



Greatly improving thermal stability of silicone resins by modification with POSS



Yaoyuan Xu ^a, Jun Long ^a, Runze Zhang ^a, Yunzhe Du ^a, Shengjie Guan ^a, Yuying Wang ^a,
Lingyun Huang ^a, Hongwei Wei ^a, Li Liu ^{a,b,**}, Yudong Huang ^{a,*}

^a School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, PR China

^b State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin, 150001, PR China

ARTICLE INFO

Article history:

Received 13 November 2019

Received in revised form

20 December 2019

Accepted 20 January 2020

Available online 23 January 2020

Keywords:

Polyhedral oligomeric silsesquioxane

Silicone resins

Thermal stability

Thermal decomposition mechanism

ABSTRACT

Silicone resins, due to its excellent high thermal stability, are widely applied in high-temperature environment. However, it is still a problem that the initial decomposition temperature of silicone resins is relatively low, which limits their wider applications. In this paper, three kinds of polyhedral oligomeric silsesquioxane (POSS) (aminopropyl, mercaptopropyl and chloropropyl) were synthesized and analyzed by FTIR, NMR and MS for structure characterization and purity analysis. Significant improvement of thermal stability was achieved by incorporating POSS into silicone resins. Three different POSS were used to modify silicone resins, and the effects of different POSS on thermal stability of silicone resins were studied. The results indicated that the thermal stability of octa-aminopropyl POSS modified silicone resins improved most significantly, with the decomposition temperature increased by nearly 45 °C compared with pure silicone resins. Moreover, the thermal decomposition mechanism of silicone resins with different POSS was studied, and chemical simulation indicated the thermal stability of silicone resins greatly improved by forming hydrogen bond between POSS and silicone resins. And the results showed one distinctive mode of increasing thermal stability, forming hydrogen bond to block resin chains' movements.

© 2020 Published by Elsevier Ltd.

1. Introduction

Silicone resins, a type of polymeric material, can be obtained by siloxane with the general formula of $R_nSiX_mO_y$, where $-R$ is a non-reactive substituent, and $-X$ is a functional group [1,2]. Its highly branched three-dimensional structure with the main chain of $-Si-O-Si-$ endows it with excellent properties such as extraordinary dielectric property, high thermal stability and short-wave irradiation resistance [3,4]. Thus, silicone resins are widely used in the fields of aerospace engineering, telecommunication industry, electronic industry and thermal insulation. Compared with homologous carbon-based polymers, silicone resins show a superior performance in thermal stability due to the physicochemical properties of the siloxane ($-Si-O-Si-$) bond [5]. However, the relatively low initial decomposition temperature limits silicone resins'

wider application. Therefore, it is of great significance to focus on modifying silicone resins in order to develop new silicone resins with higher thermal-stability.

For this purpose, extensive research has been devoted to silicone resins' modification, involving physical blending and chemical modification. As we know, the incorporation of nano- SiO_2 [6], carbon nanotubes [7], clay [8] and other nanofillers [9] can improve both thermal and mechanical properties of polymers [10,11]. However, because of the agglomeration of nanoparticles, it can hardly achieve nano-dispersion by mechanical blending. Thus, the chemical modification has a better modifying effect than physical blending in general. The chemical modification of polymer structure mainly involves two steps. First, introducing active groups into the end or side chains of polysiloxane. Then, the active groups were reacted with other polymers to form blocks, graft copolymers with interpenetrating networks in order to ameliorate silicone resins inherent deficiencies and further improve their thermal stability. Liu et al. [12] successfully synthesized a series of methylsilicone resin/POSS composites via mixing the functionalized trisilanolisobutyl POSS with hydroxylterminated methylsilicone resins, with

* Corresponding author.

** Corresponding author. School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, PR China.

E-mail addresses: liuli@hit.edu.cn (L. Liu), yduang.hit1@aliyun.com (Y. Huang).

increased decomposition temperatures and oxidation resistance. Yang [13] synthesized a series of silicone resins containing silphenylene units into the backbone to improve the thermal stability of silicone resins.

Meanwhile, hybrid organic/inorganic composites have attracted broad attention for decades. The hybrid organic/inorganic composites possess a great combination of the unique properties of both organic compound and inorganic material, owing to both the advantages of thermal stability, mechanical strength, and the ease of processing with low cost, low density. These unique qualities make such kind of materials more preferable than other conventional materials [14,15].

POSS with new organic/inorganic structure has attracted much researchers' attention. POSS, with an organic/inorganic structure, contains a silicon-oxygen based framework and eight organic corner groups on the side chains, it has been widely used to prepare high performance hybrid polymeric materials. Moreover, owing to these specific functional groups, POSS could disperse uniformly in organic polymers. By adding a little POSS into compound, the property of materials can improve dramatically, such as dielectric property, thermal stability and mechanical strength [16,17]. These characteristics make materials have promising application prospects in aerospace, medicine, national defense and other fields. Tanaka [18] used octa-isobutyl POSS as POSS-based molecular fillers to simultaneously enhance thermal and viscoelasticity of poly(methyl methacrylate) films. Pagacz [19] used octa-POSS (Hydroxyl POSS) to decrease the thermal degradation of polyurethane foams. Raimondo [20] added POSS compounds and phosphorous hardeners into an epoxy resin which was used for aeronautic applications, and improved the thermal and fire resistance of nano-filled aeronautic resins. With the development of technology, the initial decomposition temperature of silicone resins cannot satisfy the aerospace' demands. How to improve the initial decomposition temperature of silicone resins for broader applications has attracted researchers' attentions.

Here, three kinds of POSS were synthesized with various structure (aminopropyl, mercaptopropyl and chloropropyl) and the structure and the purify of POSS were characterized by NMR (^1H , ^{29}Si), FT-IR and MS tests. Silicone resins modified by POSS were studied to explore the effects of different functional groups on silicone resins' thermal stability by TGA, TGA-MS, XPS and SEM tests. The content of POSS was adjusted with 1 wt%, 5 wt%, 10 wt% and 15 wt% to investigate the optimal content of POSS and functional groups for improving the thermal stability of silicone resins. In this paper, three kinds of POSS were used to explore the thermal decomposition mechanism of different hydrogen bonds on silicone resins' thermal-stability.

2. Experimental section

2.1. Materials

3-aminopropyl triethoxysilane (APES, $\geq 99\%$), 3-chloropropyl triethoxysilane (CPOS, $\geq 99\%$), 3-mercaptopropyl triethoxysilane (MPTES, $\geq 99\%$), diethoxydimethylsilane, triethoxymethylsilane, dimethoxydiphenylsilane, trimethoxyphenylsilane, hexamethyl disilylamine were purchased from Aladdin. HCl, THF, xylene, acetone, deionized water, dichloromethane, ethanol and methanol were used without purification.

2.2. Synthesis of Octa-aminopropyl POSS($T_8\text{-NH}_2$)

This synthesis method of $T_8\text{-NH}_2$ POSS is a modification to a literature method [21]. 3-aminopropyl triethoxysilane and concentrated HCl were slowly dripped in methanol and mixed into

a heterogeneous solution. The resulting solution was heated with reflux condenser and stirred for 18 h to obtain a transparent liquid. Evaporate the solvent and add a certain amount of THF, the white precipitation could be given by filtering the liquid. The octa-aminopropyl POSS was obtained and named $T_8\text{-NH}_2$.

2.3. Synthesis of Octa-mercaptopropyl POSS($T_8\text{-SH}_8$)

This method is referring to a literature method [22] to synthesize $T_8\text{-SH}_8$. 3-mercaptopropyl trimethoxysilane and HCl were added in methanol solution. The solution was heated at 40°C and stirred for 24 h. Then the buff viscous liquid-octa-mercaptopropyl POSS was obtained and named $T_8\text{-SH}_8$.

2.4. Synthesis of Octa-chloropropyl POSS($T_8\text{-Cl}_8$)

This method is referring to a literature method [23] to synthesize $T_8\text{-Cl}_8$. 3-chloropropyl triethoxysilane, methanol and HCl were mixed to a heterogeneous solution. And solution was stirred for 5 days at 40°C . Then the white precipitation was obtained by filtering and named $T_8\text{-Cl}_8$.

2.5. Synthesis of silicone resins

The amount of each experimental reagent was determined according to the following formula. ($R/\text{Si} = 1.1$, $\text{Ph}/R = 0.4$). The total mass of four kinds of siloxane is 50 g). An oven-dried 250 ml, 3-neck bottom round flask equipped with a magnetic stirrer was fitted with 45 ml of deionized water and 8 g of acetone. Certain amount of hydrochloric acid was dropped to adjust solution pH to 4. The reactants were added dropwise to the 3-neck flask at a constant pressure in the following order: diethoxydimethylsilane, triethoxymethylsilane, dimethoxydiphenylsilane, trimethoxyphenylsilane. The hydrolysis reaction was carried out at 70°C . After reacting for 5 h, the hexamethyl disilylamine was added to adjust pH and control the molecular weight. At the end of the reaction, the silicone prepolymer in oil phase was separated by extraction. Then the prepolymer was heated up in 1 h at each of the following temperature, 80°C , 90°C , 100°C and 110°C . Finally, add certain amount of xylene and methylphenyl silicone resins were obtained.

2.6. Synthesis of POSS/resin composites

POSS/resin composites were thermal cured as follows: 100°C for 2 h, 120°C for 2 h, 150°C for 2 h, 180°C for 2 h and 220°C for 1 h, with different content of three kinds of POSS, 1 wt%, 5 wt%, 10 wt% and 15 wt%. Fig. 1 shows the structure of the three different types of POSS and silicone resins we used.

2.7. Characterizations

Thermogravimetric analysis (TGA) of the silicone resin/POSS composites was conducted by TA Instruments Q500 at a heating rate of $20^\circ\text{C}/\text{min}$ ranging from 40 to 1000°C under argon atmosphere. Fourier transform infrared (FTIR) spectra was obtained by using PerkinElmer 2200 FTIR Spectrometer between 500 and 4000 cm^{-1} . ^1H nuclear magnetic resonance (^1H NMR) and ^{29}Si nuclear magnetic resonance (^{29}Si NMR) spectra were performed on a BRUKER AVANCEIII-500 (American) with CD_3OD and CDCl_3 used as the solvent and internal standard. Mass spectra (ESI) was obtained by using Quattro Premier XE (American). The X-ray photoelectron spectroscopy (XPS) analysis was performed in an VG electron spectrometer ESCALAB Mk II (UK). Scanning electron microscopy (SEM) spectra was performed on Zeiss-SUPRA55

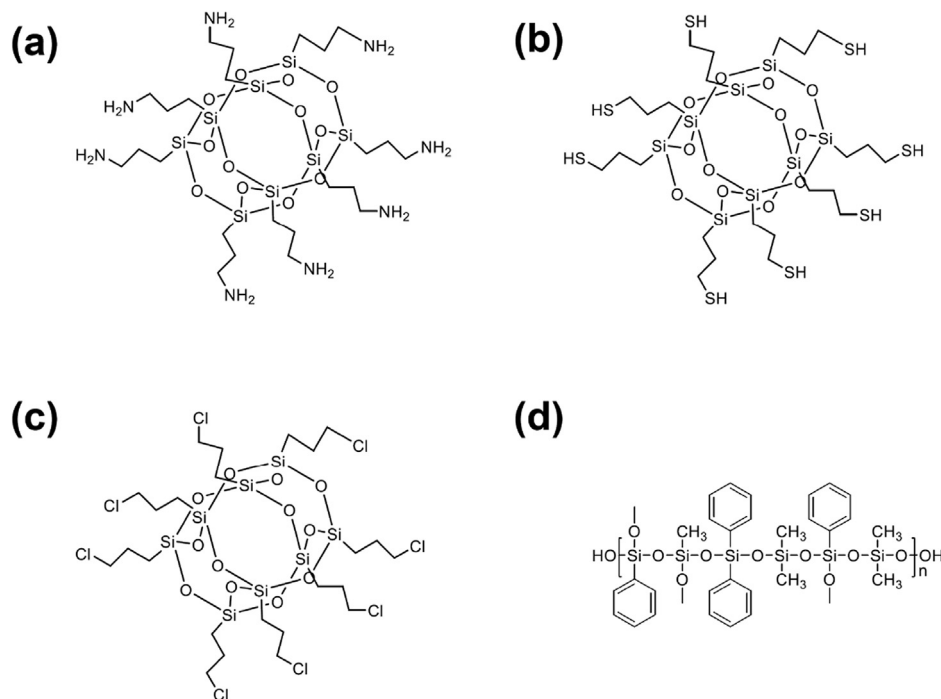


Fig. 1. The structure of synthesized three kinds of POSS, (a) $T_8\text{-NH}_2$, (b) $T_8\text{-SH}_8$, (c) $T_8\text{-Cl}_8$ and (d) silicone resins.

(Germany). TGA-MS spectra was obtained by using PerkinElmer. Hydrogen bond energy was calculated by Gaussian09 at B3LYP/gen level of theory. All geometry optimizations were carried out by using the DFT method B3LYP. H, C, N, O elements optimization uses 6-31G basis set, and Si, S, Cl elements optimization uses 6-31G(d) basis set. With using 6-311G and 6-311G(d) basis set, more accurate energy was obtained by performing single-point calculations. Frequency calculations were performed at the same theory level as optimizations to confirm the geometries presented here are local minimum of which all the frequencies are positive and to obtain zero-point energy (ZPE). All calculations were performed by using the Gaussian 09 program package. The structures were plotted with gauss-view.

3. Results and discussion

3.1. Synthesis and characterization of three kinds of POSS

The ^{29}Si NMR spectrum of three kinds of POSS were shown in Fig. 2. Three peaks were presented in -66.98 ppm, -67.05 ppm

and -67.08 ppm, respectively, attributed to the silicone chemical shift in T_8 cage structure of $T_8\text{-NH}_2$ [21], $T_8\text{-SH}_8$ [22] and $T_8\text{-Cl}_8$ [23], which were further confirmed in FTIR analysis.

The FTIR spectrum of $T_8\text{-NH}_2$, $T_8\text{-SH}_8$ and $T_8\text{-Cl}_8$ were basically indistinguishable with characteristic functional group difference, as shown in Fig. 3. The band appeared in $2890\text{--}2985\text{ cm}^{-1}$ region arose from -C-H stretching vibration and another bond in $1000\text{--}1100\text{ cm}^{-1}$ region was attributed to -Si-O-Si stretching vibration in cage structure, indicating the formation of T_8 cage structure. The characteristic vibration bond appeared in 3350 , 2560 and 701 cm^{-1} were assigned to -NH_2 , -S-H and -C-Cl stretching vibration respectively.

Fig. 4 showed ^1H NMR spectrum of POSS. The peaks can be assigned as $\delta = 4.87$ ppm (-NH_2 , 2H), $\delta = 1.75$ ppm (-SH , 1H), attributing to the functional groups -NH_2 on $T_8\text{-NH}_2$ and -SH on $T_8\text{-SH}_8$, respectively. The peaks of 0.82 , 1.91 , 2.99 ppm ($\text{-CH}_2\text{CH}_2\text{CH}_2$, 2H, 2H, 2H), 0.82 , 1.44 , 2.59 ppm ($\text{-CH}_2\text{CH}_2\text{CH}_2$, 2H, 2H, 2H) and 0.83 , 1.91 , 3.61 ppm ($\text{-CH}_2\text{CH}_2\text{CH}_2$, 2H, 2H, 2H) belongs to the propyl on $T_8\text{-NH}_2$, $T_8\text{-SH}_8$ and $T_8\text{-Cl}_8$ respectively.

MS spectra of three kinds of POSS were shown in Fig. 5. The m/z

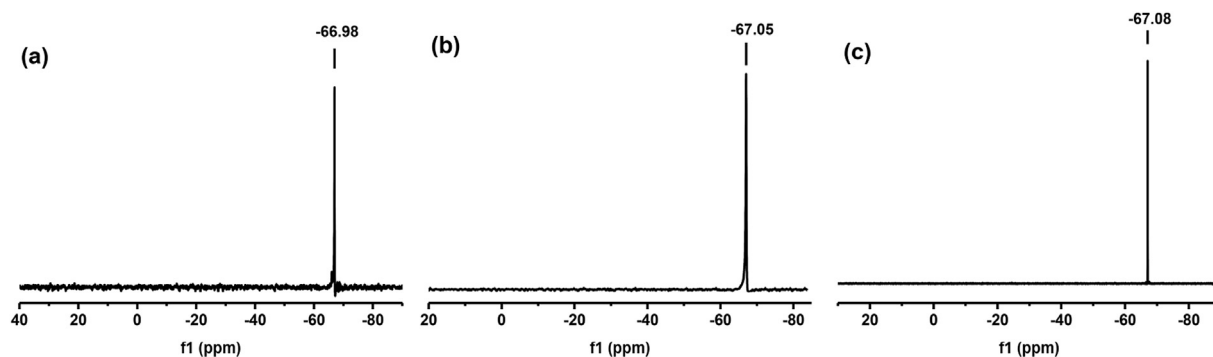


Fig. 2. ^{29}Si NMR spectra of synthesized three kinds of POSS, (a) $T_8\text{-NH}_2$, (b) $T_8\text{-SH}_8$ and (c) $T_8\text{-Cl}_8$.

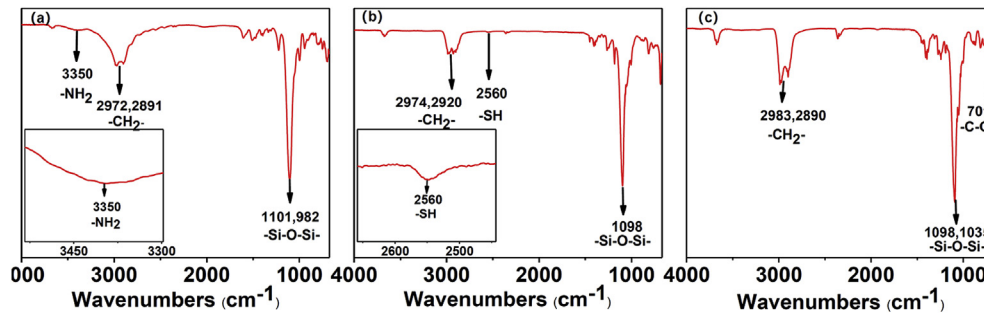


Fig. 3. FTIR spectra of synthesized three kinds of POSS, (a) T_8 -NH₂, (b) T_8 -SH₈ and (c) T_8 -Cl₈.

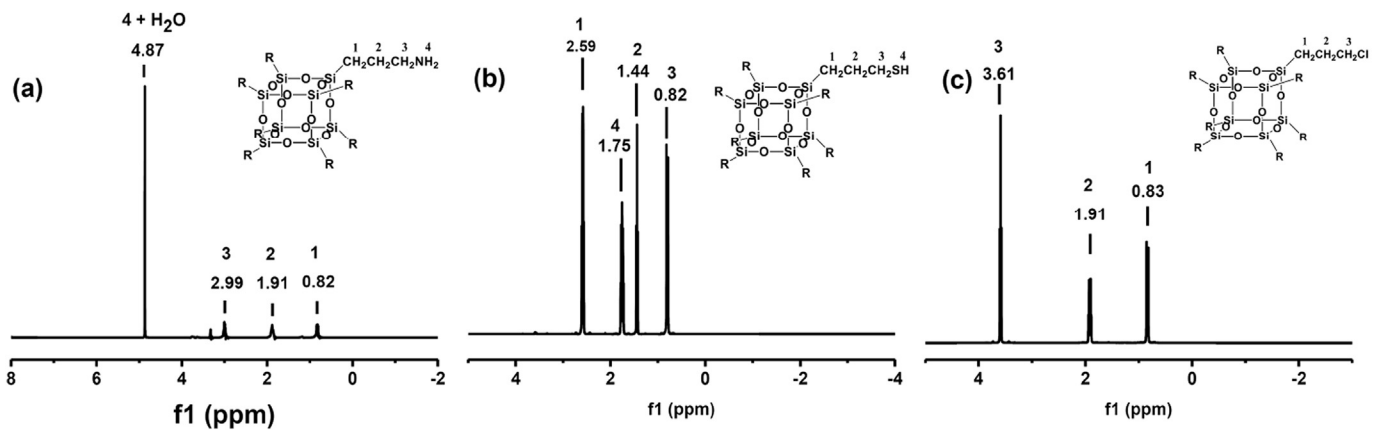


Fig. 4. ¹H NMR spectrum of synthesized three kind of POSS, (a) T_8 -NH₂, (b) T_8 -SH₈ and (c) T_8 -Cl₈.

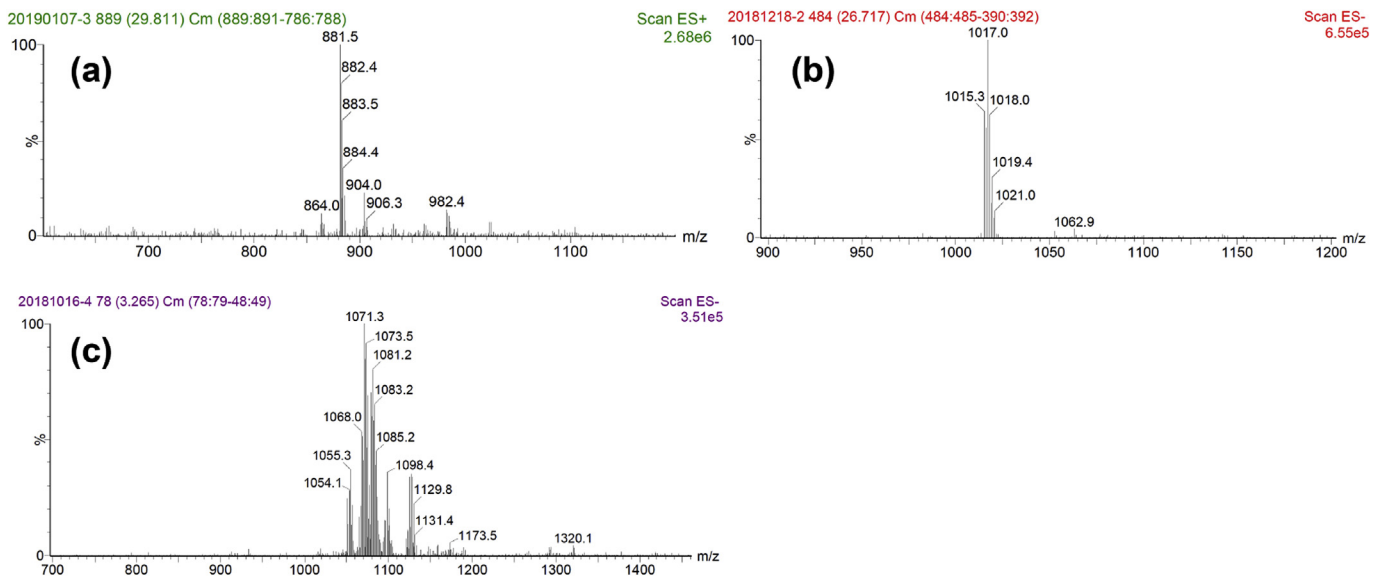


Fig. 5. MS spectrum (ESI) of synthesized three kind of POSS, (a) T_8 -NH₂ (ES⁺), (b) T_8 -SH₈ (ES⁺) and (c) T_8 -Cl₈ (ES⁻).

of $[T_8\text{-NH}_2 + \text{H}]^+$, $[T_8\text{-SH}_8 + \text{H}]^+$ and $[T_8\text{-Cl}_8 + \text{Cl}]^-$ are 881.5, 1017.0 and 1071.2 respectively. Figs. 3–5 confirmed that we synthesized three kinds of POSS successfully.

3.2. Preparation and characterization of POSS/resin composites

The surface morphology of pure resin and POSS/resin

composites were displayed in Fig. 6. It could be seen that the surface morphology of the pure resin was smooth (shown in Fig. 6d), while that of POSS/resin composites showed a wrinkled state (shown in Fig. 6a, c), which were caused by the cage structure of T_8 -NH₂ and T_8 -Cl₈, illustrating that they were aggregated uniformly in the POSS/resin composites respectively while the POSS adding is 1 wt%. The surface of T_8 -SH₈/resin composites showed an even

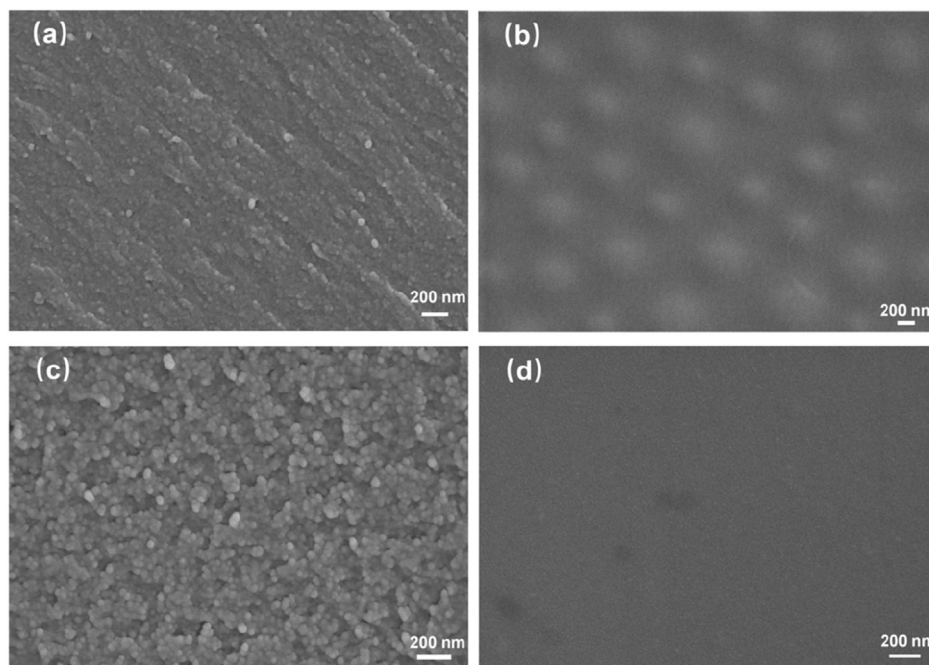


Fig. 6. SEM images of (a) T₈-NH₂/resin, (b) T₈-SH₈/resin, (c) T₈-Cl₈/resin composites with 1 wt% POSS adding and (d) neat resins.

surface with a uniform size of hemispherical bulges, indicating that T₈-SH₈ had severe agglomeration in the MP-silicone resins with 1 wt% T₈-SH₈ added (shown in Fig. 6b) [24,25]. Because of the aggregation of POSS, the scale of wrinkles and hemispherical bulges were 200 nm approximately.

The chemical compositions of pure resins and three kinds of POSS/resin composites were characterized by XPS (shown in Fig. 7). The spectral peaks of pure resins were fitted into two curves with peaks of 284.38 and 284.66 eV (shown in Fig. 7d), belonging to the -C-Si-O and -C-C on phenyl group respectively. The C 1s curves with peaks of 285.56, 285.52 and 285.90, were assigned to the -C-N on aminopropyl, -C-S on mercaptopropyl and -C-Cl bond on chloropropyl respectively (shown in Fig. 7a–c) [12,26]. It confirmed the existence of POSS in the silicone resins (shown in Figs. 6 and 7).

3.3. Thermal analysis

Fig. 8 shows the TGA curves of three kinds of POSS/resin composites measured with different content of POSS, 1 wt%, 5 wt%, 10 wt% and 15 wt%, respectively. All of three kinds of POSS improve the initial decomposition temperature with losing weight 5% (T_{5%}) of silicone resins when the POSS addition is 1 wt%. The POSS/resin composites showed a higher degradation temperature with 1 wt% POSS added. The degradation temperature was measured to be 585.5, 552.0, 561.2 and 540.5 °C at T₈-NH₂/resin, T₈-SH₈/resin, T₈-Cl₈/resin and neat resin when the content of POSS is 1 wt%. The result showed that T₈-NH₂ significantly improved the thermal stability of silicone resins with T_{5%} nearly 45° and that the thermal stability of POSS/resin composites showed a downward trend with the increasing addition of POSS, which was attributed to that POSS retarded the cross-linking of silicone resins.

The TGA-MS curves of POSS/resin composites with POSS addition is 1 wt% were shown in Fig. 9. In 400–1000 °C interval, three kinds of POSS/resin composites had similar degradation processes with ·OCH₃, ·C₆H₅, C₆H₆, ·CH₃ and CH₄ released. POSS/resin composites released H₂O from 100 °C to 300 °C, while T₈-NH₂/resin composites also released NH₃ from 100 °C to 300 °C (shown in

Fig. 9a) which can absorb most of the heat, greatly reducing the surface temperature of the polymer. And the T₈-NH₂ decomposing can accelerate the formation of C-films, which will deposit on the surface of the silicone resins. By this mean, the addition of the T₈-NH₂ (1 wt%) improved the initial decomposition temperature of silicone resins more than 45 °C [27–29]. Fig. 9b showed that from 300 °C to 500 °C, only H₂S were formed, attributed to the cleavage of -CH₂-SH on T₈-SH₈ respectively [30,31]. In 520 °C–1000 °C intervals, the decomposition of T₈-Cl₈/resin composites released HCl, attributed to the cleavage of functional groups (-CH₂-Cl) on T₈-Cl₈. During the cleavage process, amounts of ·Cl were formed, which could capture the ·OH formed by MP-silicone resins' early cleavage, improving the thermal stability of silicone resins (shown in Fig. 9c) [22,32].

3.4. Thermal decomposition mechanism

As previously reported, the initial decomposition of silicone resins at low temperature is attributed to dehydration [33,34] and "chains thawing" [35] resulted from residual terminal hydroxyl groups. With the temperature increasing, the backbone of silicone resins will bite back and release fragments. It can be seen that the decomposition temperature for 5% mass lose increases when the POSS addition is 1 wt%. This is due to the fact that the introduction of POSS into silicone resins increases the rigidity of backbones and decreases the mobility of resins' chains by forming hydrogen bonds. So adding three kinds of POSS in 1 wt% can improve the thermal stability of silicone resins.

TGA tests showed that the order of extent that POSS improved the decomposition temperature of silicone resins is: T₈-NH₂/resin > T₈-Cl₈/resin > T₈-SH₈/resin > neat resins when the POSS addition is 1 wt%. According to the formula: E_{A-B} = E_A + E_B - E_{AB}, (E_{A-B}: the bond energy of A and B; E_A, E_B: the energy of fragment A and fragment B; E_{AB}: the total energy of AB) the energy of the hydrogen bond between -NH₂ group and oxygen atom can be calculated, as shown in Fig. 10. Fig. 10a shows the structure and bond energy of the hydrogen bond (N··H-O) between -NH₂ on T₈-

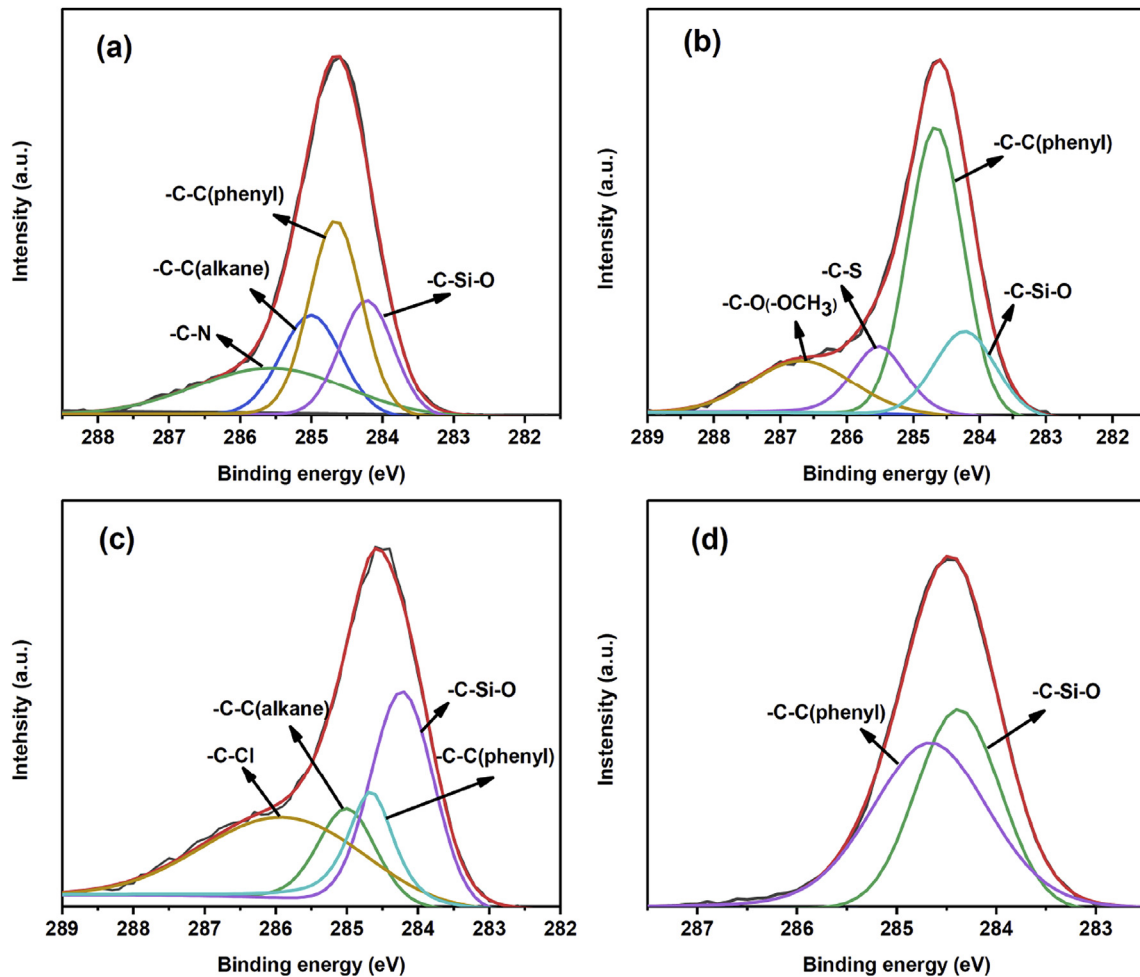


Fig. 7. XPS of C1s spectra of (a) $T_8-NH_2/resin$, (b) $T_8-SH_8/resin$, (c) $T_8-Cl_8/resin$ and (d) neat resins, while POSS adding is 1 wt%.

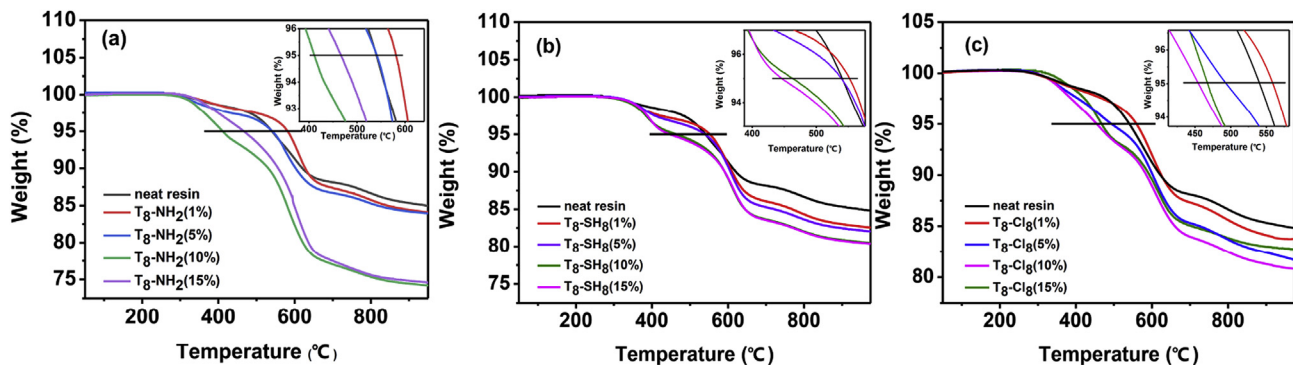


Fig. 8. TGA curves of different POSS content, 1 wt%, 5 wt%, 10 wt%, 15 wt%. (a) $T_8-NH_2/resin$, (b) $T_8-SH_8/resin$ and (c) $T_8-Cl_8/resin$ composites. “—” represents the decomposition temperature when the mass lose is 5%.

NH_2 and $-OH$ on MP-silicone resin, which is 14.67 kcal/mol. Fig. 10b shows the structure and energy of the hydrogen bond ($N-H\cdots O$) between $-NH_2$ on T_8-NH_2 and $-O-$ on MP-silicone resin, which is 3.65 kcal/mol. Because the electronegativity of O atom is higher than that of N atom, the structure of the hydrogen bond between $-NH_2$ and oxygen atom tends to form $N-H\cdots O$. Similarly, the energy of hydrogen bond between $-SH$ group and oxygen atom can be calculated, as shown in Fig. 11. It shows two kinds of hydrogen bond, $S\cdots H-O$ between $-SH$ on T_8-SH_8 and $-OH$ on silicone resins

(Fig. 11a) and $S-H\cdots O$ between $-SH$ on T_8-SH_8 and oxygen atom on silicone resins (Fig. 11b), and the hydrogen bond energy are 5.212 kcal/mol and 2.252 kcal/mol, respectively. Because the electronegativity of S atom is weaker than that of O atom, the structure of the hydrogen bond between T_8-SH_8 and MP-silicone resin tends to be $S-H\cdots O$. Fig. 12 shows the hydrogen bond ($Cl\cdots H-O$) between $-Cl$ on T_8-Cl_8 and $-OH$ on MP-silicone resin, and the bond energy is 3.78 kcal/mol. In POSS/resin composites, the hydrogen bonds are mainly existed in three distinctive forms, $N-H\cdots O$,

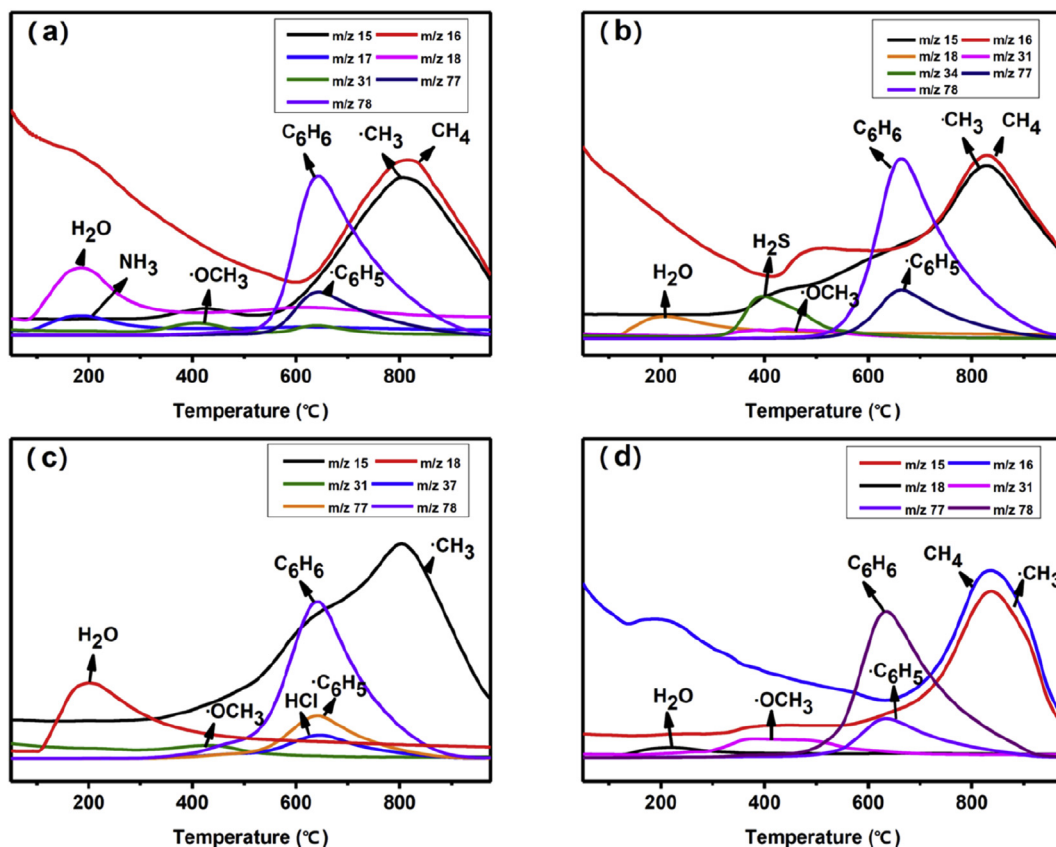


Fig. 9. TGA-MS spectra of (a) T_8 - NH_2 /resin, (b) T_8 - SH_3 /resin, (c) T_8 - Cl_8 /resin composites with POSS adding is 1 wt% and (d) neat resin.

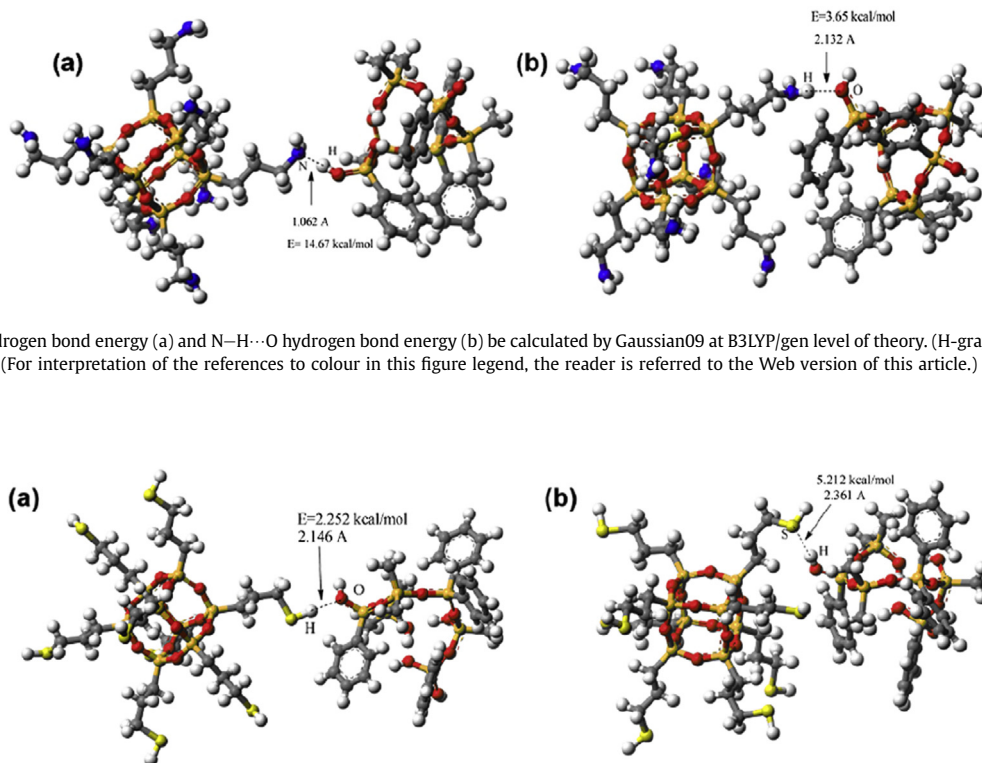


Fig. 10. The $N \cdots H \cdots O$ hydrogen bond energy (a) and $N-H \cdots O$ hydrogen bond energy (b) be calculated by Gaussian09 at B3LYP/gen level of theory. (H-gray, C-black, N-blue, O-red, 6-31G; Si-yellow, 6-31G*).

Fig. 11. The $S-H \cdots O$ hydrogen bond energy (a) and $S \cdots H \cdots O$ hydrogen bond energy (b) be calculated by Gaussian09 at B3LYP/gen level of theory. (H-gray, S-pale yellow, C-black, O-red, 6-31G; Si-yellow, 6-31G*).

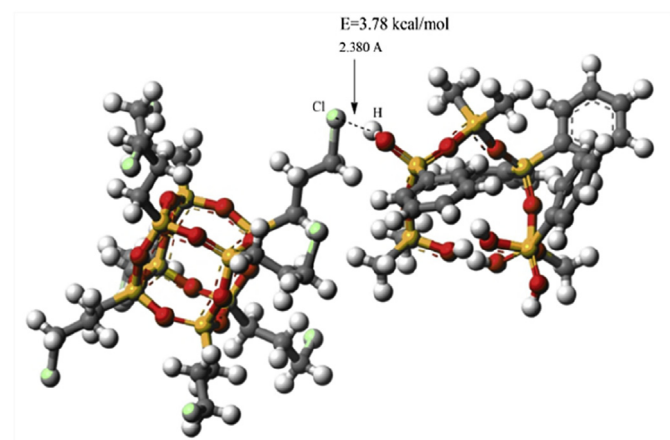


Fig. 12. The Cl \cdots H–O hydrogen bond energy be calculated by Gaussian09 at B3LYP/gen level of theory. (H-gray, C-black, O-red, 6-31G; Si-yellow, Cl-gray and green, 6-31G*). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Cl \cdots H–O and S–H \cdots O, with the hydrogen bond energy of 3.65, 3.78, 2.252 kcal/mol respectively. Due to the radius of the Cl atom is larger than H atom, the hydrogen bond is unstable and susceptible to be broken. Therefore, even though the hydrogen bond energy of Cl \cdots H–O is higher than N–H \cdots O, the thermal stability of T₈-Cl₈/resin composites is worse than T₈-NH₂/resin composites. The order of thermal stability in POSS/resin composites is as following: T₈-NH₂/resin > T₈-Cl₈/resin > T₈-SH₈/resin > neat resins with 1 wt% POSS addition, which coincided with the TGA test results above.

4. Conclusion

In this paper, three kinds of POSS (aminopropyl, mercaptopropyl and chloropropyl) were synthesized and incorporated in silicone resins. Both the effects of different kinds of functional groups and the content of POSS on the thermal stability of silicone resins were investigated. When the T₈-NH₂ content was 1 wt%, the T_{5%} of the silicone resins was dramatically increased, with the highest decomposition temperature reaching 585.5 °C, nearly 45 °C improvement compared with neat resins. Three kinds of POSS improve the thermal stability of POSS/resin composites when the POSS adding is 1 wt% by forming hydrogen bond with silicone resins. This study proposes a novel method to improve the decomposition of silicone resins by adding POSS.

Declaration of competing interest

This manuscript is approved by all authors for publication and no conflict of interest exists in the submission of this manuscript. I would like to declare on behalf of my co-authors that this paper is our original unpublished work and it has not been submitted to any other journals for reviews, in whole or in part. All the authors listed have approved the enclosed manuscript.

CRedit authorship contribution statement

Yaoyuan Xu: Conceptualization, Methodology, Writing - review & editing, Data curation, Writing - original draft, Formal analysis. **Jun Long:** Software, Project administration. **Runze Zhang:** Writing - review & editing. **Yunzhe Du:** Writing - original draft, Writing - review & editing. **Shengjie Guan:** Formal analysis. **Yuying Wang:** Formal analysis. **Lingyun Huang:** Investigation, Software. **Hongwei Wei:** Software. **Li Liu:** Software, Project administration. **Yudong**

Huang: Software, Project administration.

Acknowledgment

This work has been supported by National Key R&D Program of China.

References

- [1] R. Richter, G. Roewer, U. Böhme, et al., Organosilicon polymers—synthesis, architecture, reactivity and applications, *Appl. Organomet. Chem.* 11 (2) (1997) 71–106.
- [2] Jd Jovanovic, M.N. Govedarica, P.R. Dvornic, I.G. Popovic, The thermogravimetric analysis of some polysiloxanes, *Polym. Degrad. Stabil.* 61 (1) (1998) 87–93.
- [3] B.J. Zhang, D.X. Zhuo, A.J. Gu, Preparation and properties of addition curable silicone resins with excellent dielectric properties and thermal resistance, *Polym. Eng. Sci.* 52 (2012), 259–67.
- [4] M.W. Di, S.Y. He, R.Q. Li, D.Z. Yang, Radiation effect of 150 keV protons on methyl silicone rubber reinforced with MQ silicone resin, *Nucl. Instrum. Methods B* 248 (1) (2006) 31–36.
- [5] W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York, 1978, pp. 1–23. Materials.
- [6] H. Zhang, Z. Zhang, K. Friedrich, C. Eger, Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content, *Acta Mater.* 54 (7) (2006) 1833–1842.
- [7] W. Shen, R. Ma, A. Du, et al., Effect of carbon nanotubes and octa-aminopropyl polyhedral oligomeric silsesquioxane on the surface behaviors of carbon fibers and mechanical performance of composites, *Appl. Surf. Sci.* 447 (2018) 894–901. S016943321830905X.
- [8] Y. Lin, M. Song, C.A. Stone, S.J. Shaw, A comprehensive study on the curing kinetics and network formation of cyanate ester resin/clay nanocomposites, *Thermochim. Acta* 552 (20) (2013) 77–86.
- [9] K.C. Jajam, H.V. Tippur, Quasi-static and dynamic fracture behavior of particulate polymer composites: a study of nano- vs. micro-size filler and loading-rate effects, *Composites Part B* 43 (8) (2012) 3467–3481.
- [10] Q.S. Ma, Y. Ma, Z.H. Chen, Fabrication and characterization of nanoporous SiO₂ ceramics via pyrolysis of silicone resin filled with nanometer SiO₂ powders, *Ceram. Int.* 36 (8) (2010) 2269–2272.
- [11] G. Wu, et al., Preparation of SiO₂–GO hybrid nanoparticles and the thermal properties of methylphenylsilicone resins/SiO₂–GO nanocomposites, *Thermochim. Acta* 613 (2015) 77–86.
- [12] Y.R. Liu, Y.D. Huang, L. Liu, Effects of TriSilanollsobutyl-POSS on thermal stability of methylsilicone resin, *Polym. Degrad. Stabil.* 91 (11) (2006) 2731–2738.
- [13] Z. Yang, S. Han, R. Zhang, et al., Effects of silphenylene units on the thermal stability of silicone resins, *Polym. Degrad. Stabil.* 96 (12) (2011) 2145–2151.
- [14] D. Luo, W. Chen, Y. Mi, Incorporation of the Fe₃O₄ and SiO₂ nanoparticles in epoxy-modified silicone resin as the coating for soft magnetic composites with enhanced performance, *J. Magn. Magn. Mater.* 452 (2018) 5–9.
- [15] J.C. Huang, C.B. He, Y. Xiao, et al., Polyimide/POSS nanocomposites: interfacial interaction, thermal properties and mechanical properties, *Polymer* 44 (16) (2003) 4491–4499.
- [16] J.M. Misasi, Q. Jin, K.M. Knauer, et al., Hybrid POSS-Hyperbranched polymer additives for simultaneous reinforcement and toughness improvements in epoxy networks, *Polymer* 117 (2017) 54–63.
- [17] J.J. Chruściel, E. Leśniak, Modification of epoxy resins with functional silanes, polysiloxanes, silsesquioxanes, silica and silicates, *Prog. Polym. Sci.* 41 (2015) 67–121.
- [18] K. Tanaka, H. Kozuka, K. Ueda, et al., POSS-based molecular fillers for simultaneously enhancing thermal and viscoelasticity of poly(methyl methacrylate) films, *Mater. Lett.* 203 (2017) 62–67. S0167577X17308625.
- [19] J. Pagacz, E. Hebda, S. Michaiowski, et al., Polyurethane foams chemically reinforced with POSS -thermal degradation studies, *Thermochim. Acta* 642 (2016) 95–104. S0040603116302416.
- [20] M. Raimondo, S. Russo, L. Guadagno, et al., Effect of incorporation of POSS compounds and phosphorus hardeners on thermal and fire resistance of nanofilled aeronautic resins, *RSC Adv.* 5 (15) (2015) 10974–10986.
- [21] Z. Zhang, G. Liang, T. Lu, Synthesis and characterization of cage octa- (aminopropyl-silsesquioxane), *J. Appl. Polym. Sci.* 103 (4) (2007) 7.
- [22] H. Lin, X. Wan, X. Jiang, Q. Wang, J. Yin, A nanoimprint lithography hybrid photoresist based on the thiol-ene system, *Adv. Funct. Mater.* 21 (2011) 2960–2967.
- [23] S. Chimjarn, R. Kunthom, P. Chancharone, et al., Synthesis of aromatic functionalized cage-rearranged silsesquioxanes (T 8, T 10, and T 12) via nucleophilic substitution reactions, *Dalton Trans.* 44 (3) (2015) 916–919.
- [24] Y. Gan, X. Jiang, J. Yin, Self-Wrinkling patterned surface of photocuring coating induced by the fluorinated POSS containing thiol groups (F-POSS-SH) as the reactive nanoadditive, *Macromolecules* 45 (45) (2012) 7520–7526.
- [25] Y. Gan, J. Yin, X. Jiang, Self-wrinkling induced by the photopolymerization and self-assembly of fluorinated polymer at air/liquid interface, *J. Mater. Chem.* 2 (43) (2014) 18574–18582.

- [26] W. Zhang, G. Camino, R. Yang, Polymer/polyhedral oligomeric silsesquioxane (POSS) nanocomposites: an overview of fire retardance, *Prog. Polym. Sci.* 67 (2016) 77–125. S007967001630079X.
- [27] J. Choi, R. Tamaki, S.G. Kim, R.M. Laine, Organic/inorganic imide nanocomposites from amino-phenylsilsesquioxanes, *Chem. Mater.* 15 (2003) 3365e3375.
- [28] W.Y. Zhang, J. Barrio, C. Gervais, et al., Synthesis of Carbon-Nitrogen-Phosphorous Materials with Unprecedented High Phosphorous Amount toward an Efficient Fire-Retardant Material, *Angewandte Chemie International Edition*, 2018.
- [29] X. Mu, D. Wang, Y. Pan, et al., A facile approach to prepare phosphorus and nitrogen containing macromolecular covalent organic nanosheets for enhancing flame retardancy and mechanical property of epoxy resin, *Compos. B Eng.* 164 (2019) 390–399.
- [30] L. Li, R. Liang, Y. Li, et al., Hybrid thiol-ene network nanocomposites based on multi(meth) acrylate POSS, *J. Colloid Interface Sci.* (2013) 406.
- [31] A.F. Luo, X.S. Jiang, H. Lin, J. Yin, “Thiol-ene” photo-cured hybrid materials based on POSS and renewable vegetable oil, *J. Mater. Chem.* 21 (2011) 12753.
- [32] H. Lin, X. Wan, X. Jiang, Q. Wang, J. Yin, A “thiol-ene” photo-curable hybrid fluorinated resist for the high-performance replica mold of nanoimprint lithography (NIL), *J. Mater. Chem.* 22 (2012) 2616.
- [33] Z. Yang, S. Han, R. Zhang, et al., Effects of silphenylene units on the thermal stability of silicone resins, *Polym. Degrad. Stabil.* 96 (12) (2011) 2145–2151.
- [34] D. Bahloul-Hourlier, J. Latournerie, P. Dempsey, Reaction pathways during the thermal conversion of polysiloxane precursors into oxycarbide ceramics, *J. Eur. Ceram. Soc.* 25 (7) (2005) 979e85.
- [35] N. Grassie, K.F. Francey, I.G. Macfarlane, The thermal degradation of polysiloxanes part 4: poly(dimethyl/diphenyl siloxane), *Polym. Degrad. Stabil.* 2 (1) (1980) 67e83.