previous studies have shown that polymeric siloxanes or silicones have superior thermal stability and resistance to thermooxidative degradation.^{35–38} However, silicone resins gradually deteriorate thermally and mechanically when exposed to the combined action of atmospheric oxygen and evolved heat.³⁹ Therefore, the emphasis of this work lies in two areas: (1) the influence of methacryl-POSS on the thermal behavior of the methylsilicone resin, which was studied with thermogravimetric analysis (TGA) and isothermal TGA, and (2) the interlaminar shear strength (ILSS) and flexural strength of quartz fiber/methylsilicone resin composites, which were tested to determine the effects of POSS on the mechanical properties of the methylsilicone resin.

EXPERIMENTAL

Materials

Methyltrimethoxyl silane (MTMS) was obtained from Hangzhou Guibao Chemical Co., Ltd. (Hangzhou, China). A methacryl-POSS cage mixture was purchased from Hybrid Plastics, Inc. (Hattiesburg, USA). The molecular formula of the methacryl-POSS cage mixture was $(C_7H_{11}O_2)_n(SiO_{1.5})_n$, where n was 8, 10, or 12. The quartz fiber was obtained from the Xi'an Glass Fiber Factory (Xi'an, China).

Synthesis of the methylsilicone resin

Methylsilicone solutions were prepared by hydrochloric acid catalyzed hydrolysis and condensation of MTMS. Into a four-necked flask equipped with a stirrer, a nitrogen inlet, and a thermometer, 22.7 g of MTMS and 14 mL of methanol were placed. Water and hydrochloric acid were added with $H_2O/MTMS$ and $HCl/MTMS$ molar ratios equal to 0.60–1.64 and 0.105, respectively. The mixture was stirred at room temperature for 30 min, and this was followed by stirring at 70°C for 3 h at the rate of 150 rpm. A relatively low-molecular-weight methylsilicone resin containing OH end groups was obtained. The yield of methylsilicone was 60%. The viscosity at room temperature was 0.44 Pa s.

Preparation of the methacryl-POSS-reinforced methylsilicone

When there is no chemical reaction between POSS and a polymer matrix, POSS molecules can be

directly used as polymer additives. This is based on the fact that (1) most POSS molecules have a thermally stable structure and (2) the substituents can be tailored to enhance the compatibility of POSS. Thus, non-hydroxyl-containing POSS can be readily incorporated into a polymer matrix with the conventional melt-blending method. According to this, methacryl-POSS-modified methylsilicone was prepared through a direct blending process.

Various amounts of methacryl-POSS (from 1 to 10 wt %) were blended into the methylsilicone resin. For better mixing, a small portion of anhydrous ethanol (10 wt % with respect to the methylsilicone) was added to dissolve methacryl-POSS before it was mixed with the methylsilicone resin. These mixtures were magnetically stirred at 90°C for 5 h. Methacryl-POSS appeared to completely dissolve in each case into the methylsilicone resin. After mixing, a dark brown solution was obtained. The solution was condensed through vacuum distillation at 70–80°C for 1 h.

Fabrication of the composites

The quartz fiber/methylsilicone composites and the quartz fiber/5 wt % methacryl-POSS-reinforced methylsilicone composites were fabricated to study the effects of methacryl-POSS on the mechanical properties of the methylsilicone resin.

The unidirectional long quartz fiber reinforced methylsilicone composites were fabricated by the filament winding method. Curing was performed in a compression-molding machine by the method of compression molding, and the content of the resin in the composites was kept in the range of 35–40 wt % by the control of the concentration of the methylsilicone resin. The cure protocol was as follows: at first, the sample was heated from room temperature to 100°C and held for 45 min, and then the temperature was raised to 130 and 160°C and held for 2 h. Each sample was postcured at 200°C for 2 h. The mold was cooled to room temperature, with the pressure being maintained. All composite samples were about 12 mm wide and 2 mm thick.

Measurements

Fourier transform infrared (FTIR) spectra were measured with a spectral resolution of 1 cm^{-1} on a Nicolet Nexus 670 FTIR spectrophotometer (Nicolet Instrument Co., Madison, WI., USA) with KBr disks or pellets at room temperature.

Atomic force microscopy (AFM) experiments were carried out on a Solver P47 AFM/[Scanning Tunneling Microscope (STM)] system (NT-MDT Co., Moscow, Russia), and the AFM images were taken with a $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ scan area from methacryl-POSS-reinforced methylsilicone films.

TGA was performed on a ZRT-2P thermoanalyzer (Cany Precision Instrument Co., Shanghai, China). Samples weighing about 10.0 mg were heated from 30 to 1000°C at a heating rate of 10°C/min in a dynamic air atmosphere.

Isothermal TGA was performed in a muffle furnace. Samples weighing about 50 mg were evaluated. The samples were air-pyrolyzed in the muffle furnace under isothermal conditions at nine different temperatures (200, 300, 400, 500, 600, 700, 800, 900, and 1000°C) for 3 h and 1 min. Each sample was evaluated three times, and the average weight loss was calculated.

ILSS of the quartz fiber/methylsilicone composites was tested on a universal testing machine (WD-1, Changchun, China) with a three-point short-beam bending test method according to GB3357-82. Specimen dimensions were nominally 20 mm × 6 mm × 2 mm. The specimens and an enclosed space in which the test was conducted were maintained at room temperature. The specimens were tested at a rate of cross-head movement of 2 mm/min. ILSS for the composite test was calculated with the following equation:

$$\text{ILSS} = \frac{3P_b}{4bh} \quad (1)$$

where P_b is the maximum compression load at fracture (N), b is the breadth of the specimen (mm), and h is the thickness of the specimen (mm). Each reported ILSS value was the average of more than 10 successful measurements.

The flexural strength of quartz fiber/methylsilicone composites was also tested on a universal testing machine (WD-1) with a three-point short-beam bending test method according to GB3356-82. Specimen dimensions were nominally 32 mm × 12 mm × 2 mm, with a span to thickness ratio of 16. The specimens were tested at a rate of crosshead movement of 2 mm/min. The flexural strength (σ_f) for the composites test was calculated with the following equation:

$$\sigma_f = \frac{3P_b \cdot l}{2b \cdot h^2} \quad (2)$$

where P_b is the maximum compression load at fracture (N), b is the breadth of the specimen (mm), l is the length of the span of the specimen (mm), and h is the thickness of the specimen (mm). Each reported flexural strength value was the average of more than five successful measurements.

RESULTS AND DISCUSSION

FTIR spectrum analysis

Figure 1 shows the FTIR spectra for pure methylsilicone, methacryl-POSS, and 5 wt % methacryl-POSS-reinforced methylsilicone from 4000 to 500 cm^{-1} . The

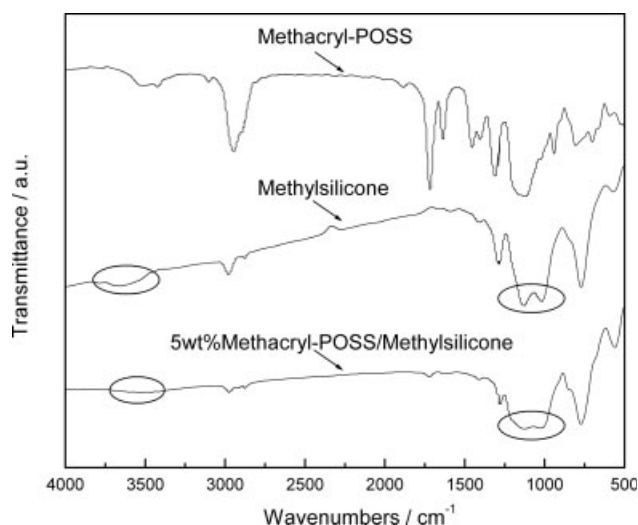


Figure 1 FTIR spectra of methacryl-POSS, methylsilicone, and 5 wt % methacryl-POSS-reinforced methylsilicone.

peaks at 3458 (Si—OH stretching), 2974 (C—H stretching of Si—CH₃), 1124 and 1027 (Si—O—Si asymmetric stretching), and 781 cm^{-1} (Si—O—Si symmetric stretching) are shown in the FTIR spectrum of pure methylsilicone and indicate that the synthesized product was the hydroxyl-terminated methylsilicone resin. The peaks at 3419 (Si—OH stretching), 2956 (C—H stretching of Si—C), 1720 (C=O stretching), and 1116 cm^{-1} (Si—O—Si stretching) are shown in the FTIR spectrum of methacryl-POSS. The Si—OH absorption band in the FTIR spectrum of methacryl-POSS indicates that there were a small number of hydroxyl groups in the methacryl-POSS cage mixture. These hydroxyl groups originated from some partial-cage-structured methacryl-POSS mixtures, which were produced by the incomplete condensation reaction during the preparation of the methacryl-POSS cage mixture.

Two distinct changes can be observed in the FTIR spectrum of POSS-reinforced methylsilicone. First, the absorption peaks of the Si—OH groups at 3500–3000 cm^{-1} decrease in intensity. Second, the Si—O—Si absorption band between 1000 and 1300 cm^{-1} becomes wider and broader with the incorporation of POSS. These results suggest that a condensation reaction of the small number of Si—OH groups between methacryl-POSS and hydroxyl-terminated methylsilicone took place. Because methacryl-POSS cage mixtures have only a minute quantity of Si—OH groups and a large quantity of POSS creating strong steric hindrance, this kind of condensation reaction is limited to a small extent.

AFM

AFM has become a very powerful tool for studying surface properties at the nanometer level. An AFM

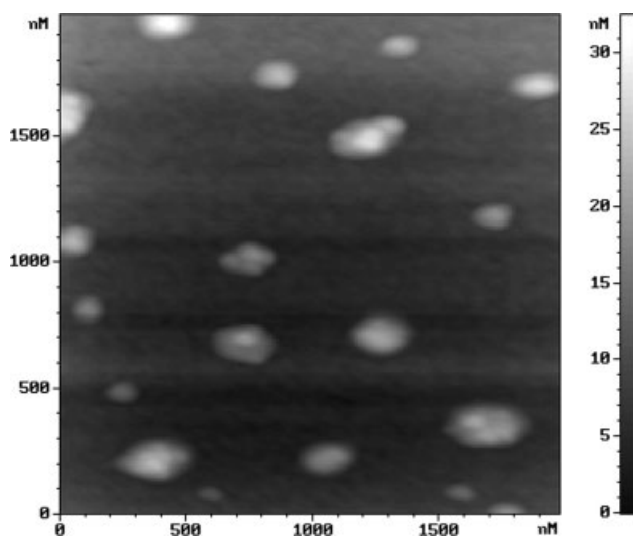


Figure 2 Two-dimensional AFM image of the surface of the methacryl-POSS-reinforced methylsilicone films.

image taken from methacryl-POSS-reinforced methylsilicone films is shown in Figure 2. In the two-dimensional image, the bright domains are the inorganic particles. We can see from the AFM image that in the random copolymers of POSS and methylsilicone, the POSS groups associated to form a POSS network within the polymer matrix; it is likely that POSS reacted with itself to form a network with the double bonds opening and polymerizing at 90°C. Most of the aggregates had diameters less than 350 nm. Presumably, it was this network of physical crosslinking that caused the increases in the thermal stability. The tendency of methacryl-POSS to aggregate in the methylsilicone resin was decided by two features of the physically blended POSS system: there were no covalent POSS-polymer linkages, and the POSS molecules may have had a much broader size distribution in the final composite (a chemically grafted POSS system generally has POSS molecules dispersed at the molecular level).

Thermal properties of the methylsilicone and POSS-reinforced methylsilicone

Effects of methacryl-POSS on the short-term thermal stability of methylsilicone

The cured methylsilicone and 5 wt % methacryl-POSS modified methylsilicone were ablated for 1 min isothermally to evaluate the effects of methacryl-POSS on the short-term thermal stability of methylsilicone. The weight loss of a sample as a function of the isothermal heating temperature is presented in Figure 3. Each of the data points represents the weight loss following 1 min of isothermal heating at the specific temperature. The error bars represent the standard deviation from three independent evaluations under each condition. It can be

observed from Figure 3 that the weight loss of the methacryl-POSS-reinforced methylsilicone was much less than that of methylsilicone at the corresponding temperature, and this indicated that the short-term thermal stability of methylsilicone was improved with the incorporation of methacryl-POSS.

The Si—C bond is thermodynamically less stable than the Si—O bond, and the activation energy of thermooxidative degradation is lower than the degradation of the main chain. Therefore, thermooxidative degradation is easier than the decomposition of the main chain when methylsilicone experiences short-term exposure to a high temperature. Therefore, the weight loss of methylsilicone was mainly caused by the oxidization of organic substituent groups when it was ablated in air for only 1 min. According to the literature,⁴⁰ the interaction of oxygen with a methylsilicone resin depends on the oxygen diffusion and solubility in the methylsilicone resin. The diffusion rate and solubility of oxygen in the methylsilicone resin decreased with the incorporation of methacryl-POSS. Because the nanostructure of the POSS cages prevented the diffusion of oxygen, this resulted in the improvement of the short-term thermal stability of the methylsilicone resin.

Effects of methacryl-POSS on the long-term thermal stability of methylsilicone

Figure 4 shows the weight loss of methylsilicone before and after reinforcement with methacryl-POSS as a function of the isothermal heating temperature. Each data points represents the weight loss following 3 h of isothermal heating at the specific temperature. The error bars also represent the standard derivation from these independent evaluations under

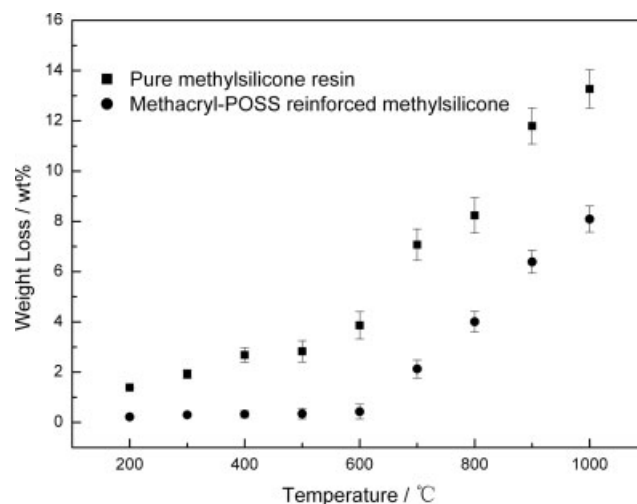


Figure 3 Weight loss of the pure methylsilicone resin and methacryl-POSS-reinforced methylsilicone after air pyrolysis for 1 min as a function of the isothermal degradation temperature.

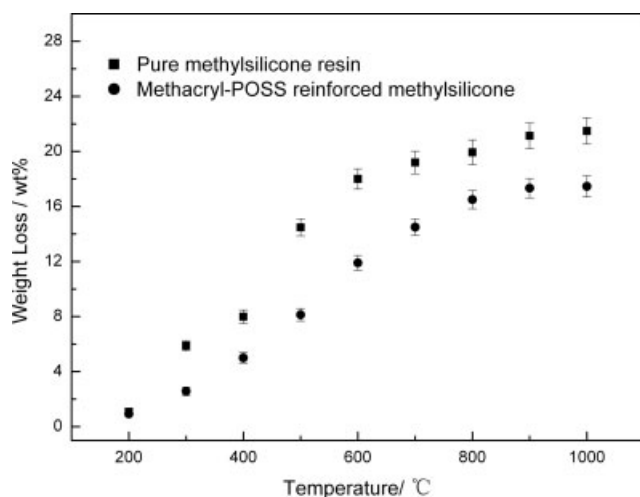


Figure 4 Weight loss of the pure methylsilicone resin and methacryl-POSS-reinforced methylsilicone after air pyrolysis for 3 h as a function of the isothermal degradation temperature.

each condition. As shown in Figure 4, the weight losses of both methylsilicone samples were small and close to each other at 200°C. The weight loss of methylsilicone increased rapidly after 300°C and was more than that of methacryl-POSS-reinforced methylsilicone at the corresponding temperature. Therefore, the long-term stability of methylsilicone improved when methacryl-POSS was used as a reinforcing agent. The mechanisms accounting for these results are discussed in the following section.

Thermal degradation mechanism of methylsilicone under the effects of methacryl-POSS

TGA was applied to evaluate the thermal stability of the POSS-containing methylsilicone nanocomposites. Shown in Figure 5 are the TGA curves of methylsilicone and its nanocomposites with POSS, which were recorded in an air atmosphere at 10°C/min. Within the experimental temperature range, the TGA curve of methylsilicone displays two-stage degradation mechanisms. According to the TGA measurements, there were at least two chemical processes between 200 and 300°C. At first, SiOH end groups reacted, and H₂O was set free. At a slightly higher temperature (ca. 250°C), OCH₃ end groups were involved in the reaction, and CH₃OH was produced as an additional volatile product. A weight loss of 10.5% was found in this step. The main reason for this high weight loss was the formation of an isolated, cage-like (CH₃SiO_{3/2})_n structure, which sublimated and led to a weight loss of the resin; one of the mechanisms for the formation of cyclics involved the hydroxyl chain ends biting into the chain a few units back. The second step of cleavage, shown by TGA between 400 and 500°C, can be easily explained. The Si—CH₃

groups in the resin were oxidized, and CO₂ and H₂O were released. SiO₂ remained in the crucible.

For the POSS–methylsilicone hybrids, Figure 5 shows that the heat resistance of the methylsilicone resin was greatly improved by the introduction of methacryl-POSS. The effect of the addition of POSS to the methylsilicone was maximized at the 5 wt % level, which showed only a 13 (w/w) total weight loss. As shown, when a smaller quantity of POSS was incorporated into methylsilicone, its thermal stability did not increase as would be expected. However, at larger loadings of POSS, the trend was reversed because two factors affect the thermal properties of methylsilicone/methacryl-POSS hybrids.²³ First, the massive unit of methacryl-POSS tends to restrict the segment's motions in methylsilicone because of its rigid nature, which increases both the rigidity and the thermal stability. On the other hand, methacryl-POSS may also increase the free volume, and this allows increased segmental motions and lowers the thermal stability of the methylsilicone resin.

Therefore, the quantity of POSS added to the methylsilicone had an optimum value. The second pyrolysis step of the POSS-reinforced methylsilicone resin occurred above 500°C; the organic substituents of POSS macromers were oxidized, and this was then followed by subsequent crosslinking reactions that formed a layer of SiO₂ on the surface of the POSS-reinforced methylsilicone resin, whereas the side group and main chain remained intact.³²

Mechanical properties of the composites

Effects of methacryl-POSS on ILSS of the methylsilicone composites

ILSS of quartz fiber/methylsilicone composites before and after reinforcement by methacryl-POSS

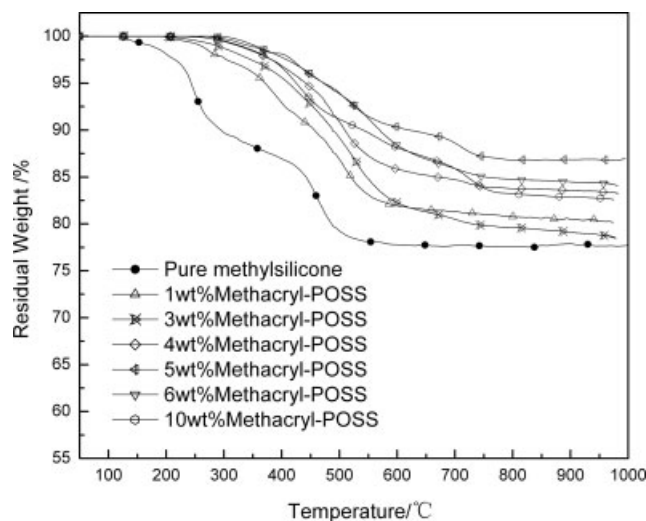


Figure 5 TGA curves of pure methylsilicone and its nanocomposites with POSS in an air atmosphere.

was calculated with eq. (1). The results of the test are shown in Table I. ILSS of the quartz fiber/methylsilicone composites decreased with an increase in the temperature, from 20.01 MPa at room temperature to 14.02 MPa at 500°C. ILSS could be increased by 27.84% at room temperature after the incorporation of methacryl-POSS. After pyrolysis at 500°C for 30 min, ILSS of the quartz fiber/POSS-reinforced methylsilicone composites remained at 16.37 MPa, which was still higher than that of unmodified methylsilicone composites.

It is well known that the interface adhesive strength influences the efficiency of load delivery between the matrix and fiber and further affects the mechanical performance. Therefore, the thermal degradation of methylsilicone was the main reason for the decrease in ILSS of the methylsilicone composites at a high temperature. As we mentioned previously, the thermal stability of the methylsilicone resin was greatly improved by the introduction of methacryl-POSS. Therefore, ILSS of the methylsilicone composites was raised correspondingly by the incorporation of POSS.

Effects of methacryl-POSS on the flexural strength of the methylsilicone composites

The flexural strength of the quartz fiber/methylsilicone composites before and after reinforcement by methacryl-POSS was calculated with eq. (2). The results of the test are shown in Table II. The flexural strength of the quartz fiber/methylsilicone composites decreased with an increase in temperature, from 267.01 MPa at room temperature to 128.01 MPa at 500°C. After the incorporation of methacryl-POSS into the methylsilicone resin, the increasing percentage of the flexural strength was 19.75 at room temperature and 26.83 at 500°C versus that of the control.

As mentioned previously, the effect of reactive Si—OH end groups on thermolysis was reduced through the addition of the methacryl-POSS cage mixture, which was necessary to obtain a comparatively completely cured network. On the other hand, the inorganic SiO₂ layer, formed by the selective removal of the organic substitute of POSS, contributed

TABLE I
Effect of Methacryl-POSS on the ILSS of the Quartz Fiber/Methylsilicone Resin Composites

	ILSS (MPa)		Increasing rate (%)
	Methylsilicone composite	POSS-modified methylsilicone composite	
Untreated	20.01	25.58	27.84
After treatment at 500°C	14.02	16.37	16.76

TABLE II
Effect of Methacryl-POSS on the Flexural Strength of the Quartz Fiber/Methylsilicone Resin Composites

	Flexural strength (MPa)		Increasing rate (%)
	Methylsilicone composite	POSS-modified methylsilicone composite	
Untreated	267.00	319.74	19.75
After treatment at 500°C	128.01	162.35	26.83

to rigidizing the virgin polymer materials. Therefore, the flexural strength was improved with the increase in the cure degree and rigidity of the polymer.

CONCLUSIONS

The effects of methacryl-POSS on the thermal stability and mechanical properties of a methylsilicone resin have been investigated and discussed in this article. It has been proposed that the mechanism of thermal property improvements in methacryl-POSS/methylsilicone nanocomposites is due to the retardation of polymer chain motion and the formation of a protective layer of SiO₂. The mechanical properties, including the ILSS and flexural strength, have also been improved with increases in the cure degree and rigidity of the polymer.

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