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Influences of MonoSilanolIsobutyl-POSS on thermal stability of polymethylsilxoane

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Abstract Incorporation of polyhedral oligomeric silsesquioxane (POSS) molecules into polymer matrix resulted in increased used and decomposition temperatures. Polymethylsiloxane (PMS)/MonoSilanolIsobutyl-POSS hybrid copolymers containing various proportions of MonoSilanolIsobutyl-POSS were prepared. The structures and thermal properties of the obtained products were characterized with Gel Permeation Chromatography (GPC), Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG) and X-ray photoelectron spectroscopy (XPS). The GPC and FTIR spectra suggested successful bonding of MonoSilanolIsobutyl-POSS and PMS. TGA, DTG and XPS analysis revealed that MonoSilanoIsobutyl-POSS reinforced PMS are thermally more stable than the original PMS, primarily by the elimination of SiOH effects, the nanoreinforcement effect of POSS, the retardation of polymer chain motion and the formation of SiO_2 protective layer.

Introduction

Silicone resins have been widely used at elevated temperatures because of their outstanding thermal stability [1, 2]. However, their major drawback is their degradation at high temperature. The thermal degradation of silicones in air occurs primarily through the cleavage of organo-groups bound to the silicon atoms resulting in the formation of gaseous products [3, 4]. Another process is due to the terminal hydroxyl groups of silicones can participate in a ‘‘back-biting’’ reaction through which a Si–O chain branch is formed [5, 6].

Some traditional fillers (e.g., silica [7], titania [8], ferric oxide [9], aluminum oxide and zinc oxide [10], etc.) have been used to stabilize the siloxane structures against depolymerization. However, fillers are conventionally utilized to macroscopically reinforce large associated or nearby groups of polymers rather than the individual chains and segments within these polymers. Furthermore, the mismatch of chemical potential (e.g., solubility, miscibility, etc.) between hydrocarbon-based polymers and inorganic-based fillers resulted in a high level of heterogeneity in compounded polymers. Therefore, there exists a need for appropriately sized reinforcements for polymer systems with controlled diameters, distributions and with tailorable chemical functionality [11].

One class of inorganic component–polyhedral oligomeric silsesquioxanes (POSS) has nanometer-sized structures with high surface area and controlled porosity, and has been demonstrated to be an efficient method in the design of hybrid materials. POSS consists of a rigid, cubic silica core and has organic functional groups connected to the vertexes of the cubic core for further reaction. Their incorporation into some polymers has led to enhancements in thermal stability and mechanical properties. For instance, POSS molecules have been successfully incorporated into methacrylates [12], styrenes [13], norbornenes [14], ethylenes [15], polypropylene [16], epoxy [17] and siloxanes [18]. Moreover, nanostructured POSS dissolves in polymer matrix at the molecular level thus solving the long-standing dispersion problem associated with traditional particulate fillers.

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The copolymerization of disilanol functional POSS macromers with difunctional silane and siloxane monomers has been reported [19–24]. However, Polymethylsiloxane (PMS) was used in this study. There are two reasons why we have chosen PMS as one of the siloxane polymer models for the studying of POSS/polymer blends. First, because of their similarity in chemical compositions, POSS macromers have better compatibility with PMS than with other polymers, and good compatibility is a crucial requirement for fabricating multi-component systems with specific properties. Second, because of their organic/inorganic feature and the nanometer-size, POSS macromer has the potential to be a reinforcing filler for PMS. We report the preparation of hydroxyl-terminated PMS/MonoSilanolIsobutyl-POSS hybrid copolymers through silanol–silanol condensation reaction, and we also examine the influences of MonoSilanolIsobutyl-POSS on the thermal stability and degradation behavior of PMS.

Experiment

Materials

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

Synthesis of hydroxyl-terminated PMS

Hydroxyl-terminated PMS 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 PMS containing OH end groups were obtained.

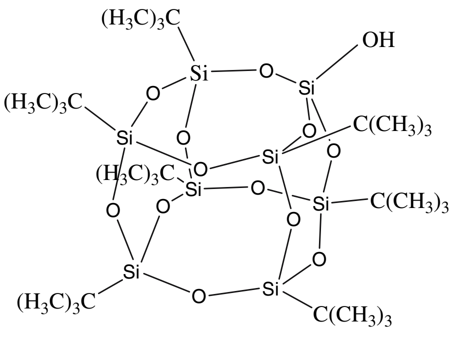

Fig. 1 The structure image of MonoSilanolIsobutyl-POSS

Preparation of the PMS/POSS hybrid copolymers

Systematic design of the PMS/POSS hybrid copolymers was shown in Fig. 2. Various amounts of MonoSilanolIsobutyl-POSS (from 1 wt.% to 10 wt.%) were blended into silanol-terminated PMS before end crosslinking. For better mixing, a small portion of anhydrous ethanol (amounting to 10 wt.% PMS) was added to dissolve MonoSilanolIsobutyl-POSS before it was mixed with PMS. The mixture was stirred vigorously, and the solvent was removed at an elevated temperature by evacuation. The resulting solution was poured into Teflon molds and put into an oven to thermal cure. The cure protocol was as follows: heat to 80 °C and hold for 30 min, then 100 °C for 2 h, 130 °C for 2 h, 160 °C for 2 h and 180 °C for 2 h. Each sample was then postcured at 200 °C for 30 min. After curing, a dark-brown solid was obtained.

Measurements

The molecular weight of samples was measured by a Shimadzu Gel Permeation Chromatograph (GPC-802, made in Japan). A series of narrow polystyrene molecular weight standards with molecular weight ranging from 30,000 Da to 500 Da were used to calibrate the GPC column set. Tetrahydrofuran (THF) was used as the mobile phase that was flowed at 1.0 ml/min. The column temperature was set at 25 °C.

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.

Thermogravimetric analysis (TGA) was performed on a CANY thermoanalyzer (ZRT-2P, made in China). Samples weighting about 10.0 mg were heated from 50 °C to 1,000 °C at a heating rate of 10 °C/min in a dynamic air atmosphere.

The X-ray photoelectron spectroscopy (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.

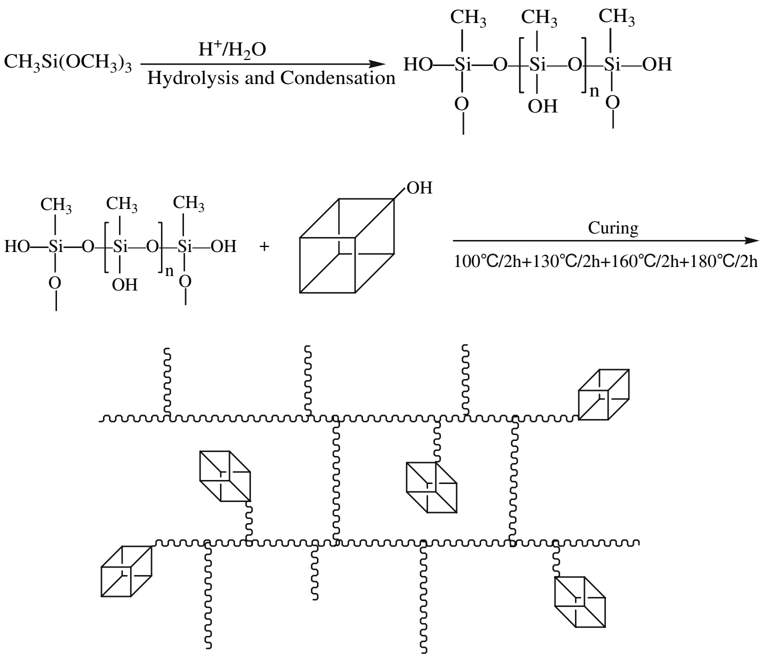

Fig. 2 Chemical incorporation of POSS cages into PMS networks

Results and discussion

The molecular weights of PMS and PMS/POSS copolymers

The molecular weights of the PMS and PMS/POSS hybrid polymers (PMS + 4 wt.% MonoSilanolIsobutyl-POSS) were determined by GPC in THF using Polystyrene standards for the calibration. The GPC chromatograms of the polymers are shown in Fig. 3 and the molecular weights of the polymers are reported in Table 1. The chromatograms of PMS and PMS/POSS hybrids show the expected monomodal distribution for solution polymerizations. This indicates the formation of one type of polymer chains in the PMS and PMS/POSS synthesis. The molecular weights of PMS/POSS hybrid polymers are higher compared to that of PMS. The formation of higher molecular weight polymers suggests that the conditions employed for the synthesis of PMS/POSS hybrid polymers is highly effective.

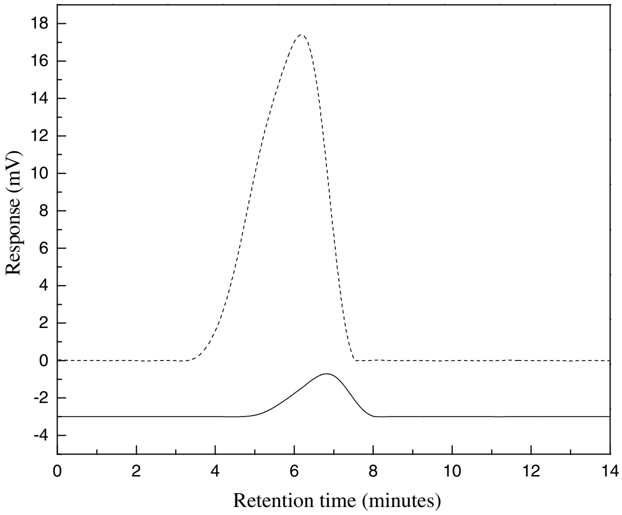

Fig. 3 The GPC chromatograms of PMS (straight line) and PMS/POSS hybrid polymers (dashed line)

Table 1 The molecular weights of PMS and PMS/MonoSilanolIsobutyl-POSS copolymers determined by GPC

Polymer	M_w (g/mol)	M_n (g/mol)	M_z (g/mol)	M_w/M_n
PMS	2396	2351	2445	1.019
PMS/POSS copolymer	2735	2671	2803	1.024

FT-IR analysis

Figure 4 shows the FT-IR spectra for MonoSilanolIsobutyl-POSS, PMS and 4 wt.% MonoSilanolIsobutyl-POSS reinforced PMS. The peaks at 3,425 cm^{-1}(Si–OH stretching), 2,956 cm^{-1}(C–H stretching of Si–C(CH$_3$)$_3$), 1,113 cm^{-1}(Si–O–Si asymmetric stretching), and 815 cm^{-1}(Si–O–Si symmetric stretch) are shown in the Fourier transform infrared (FTIR) spectrum of MonoSilanolIsobutyl-POSS, however, at 1,717 cm^{-1} exists the absorption band of C=O, which originates from the intermediate products or some partial cage structured POSS mixtures during the preparation of MonoSilanolIsobutyl-POSS. The peaks at 3,458 cm^{-1}(Si–OH stretching), 2,974 cm^{-1}(C–H

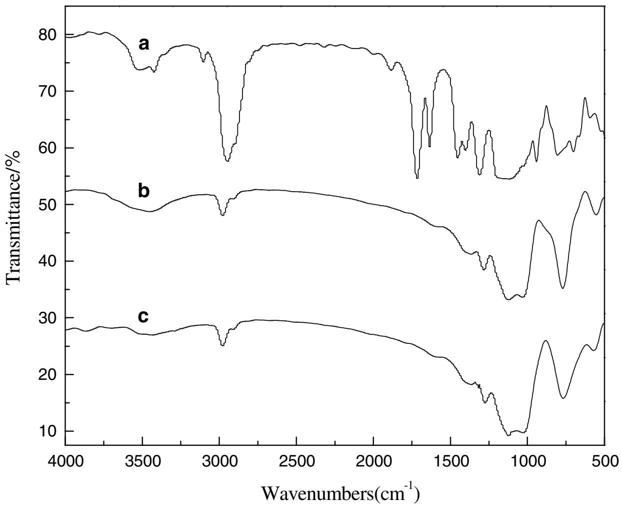

Fig. 4 FT-IR spectra of MonoSilanolIsobutyl-POSS (**a**), PMS (**b**) and 4 wt.% MonoSilanolIsobutyl-POSS reinforced PMS (**c**) in the regions from 4,000 cm^{-1} to 500 cm^{-1}

stretching of Si–CH$_3$), 1,124 cm^{-1} and 1,027 cm^{-1} (Si–O–Si asymmetric stretching), and 781 cm^{-1}(Si–O–Si symmetric stretch) are shown in the FTIR spectrum of PMS, which indicates that the synthesized products are the hydroxyl terminated PMS. The Si–O–Si band of the prepared PMS splits into two bands at 1,124 and 1,027 cm^{-1} and the detailed peak assignment can be found in the literature [25]. The peak position of the Si–O–Si band at 1,127 cm^{-1} suggests the existence of the Si–O–Si cage structure in the prepared PMS polymers. The 1,027 cm^{-1} band can be assigned to the Si–O–Si network absorption band.

Two distinct changes can be observed from a comparison of the FTIR spectra of Fig. 4b and Fig. 4c. One difference is observed between the Si–OH contents in the prepared PMS and PMS/POSS copolymers. The absorption peaks of the Si–OH groups at about 3,450 cm^{-1} decrease significantly in Fig. 4c. This suggests that the condensation reaction of the Si–OH groups of PMS and MonoSilanolIsobutyl-POSS have taken place. Thus, MonoSilanolIsobutyl-POSS promotes the condensation reaction of the Si–OH group and reduces the Si–OH content of PMS. Another change is the absorption bands between 1,000 cm^{-1} and 1,300 cm^{-1} become wider and broader in Fig. 4c. The intensity of the Si–O–Si absorption band of the cage structure at 1,124 cm^{-1} increases after the incorporation of POSS. However, the Si–O–Si absorption band of the network structure at 1,027 cm^{-1} shows the opposite trend. This indicates that the Si–O–Si cage structure of POSS has been linked to the network structure of PMS.

The above FT-IR results suggest that the presence of MonoSilanolIsobutyl-POSS in PMS polymer matrix has significantly affected the reaction during the condensation stage, which resulted in a higher crosslinked PMS-POSS network. The FT-IR results agree with our previous conclusions as demonstrated using GPC results.

Comparison of TGA and DTG curves of PMS and PMS/POSS copolymers

TGA and differential thermogravimetric analysis (DTG) are applied to evaluate the effects of MonoSilanolIsobutyl-POSS on the thermal stability and degradation behavior of the PMS. The TGA curves of PMS and PMS/MonoSilanolIsobutyl-POSS hybrid copolymers in air at a heating rate of 10 °C/min are shown in Fig. 5a, and the corresponding DTG curves are shown in Fig. 5b. The most important other features of the thermograms for all six samples are given in Table 2.

As can be seen from the TGA curve of pure PMS in Fig. 5a, the PMS shows 22 w/w total weight loss. The DTG curves of PMS are characterized by two maxima, the

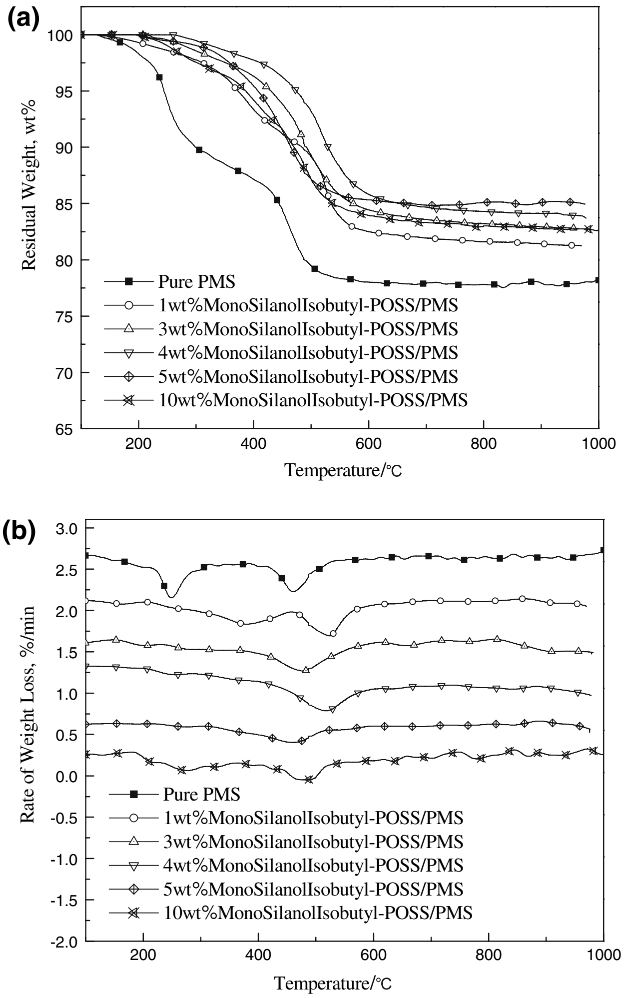

Fig. 5 TGA(**a**) and DTG(**b**) curves of PMS and PMS/ MonoSilanolIsobutyl-POSS hybrid copolymers in air at a heating rate of 10 °C / min

Table 2 TGA and DTG results for the PMS and PMS/POSS hybrid copolymers

Wt.% POSS	Onset of degradation* (°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	222.4	380.1	449.2
	478.7	523.6	581.6
3	279.8	477.9	581.5
4	328.5	516.8	598.1
5	303.9	457.8	512.2
10	251.9	276.5	388.7
	410.7	476.3	532.7

* Temperature for 1% weight loss

first at about 254.4 °C and the second at about 456.3 °C, which can be explained by the existence of a two-stage decomposition mechanism. There are at least two chemical processes at the first degradation stage. At the beginning, 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 of 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 $(CH_3SiO_{1.5})_n$-structure, which sublimate and lead to the weight 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 [26–28]. The second step of cleavage shown by TGA between 400 °C and 500 °C can be easily explained. The Si–CH_3 groups in the PMS polymers are oxidized, CO_2 and H_2O are released. SiO_2 remains in the crucible [29].

According to the TGA curves of PMS/POSS hybrids, the heat resistance of the PMS can be greatly improved by the introduction of MonoSilanolIsobutyl-POSS, which shows 16 w/w total weight loss for 4 wt.% MonoSilanolIsobutyl-POSS/PMS hybrid polymers. The DTG curves for 1 wt.% and 10 wt.% MonoSilanolIsobutyl-POSS reinforced PMS are characterized by two maximums and the others are characterized by only one maximum. This indicates that 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. Since MonoSilanolIsobutyl-POSS can react with hydroxyl-terminated PMS by thermally induced SiOH condensations, the influence of Si–OH on the thermal stability of PMS was diminished to a certain extent [30]. However, the SiOH groups of MonoSilanolIsobutyl-POSS can themselves cause chain cleavage [31–33]. 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 excessive SiOH groups of POSS can cause cleavage of the PMS chains. This would explain the observation that the effect of this stabilization is most pronounced at the lower concentrations of POSS. So, if the quantity of POSS added to the PMS is proper to scavenge the silanol groups of PMS, the first decomposition stage caused by silanols can be eliminated. The second pyrolysis step of POSS reinforced PMS occurs at above 500 °C, the organic substituents of PMS and POSS macromers are oxidized.

These results suggest that the thermal stability of the PMS has been greatly improved by the introduction of POSS cages. One of the thermal degradation mechanisms of PMS under effects of POSS is the elimination of SiOH effects, as we have mentioned above. The second reason for the enhancement of thermal stability could be ascribed to the nanoreinforcement effect of POSS on the polymer matrix. Chemical bonding acts as an attractive force between the PMS and the POSS, leading to increased compatibility, therefore, POSS is molecularly dispersed and substantial reinforcement is possible. We further hypothesize that in a well-dispersed POSS-polymer system, such as the chemically synthesized POSS polymer hybrids, the particle-to-matrix interactions are dominant since the number of molecularly dispersed POSS molecules is large. Furthermore, the incorporation of the large mass and steric bulk of the POSS units in polymer matrix generally serves to reduce chain mobility, often improving thermal properties [34].

XPS analysis

The C1s peak, shown in Fig. 6a, is centered at about 284.2 eV, indicating that the predominant form of carbon present for the room temperature (R.T.) PMS is CH_3–Si. In spectra b and c, the C1s peaks shift to higher binding energy. This observation is consistent with the relative amounts of CH_3–Si decrease and the concentrations of C=O (BE = 288.8 eV) and C–O (BE = 286.5 eV) increase.

The C1s spectra obtained from POSS reinforced PMS is shown in Fig. 7. The predominant form of carbon present in the room temperature sample corresponds to the CH_3–Si (BE = 284.2 eV) of PMS and $(CH_3)_3C$–Si (BE = 284.5 eV) of the POSS cages. After oxidation at 300 °C, the C1s peak shifts slightly to higher binding energy, which indicates that there is no thermal degradation at 300 °C (see Fig. 7b). In spectra c, only the concentration of the singly oxidized carbon atoms (BE = 286.5 eV) increases. These changes imply that the isobutyl groups are being removed selectively leaving the methyl groups. This

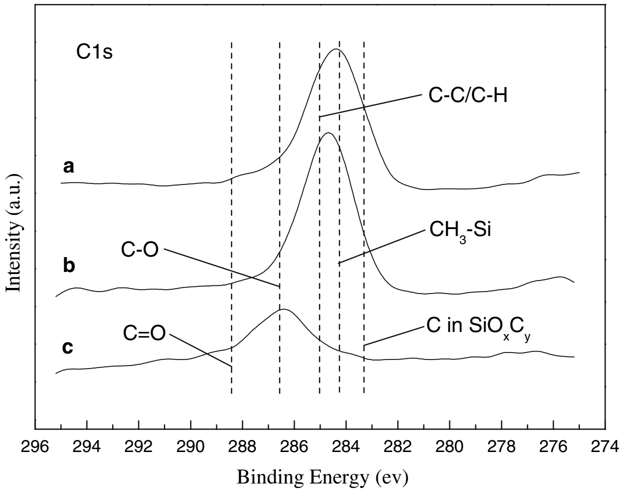

Fig. 6 C1s spectra obtained from PMS (**a**) R.T., (**b**) after pyrolysis in air atmosphere at 300 °C, (**c**) after pyrolysis in air atmosphere at 700 °C

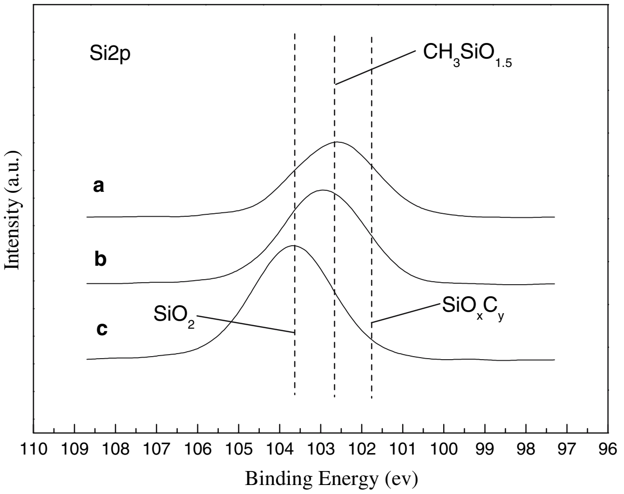

Fig. 8 Si2p spectra obtained from PMS (**a**) R.T., (**b**) after pyrolysis in air atmosphere at 300 °C, (**c**) after pyrolysis in air atmosphere at 700 °C

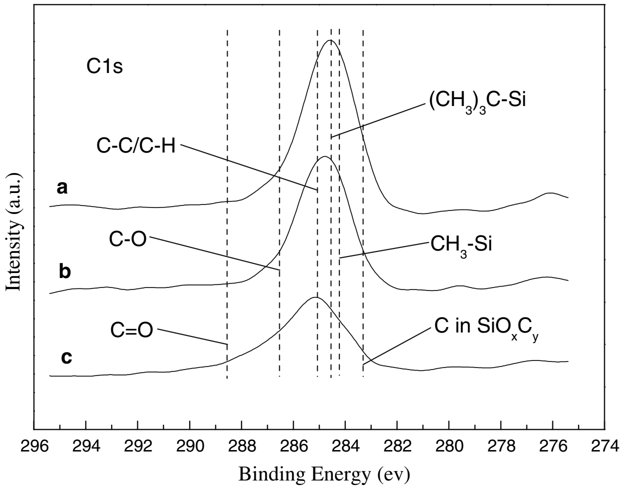

Fig. 7 C1s spectra obtained from POSS reinforced PMS (**a**) R.T., (**b**) after pyrolysis in air atmosphere at 300 °C, (**c**) after pyrolysis in air atmosphere at 700 °C

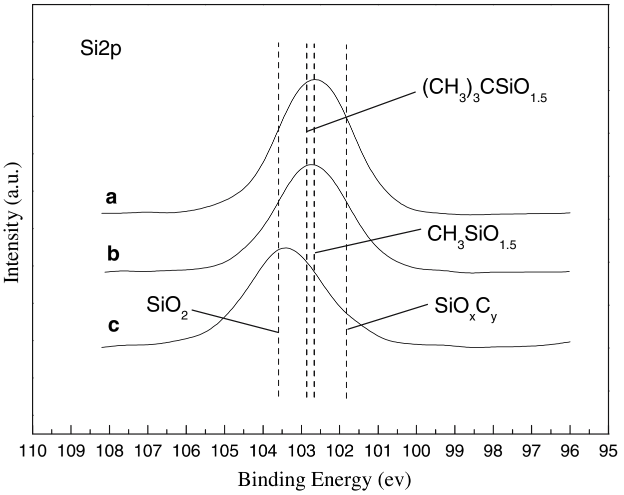

Fig. 9 Si2p spectra obtained from POSS reinforced PMS (**a**) R.T., (**b**) after pyrolysis in air atmosphere at 300 °C, (**c**) after pyrolysis in air atmosphere at 700 °C

selective removal could be due to the larger size of the POSS cage compared to the PMS chains. It could also be attributed to the weaker Si–C bond and the possibility that the POSS nanostructures could be surface segregating [35].

The Si2p peaks obtained from PMS are shown in Fig. 8. The spectrum of room temperature sample is centered at a BE a 102.6 eV, which corresponds to $CH_3SiO_{1.5}$ in the PMS chains. The spectra b shift to higher binding energy. After pyrolysis at 700 °C, the center of Si2p peak shifts to 103.6 eV, which corresponds to inorganic SiO_2.

However, in the Si2p region of the POSS reinforced PMS (see Fig. 9), the predominant forms of silicon are $CH_3–SiO_{1.5}$ (BE = 102.6 eV) on the PMS chains and $(CH_3)_3C–SiO_{1.5}$ (BE = 102.9 eV) on the POSS cages. The fact that little difference is observed in the spectra b indicates that the POSS reinforced PMS are thermally stable at 300 °C. This agrees with the change of C1s peaks for the same sample. After treated at 700 °C, only a small portion of SiO_2 is formed on the surface of POSS reinforced PMS which acts as a protective barrier preventing further degradation of the virgin polymer matrix [36].

Figure 10 shows the SiO_2 protective layer formation mechanism in PMS/POSS hybrid copolymers. The thermochemistry and SiO_2 protective layer formation

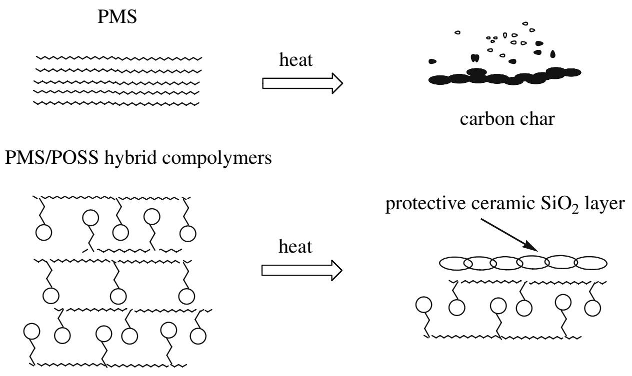

Fig. 10 The SiO_2 protective layer formation mechanism in PMS/POSS hybrid copolymers

mechanism operating for POSS-polymers have been previously reported [37]. 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. 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 polymers thereby enabling their facile incorporation into conventional polymer matrix.

Conclusions

MonoSilanolIsobutyl-POSS was used to reinforce hydroxyl terminated PMS polymers. The formation of higher molecular weight polymers suggested that the conditions used for the fabrication of PMS/POSS hybrid copolymers was very effective. TGA and XPS results have shown that PMS/POSS hybrid copolymers have much better thermal stability than pure PMS polymers. The enhancement of thermal stability could be ascribed to the elimination of SiOH effects, the nanoreinforcement effect of POSS on the polymer matrix, the retardation of polymer chain motion and the formation of SiO_2 protective layer. The promising results contained herein combined with the numerous property enhancements previously reported for POSS incorporation into traditional polymer systems made their use an attractive alternative to traditional fillers or coating systems when applied to space-based material applications.

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