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Effects of TriSilanolIsobutyl-POSS on thermal stability of methylsilicone resin

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Abstract

Methylsilicone resin/polyhedral oligomeric silsesquioxane (POSS) composites with various proportions of POSS monomer were synthesized by the reaction of functionalized TriSilanolIsobutyl-POSS macromonomer with hydroxyl-terminated methylsilicone resin. The structures of the obtained hybrid polymers were characterized with Fourier-transformed infrared (FT-IR) and transmission electron microscopy (TEM). The FT-IR spectra suggested successful bonding of TriSilanolIsobutyl-POSS and methylsilicone resin. TEM analysis showed that POSS can dissolve in methylsilicone resin at the molecular level. The influences of TriSilanolIsobutyl-POSS on the thermal stability and degradation behavior of methylsilicone resin were studied by thermogravimetric analysis (TGA), solid-state ^{29}Si NMR and X-ray photoelectron spectroscopy (XPS). All these techniques showed that TriSilanolIsobutyl-POSS incorporation results in increased decomposition temperatures and oxidation resistance, primarily by reducing the effect of silanol end groups on the thermolysis through condensation reaction of Si–OH groups and partial loss of isobutyl followed by the formation of an inorganic SiO_2 layer to prevent methylsilicone from further degradation.

Keywords: TriSilanolIsobutyl-POSS; Methylsilicone resin; Thermal stability; Thermogravimetric analysis (TGA)

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1. Introduction

Methylsilicone resins have long been used in high temperature applications owing to their excellent thermal stability and resistance to thermal oxidative degradation [1]. Continuous use temperature of 200 °C with peak temperature above 300 °C is not uncommon [2]. Although the siloxane bonds which make up the backbone of silicone resins are intrinsically resistive to heterolytic bond cleavage [3], the methyl side groups attached to the silicon atom of typical silicone resins are prone to thermal oxidative degradation leading to the formation of siloxane crosslinks [4] and terminal hydroxyl groups can participate in a ‘‘back-biting’’ reaction through which a Si–O chain branch is formed [5]. Therefore, silicone resin used in high temperature applications in the presence of air typically fails due to embrittlement beyond a point which can be tolerated.

Stabilization of silicone resins against thermal oxidative degradation is most frequently accomplished by incorporation of fillers (e.g. silica [6], ferric oxide [7], aluminum oxide and zinc oxide [8], etc.). However, the filled systems have particles on the range of a micron and in some cases even on the nanoscale, they have a tendency to aggregate to give even larger domains. Preceramic polymers such as poly(carborane-siloxane) systems have shown superior resistance to thermal oxidative degradation, however, high cost and availability issues have limited their use [9].

POSS are structurally well defined compounds composed of a silicon–oxygen framework having the general formula ($RSiO_{3/2}$), and can be easily functionalized with a wide variety of organic groups that are commonly employed in polymerization or grafting reactions. Research has shown that incorporation of POSS monomers into polymers can result in increased use and decomposition temperatures and improved oxidation

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resistance [10–15]. Moreover, nanostructured POSS dissolves in polymer matrix at the molecular level thus solving the longstanding dispersion problem associated with traditional particulate fillers.

POSS silanols possess a hybrid inorganic–organic three-dimensional structure which contains from one to four stable silanol (Si–OH) groups. Stable silanols are unique given the proclivity of most Si–OH groups to eliminate water and form siloxane (Si–O–Si) linkages. POSS silanols can be incorporated into a polymer by copolymerization or grafting methods. The copolymerization of a disilanol functional POSS macromer with difunctional silane and siloxane monomers has been reported [16–18]. However, very little is known about the incorporation of trisilanol functionalized silsesquioxanes into polymethylsiloxane. Here, we report the preparation of hydroxyl-terminated methylsilicone/TriSilanolIsobutyl-POSS hybrid copolymers with various proportions of POSS synthesized by silanol–silanol condensation reaction, and we also examine the high temperature stability and degradation behavior of the obtained products.

2. Experiment

2.1. Materials

Methyltrimethoxy silane (MTMS) was obtained from Hangzhou Guibao Chemical Co., Ltd, China. TriSilanolIsobutyl-POSS was purchased from Hybrid Plastics, Inc, USA. The structure of TriSilanolIsobutyl-POSS is shown in Fig. 1.

2.2. Synthesis of hydroxyl-terminated methylsilicone resin

Hydroxyl-terminated silicone solutions were prepared by 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 MTMS and 14 ml methanol were placed. Water and hydrochloric acid were added in the molar ratios of H_2O/MTMS equal to 0.60–1.64 and HCl/MTMS equal to 0.105. The mixture was stirred at room temperature for 30 min, followed by stirring at 70 °C for 3 h at the rate of 150 rpm under a regulated nitrogen flow. The relatively low molecular methylsilicone resin containing OH end groups was obtained.

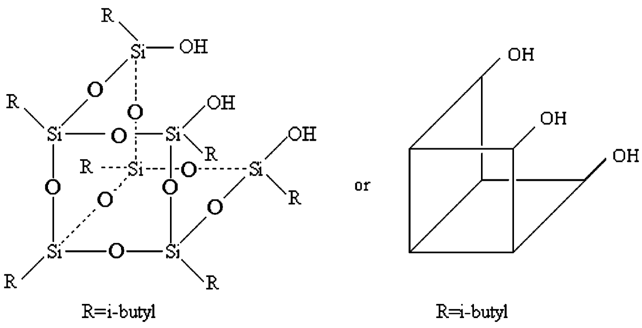

Fig. 1. The structure image of TriSilanolIsobutyl-POSS.

2.3. Preparation of the methylsilicone-POSS hybrid polymers

Systematic design of the methylsilicone-POSS hybrid polymers is shown in Fig. 2. Various amounts of TriSilanolIsobutyl-POSS were blended into silanol-terminated methylsilicone resin before end linking. For better mixing, a small portion of anhydrous ethanol (amounting to 10 wt% methylsilicone) was added to dissolve the POSS before it was mixed with methylsilicone resin. The mixture was stirred vigorously, and the solvent was removed at an elevated temperature and then by evacuation. The resulting solution was poured into Teflon molds and put into an oven to thermal cure at 100 °C, 130 °C, 160 °C and 180 °C for 2 h. After curing, a dark-brown solid was obtained.

2.4. Transmission electron microscopy (TEM)

The TEM instrument used was a FEI transmission electron microscope (Tecnai 20, made in the USA), with an acceleration voltage of 200 kV. Samples for the TEM study were microtomed with Leica Ultracut Uct into 50–100 nm-thick slices. Subsequently, these slices were placed on mesh 200 copper nets for TEM observation.

2.5. Fourier-transformed infrared (FT-IR) spectrum analysis

FT-IR spectra were measured with a spectral resolution of 1 cm^{-1} on a Nicolet FT-IR spectrophotometer (Nexus670, made in the USA) using KBr disks or pellets at room temperature.

2.6. Thermogravimetric analysis (TGA)

TGA was performed on a CANY thermoanalyzer (ZRT-2P, made in 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.

2.7. Solid-state ^{29}Si NMR

Solid-state ^{29}Si NMR measurements of the resultant solid products were performed on a Bruker spectrometer (AV-400, made in Swiss) equipped with a 4 mm CP/MAS (cross-polarization/magic angle spinning) probe. A single pulse ^{29}Si excitation frequency of 79.46 MHz was employed with a 45° pulse length (3 μs) and 60 s repetition delay. The Hartmann–Hahn condition in the ^{1}H–^{29}Si CP/MAS NMR experiments was optimized with kaolinite using a contact time of 1 ms and a 5 s recycle delay. ^{29}Si scale was calibrated by external standard M_8Q_8 (−109.8 ppm). All solid-state ^{29}Si NMR spectra were referenced to $(CH_3)_4Si$.

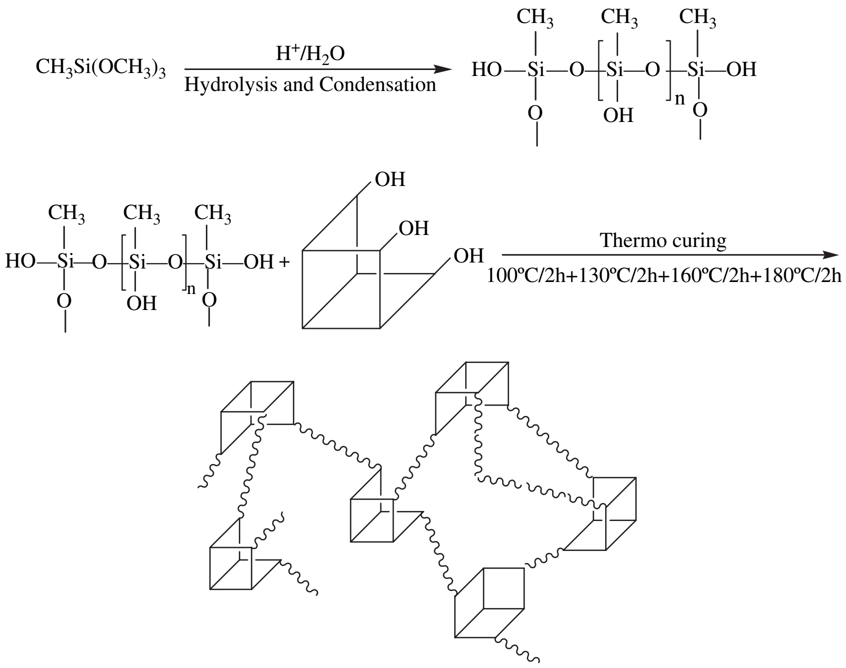

Fig. 2. Preparation of methylsilicone/POSS hybrid materials.

2.8. X-ray photoelectron spectroscopy (XPS)

The XPS analysis of the samples was carried out in an VG electron spectrometer (ESCALAB Mk II, made in UK) at base pressures in the preparation and analysis chambers of 2×10^{-8} and 1×10^{-8} Pa. The photoelectrons were excited by an X-ray source using Mg Kα (h$\nu = 1256.6$ eV). The instrumental resolution measured as the full-width at half-maximum of the Ag $3d_{5/2}$ photoelectron peak was 1.2 eV for a pass energy in the analyser of 20 eV. The C1s and Si2p photoelectron peaks were recorded.

3. Results and discussion

3.1. Fourier-transformed infrared spectrum analysis

Fig. 3 shows the FT-IR spectra of methylsilicone (a), TriSilanolIsobutyl-POSS (b) and 5 wt% TriSilanolIsobutyl-POSS reinforced methylsilicone (c). As discussed in literature [19], the Si–OH and Si–O–Si absorption bands of silicone resin are shown at 3500–3000 cm^{-1} and 1300–1000 cm^{-1}, respectively. Two distinct changes can be observed in Fig. 3c. The absorption peaks of the Si–OH groups at 3500–3000 cm^{-1} decrease in intensity obviously. This suggests that the condensation reaction of the Si–OH group between POSS and methylsilicone have taken place. Another distinct change is the peak intensity between 1000 and 1300 cm^{-1}. The intensity of the Si–O–Si absorption band increases with the incorporation of POSS. These results further confirm that the POSS is indeed incorporated into the metylsilicone resin rather than as a mixture.

3.2. TEM analysis

A transmission electron micrograph taken from the POSS reinforced methylsilicone (methylsilicone + 10 wt% TriSilanolIsobutyl-POSS) is shown in Fig. 4, which illustrates the molecular level dispersion of POSS that can be achieved in methylsilicone resin via compounding. Specifically, the black dots in Fig. 4 represent TriSilanolIsobutyl-POSS dispersed at

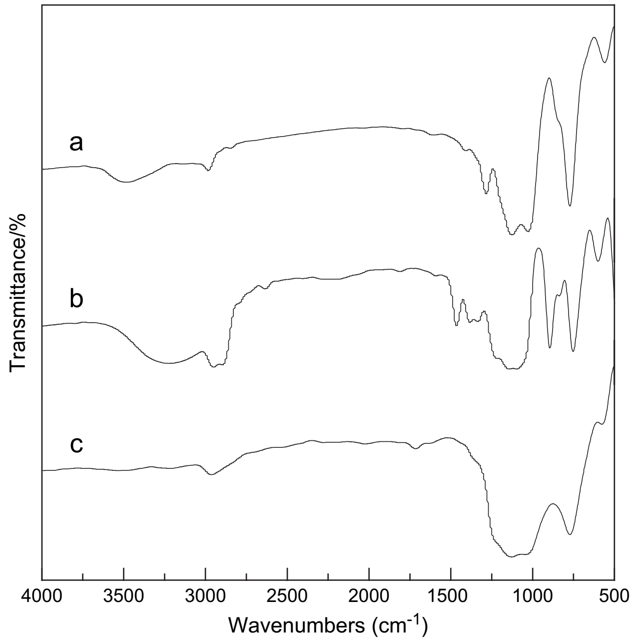

Fig. 3. FT-IR spectra of methylsilicone (a), TrisilanolIsobutyl-POSS (b) and 5 wt% TrisilanoIsobutyl-POSS reinforced methylsilicone (c) in the regions from 4000 to 500 cm^{-1}.

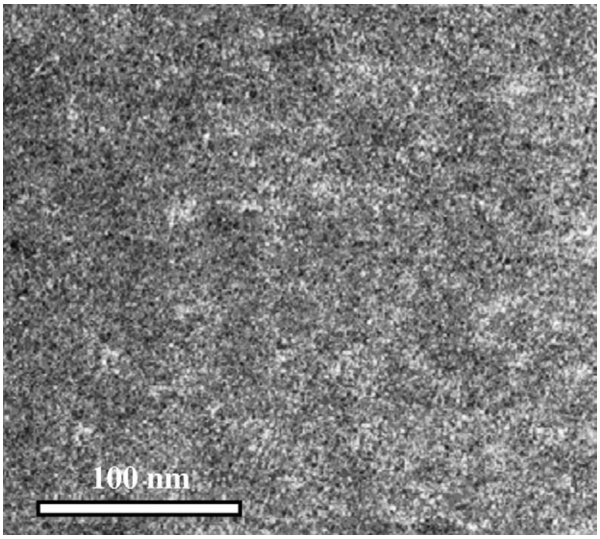

Fig. 4. TEM of 10 wt% TriSilanoIsobutyl-POSS/methylsilicone nanocomposite.

the 1–5 nm level and the white scale bar represents 100 nm. Since each POSS molecule has a three-dimensional inorganic core covered with seven organic side groups and three hydroxyl groups, it is believed that better dispersion may result from the chemical bonding of hydroxyl groups and increased interaction of compatible side groups with methylsilicone resin's network.

3.3. Thermogravimetric analysis

TGA is applied to evaluate the thermal stability of the POSS-containing methylsilicone nanocomposites. In Fig. 5 the TGA curves of methylsilicone and its nanocomposites with POSS, recorded in air atmosphere at 10 °C/min are shown. The most important other features of the thermograms for all seven samples are given in Table 1.

It is noted that within the experimental temperature range, the TGA curve of methylsilicone displays two stage degradation mechanisms. According to the TGA measurement, there are at least two chemical processes between 200 and 300 °C. At first SiOH end groups have reacted and H_2O is set free. At slightly higher temperature (approx. 250 °C), OCH_3 end groups are involved in the reaction and CH_3OH is produced as additional volatile product. If all chemically analyzed end groups react under condensation and release H_2O and CH_3OH, a weight loss of approx. 4% should be expected in this step. However, a weight loss of 10.5% is found. The main reason for this high weight loss is the formation of isolated cage-like $(CH_3SiO_{3/2})_n$-structure, which sublimate and leads to a loss of resin, one of the mechanisms for the formation of cyclics involves the hydroxyl chain ends "biting" into the chain a few units back [20–22]. The second step of cleavage shown by TGA between 400 and 500 °C can be easily explained. The $Si-CH_3$ groups in the resin are oxidized, CO_2 and H_2O are released. SiO_2 remains in the crucible [23].

Table 1
TGA results for the methylsilicone resin nanocomposites containing POSS

wt% POSS	Onset of degradation[a] (°C)	Temperature of maximal rate of weight loss (°C)	End of degradation (°C)
0	186.8	254.4	355.2
	416.7	456.3	497.0
1	242.1	316.2	339.1
	417.2	483.2	529.7
3	302.6	487.9	512.4
4	372.5	491.1	552.7
5	429.2	564.2	628.3
6	294.1	527.3	589.8
10	296.9	418.1	432.8
	446.9	505.0	531.1

[a] Temperature for 1% weight loss.

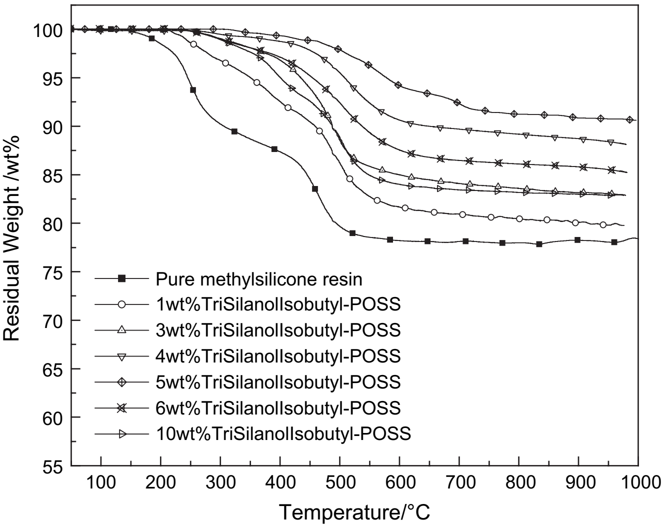

Fig. 5. TGA curves for the methylsilicone resin nanocomposites containing POSS.

For the POSS-methylsilicone hybrids, decomposition occurs by a two-step process only in the 1 wt% and 10 wt% hybrids and the others degrade by a single-step process, implying that the existence of POSS significantly affects the degradation mechanism of the matrix polymer. Since the TriSilanolIsobutyl-POSS can react with hydroxyl-terminated methylsilicone resin by thermally induced SiOH–SiOH condensations, the influence of Si–OH on the thermal stability of methylsilicone resin was diminished to a certain extent [24]. However, the SiOH groups of TriSilanolIsobutyl-POSS can themselves cause chain cleavage [25–27]. Thus, at low concentrations of POSS (≤5 wt%), most of the SiOH groups of POSS seem to have been used up in binding the polymer chain ends. As the concentration of POSS is high, the excess SiOH groups in POSS can cause cleavage of the methylsilicone chains. This would explain the observation that the effect of this stabilization is most pronounced at the lower concentrations of POSS. The second pyrolysis step of POSS reinforced methylsilicone resin occurs at above 500 °C, the organic substituents of POSS macromers are oxidized, which is then followed by subsequent cross linking reactions that form a silica layer on the surface of POSS reinforced methylsilcone resin, while the side group and main chain remain intact.

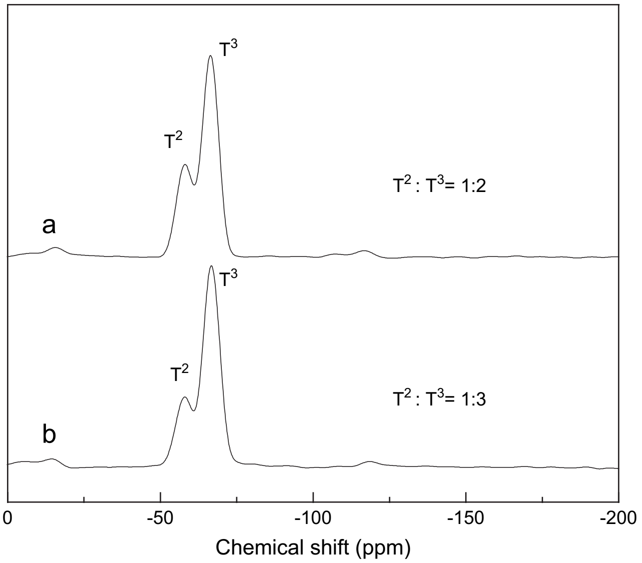

Fig. 6. ^{29}Si NMR spectra of methylsilicone (a) and POSS reinforced methylsilicone (b) at room temperature.

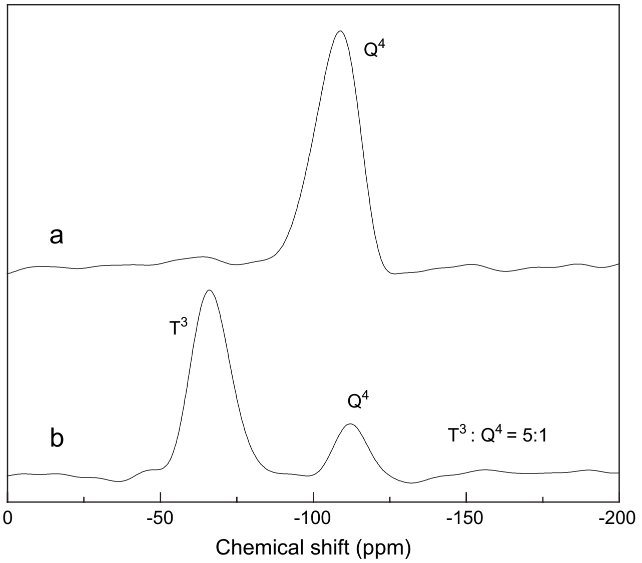

Fig. 7. ^{29}Si NMR spectra of methylsilicone (a) and POSS reinforced methylsilicone (b) prepared by pyrolysis in air atmosphere at 700 °C.

The thermal stability of the methylsilicone resin has been greatly improved by the introduction of POSS cages. These results suggest that the incorporation of POSS into polymer resins greatly retards polymer chain motion. An explanation of this retardation in chain motion by POSS molecules has been suggested [28]. The retardation is formed either by intermolecular interactions between POSS molecules and the polymer chains, or by the large inertia exhibited by polymer segments containing the massive POSS molecules. Furthermore, the large mass and steric bulk of the POSS units prevent rapid shifts in the physical location of POSS units, thereby retarding segmental motion. Therefore, POSS incorporation in polymer resin generally serves to reduce chain mobility, often improving thermal properties.

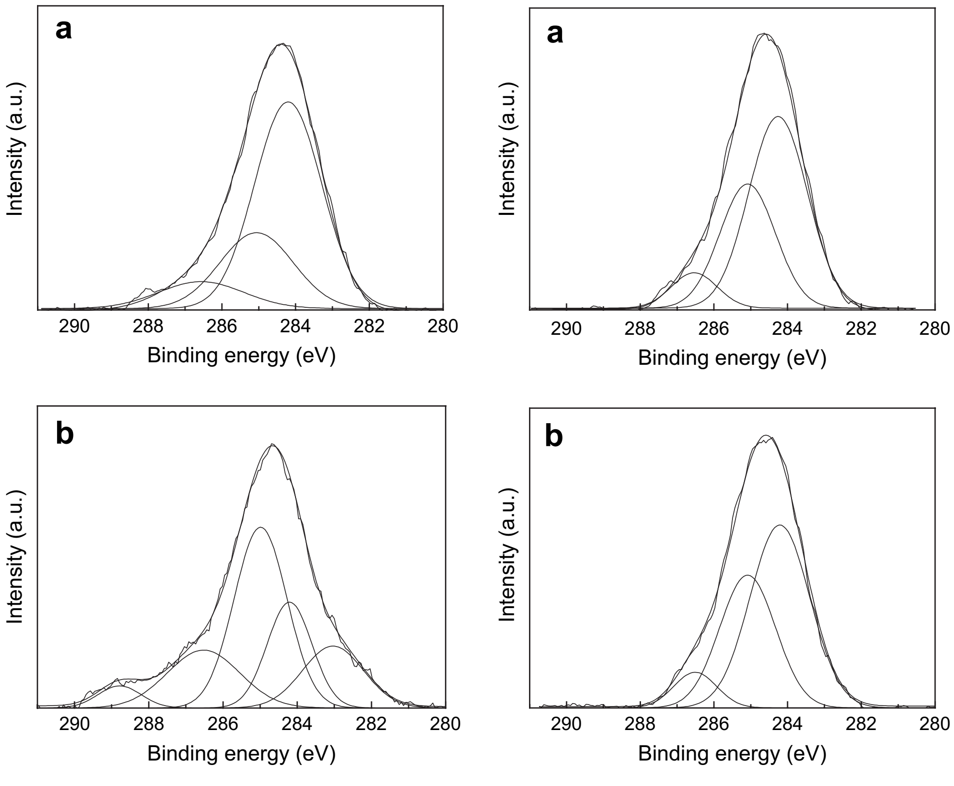

Fig. 8. Comparison of the C1s line (a) room temperature, (b) pyrolysis at 700 °C for 30 min for the methylsilicone resin (left-hand side) and POSS reinforced methylsilicone resin (right-hand side).

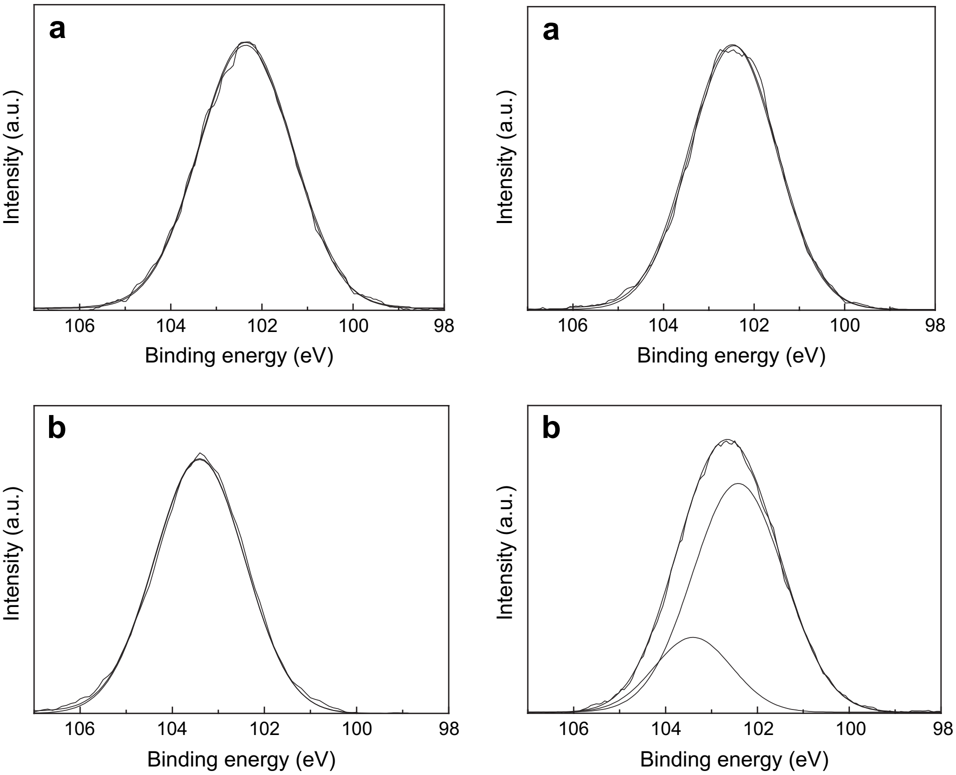

Fig. 9. Comparison of the Si2p line (a) room temperature, (b) pyrolysis at 700 °C for 30 min for the methylsilicone resin (left-hand side) and POSS reinforced methylsilicone resin (right-hand side).

3.4. NMR analysis

^{29}Si NMR provides structural information concerning the type of silicons present in the resin network.

The ^{29}Si NMR spectrum of methylsilicone resin (Fig. 6a) shows two broad signals centered at about −58.2 ppm and −66.3 ppm. These signals show that the resin predominantly consists of T^2 and T^3 units, where T^n indicates the siloxane unit structures $RSi(OSi)_nX_{3-n}$ [$n = 2$ (T^2) and 3 (T^3); R = Me and isobutyl; X = OH, OMe]; and the ratio of the T^2 unit to the T^3 unit is 1:2. They are similar to those reported in literature [29]. The chemical shift of the MTMS monomer has been reported from −37 to −41 ppm [30], which is not observed in Fig. 6a. These results suggest the complete hydrolysis and condensation reactions of MTMS.

POSS reinforced methylsilicone resin exhibits similar distributions of T^2 (−58.5 ppm) and T^3 (−66.5 ppm) silicons (Fig. 6b) and the unit ratio is 1:3. In contrast to pure methylsilicone signals, these resonance peaks shift slightly to higher field. Such a very small chemical shift change was occurred by only conformation change around the ^{29}Si nuclei in T^2 and T^3 sites. The decrease of T^2 groups and increase of T^3 groups are due to the reduction of −OH bond in POSS-methylsilicone system. This suggests that the condensation reaction of the Si−OH group has taken place.

Fig. 7a shows the ^{29}Si NMR spectrum of methylsilicone resin treated at 700 °C in air. Clearly, the T^2 and T^3 peaks disappear and Q^4 structure ($SiO_{4/2}$) unit forms at −110.4 ppm. This suggests that dramatic changes in the structure of the siloxane network can be observed after oxidation at 700 °C. The new Q^4 sites result from the replacement of $Si-CH_3$ by Si−O through nucleophilic attack by Si−OH groups.

Fig. 7b shows the ^{29}Si NMR spectrum of POSS reinforced methylsilicone resin treated at 700 °C in air. Resulting products are formed by two basic structure units T^3 and Q^4, which are indicated by ^{29}Si NMR signals at −64.1 and −111.0 ppm, respectively; and the unit ratio of T^3 to Q^4 is 5:1. In contrast to the spectrum of methylsilicone resin treated at 700 °C, T^3 structure units are still present in the spectrum of POSS reinforced methylsilicone resin. On the basis of the results of ^{29}Si NMR, it is obvious that TriSilanolIsobutyl-POSS has been shown to stabilize the siloxane structures against depolymerization and increase the resistance of the methylsilicone to oxidation reactions strongly under high temperatures.

3.5. XPS spectra analysis

The peak shape analysis gives further information on the chemical changes concerned. Fig. 8 shows the C1s peaks for the methylsilicone and for the POSS reinforced methylsilicone at room temperature (R.T.) and pyrolysis at 700 °C for 30 min. Fig. 9 depicts the corresponding Si2p peaks. Table 2 summarizes the results of peak synthesis for the C1s and the Si2p peaks.

The C1s peaks shown in Fig. 8 are centered about 284.2 eV for room temperature samples. This value is characteristic of methyl groups on the methylsilicone chain. The distribution of the C1s components of the degraded surfaces is remarkably different for the methylsilicone and

Table 2
Peak synthesis results of the C1s and Si2p peaks for the thermal treated methylsilicone resin (a) and POSS reinforced methylsilicone samples (b)

Sample		Peak area (%)						
		C1s (eV)					Si2p (eV)	
		288.8	286.5	285.0	284.2	283.0	103.4	102.4
a	R.T.	–	10.53	25.68	63.79	–	–	100
	700 °C	4.09	18.08	41.17	20.37	16.29	100	–
b	R.T.	–	8.19	34.86	56.95	–	–	100
	700 °C	–	8.68	36.31	55.01	–	21.66	78.34

POSS reinforced methylsilicone after pyrolysis at 700 °C for 30 min. In the case of methylsilicone sample, the relative amounts of CH_3–Si– decrease substantially, and two new lines appear at BE = 288.8 eV (highly oxidized carbons) and BE = 283.0 eV (amorphous or graphites carbon), respectively. While in the case of the POSS reinforced methylsilicone sample, it is only the concentration of the singly oxidized carbon atoms (BE = 286.5 eV) that increases slightly after oxidation at 700 °C. These changes imply that the isobutyl groups are being removed selectively leaving the methyl groups. This selective removal could be due to the larger size of the POSS cage compared to the methylsilicone chain. It could also be attributed to the weaker Si–C bond and the possibility that the POSS nanostructures could be surface segregating [31].

The Si2p peaks obtained from the sample before and after pyrolysis at 700 °C are shown in Fig. 9. These peaks are centered at a BE of 102.4 eV which corresponds to $RSiO_{3/2}$ in the methylsilicone chain and POSS cage. However, in the Si2p region of the methylsilicone chain a new component appears after pyrolysis at 700 °C for 30 min. In literature [32] the Si2p peak at 103.4 eV is assigned to an "inorganic silica-like phase". The percentage of inorganic silica after pyrolysis at 700 °C for 30 min reaches 100% in the methylsilicone sample, which is only 21.66% in the POSS reinforced methylsilicone sample. The fact that the difference is observed in the Si2p spectra obtained after oxidation at 700 °C indicates that the silica layer forms a protective barrier on the surface of POSS reinforced methylsilicone, which prevents further degradation of the methylsilicone chain. These agree well with the ^{29}Si NMR data from the same samples.

The thermochemistry and SiO_2 protective barrier formation mechanism operating for POSS-resins have been previously reported [33]. The organic substituents on POSS cages undergo hemolytic Si–C bond cleavage at first. This process is immediately followed by fusion of POSS cages to form a thermally insulated and oxidatively stable silica layer. Fig. 10 shows the SiO_2 protective layer formation mechanism in methylsilicone/POSS nanocomposites. On the other hand, the nanoscopic size and composition of the POSS nanostructured chemicals deter the formation of appreciable vapor pressure, and hence, the system is inherently of the excellent thermal and oxidative stability. This is largely due to the inorganic POSS component. The organic portion of their composition provides compatibility with existing resins thereby enabling their facile incorporation into conventional plastics.

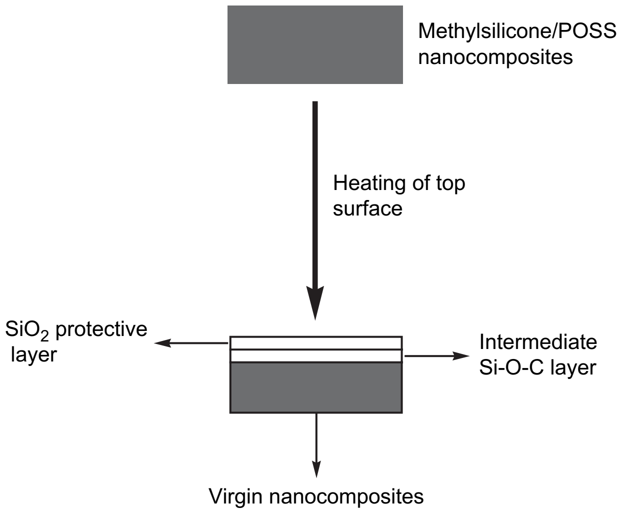

Fig. 10. Depiction of the SiO_2 protective layer formation mechanism in methylsilicone/POSS nanocomposites.

4. Conclusions

The effects of TriSilanolIsobutyl-POSS on the thermal stability of methylsilicone resin were investigated and discussed in this paper. It was proposed that the terminal hydroxyl groups of polymer matrix and POSS silanol were crucial to improvement in thermal stabilities of POSS-containing nanocomposites, which reduce the effect of reactive Si–OH end groups on the thermolysis. Moreover, the nanoscaled dispersion of POSS cages in methylsilicone matrixes is also an important factor to contribute to the enhanced thermal stability. It is plausible to propose that mass loss from segmental decomposition via gaseous fragments would be suppressed by well-dispersed POSS cubes at the molecular level.

On the other hand, TGA, ^{29}Si NMR and XPS measurements showed that the degradation process at higher temperatures observed in TriSilanolIsobutyl-POSS reinforced methylsilicone is predominantly due to the retardation of chain motions by POSS molecules and the selective removal of isobutyl group followed by the resulting inorganic SiO_2 layer to rigidize the polymer materials and prevent further degradation of the virgin polymer. The promising results contained herein combined with the numerous property enhancements previously reported for POSS incorporation into traditional polymer systems make their use as an attractive alternative to filler or coating systems when applied to space-based material applications.

Acknowledgement

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