Effect of homologous nano-composites on the thermal degradation of the silicone resin

Bo Jiang\textsuperscript{a,b}, Kuiyuan Zhang\textsuperscript{b}, Qingfu Cai\textsuperscript{b}, Tianyou Zeng\textsuperscript{a,b}, and Meifang Zhu\textsuperscript{a}

\textsuperscript{a}State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, China; \textsuperscript{b}Polymer Materials and Engineering Department, School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, People’s Republic of China

**ABSTRACT**

Effect of homologous of nano-composites on the thermal degradation of the silicone resin was researched based on graphene oxide (GO)/polyhedral oligomeric silsesquioxane (POSS). First, the amino-POSS was grafted onto the GO surface (GO/POSS) via the amide bond. Second, GO/POSS was incorporated into the silicone with active epoxy group via chemistry grafting. The reaction kinetics of the thermal decomposition of the epoxy–silicone resin based on nano-composite homologous effect is developed. The initial decomposition temperature of the modified silicone resin is improved by 77.2°C. At high temperatures, GO/POSS-modified silicone molecular end forms homologous nano-structures, which can restrain silicone future degradation. The developed strategy has potential to restrain the degradation of the polymer molecular chain.

**Introduction**

Silicone resin matrix composites, which are a type of heat-resistant materials that exhibit good dielectric properties, low heat expansion coefficient, and are light weight, are applied in the aerospace industry, specifically on space shuttles (1–5). With the advancement of national defense and scientific technology, new emerging aerospace materials require that resin matrices exhibit high performance, especially heat resistance (6). However, the low initial onset thermal decomposition temperature of common silicone resin of about 200–400°C makes it difficult to be applied in high-temperature conditions. To be more specific, the end alkoxy groups of polysiloxane silicon molecular chains can be easily decomposed at high temperatures. The mechanisms of these degradation behaviors have been explored. Sun (7) studied the thermal degradation kinetics of poly (methylphenylsiloxane) containing methacryloyl groups and explain that thermal degradation of the poly-siloxane system undergoes two processes: “unzipping degradation” and “rearrangement degradation” at the high temperature. Camino (8, 9) studied polydimethylsiloxane (PDMS) thermal degradation via Si–O bond scission in a chain-folded cyclic conformation energetically favored by the overlapping of empty silicon d-orbitals with orbitals of oxygen and carbon atoms. PDMS thermal decomposition process was controlled by the different rate of the diffusion and evaporation of oligomers produced.

The property of thermal degradation of the silicone resin influences the application fields. Some physical and chemical strategy was developed to improve the thermal decomposition temperature. Zeng (10) prepared the allyloxyethoxysilane modified liquid silicone rubber by hydrosilylation reaction. The result shown that decomposition temperature of the modified liquid silicone rubber increased by 31°C and 60°C at 10% and 20% weight loss, respectively.

The stabilization of silicone resin against thermal oxidative degradation is most frequently accomplished by the incorporation of polyhedral oligomeric silsesquioxane (11), ferric oxide (12), aluminum oxide, or zinc oxide (13). Pradhan (14) developed the multi-walled carbon nanotube and fine powders of montmorillonite-reinforced silicone rubber nano-composites, which also exhibit the maximum improvement in thermal stability corresponding to 10% weight loss by 70°C. Lu (15) studied the aluminum oxide fibers modified the silicone elastomer, and when 30 wt% fiber was added to silicone elastomer, decomposition temperature increased to 49°C.

These nano-particles have high thermal stability and can act as “heat sink” which can limit the thermal conduction inside the material. In addition, the incorporation
nano-particles have protection effect (16, 17). Backbone structure of silicone resin is Si–O with side chain –CH₃, the homology structure incorporated into silicone resin molecular chain is excellent strategy from compatibility and stability of the molecular size.

Graphene is a single atomic plane of graphite that is sufficiently isolated from its environment, which is considered to be freestanding (18). Graphene nano-sized reinforced polymer composites have exhibited promising results for enhanced heat resistance (19, 20). Since the pioneering study of graphene as a new nano-sized carbon structure by Novoselov et al. (21). Graphene oxide (GO) is often used as nano-particles to functionalize the material’s surface owing to the carbonyl and carboxyl groups at the GO surface. Polyhedral oligomeric silsesquioxanes (POSS) has emerged as a novel organic–inorganic hybrid, which is Si–O cage structure of nano-particles containing a designed functional group that can participate in specific chemical reactions. The heat resistance of POSS is great and it can be used as a modified material. GO-grafted POSS (GO/POSS), a new type of reinforced filler in polymer matrix, can be used to modify dielectric properties, heat resistance properties, infiltration properties, mechanical properties, and interface properties of materials (22–24). The nano-composites show excellent performance due to the synergistic effect between GO and POSS.

No studies on effect of homologous nano-composite modified silicone resin have been reported. To increase the thermal decomposition temperature of silicone with epoxy group, we prepared the GO/POSS nano-structure modified silicone resin. The reaction kinetics of the modified silicone resin was studied.

**Experimental**

**Materials**

Nano-graphite powder, dicyclohexylcarbodimide (DCC) and 4-dimethylamino-pyridine (DMAP) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Octaaminophenyl polyhedral oligomeric silsesquioxanes (Oap-POSS) was provided by Hybrid Plastics Incorporation (Hattiesburg, Mississippi, USA). Methyl triethoxysilane, silane coupling agent (A1871), and dimethyldiethoxysilane were purchased from Chenguang Chemical Reagent Co. Ltd. (Shandong, China). Concentrated sulfuric acid (98%), tetrahydrofuran (THF), ethanol, ammonia water, concentrated hydrochloric acid (36.5%), sodium nitrate, potassium permanganate, and ethylenediamine were provided by Tianjin Fu Yu Fine Chemical Co. Ltd. (Tianjin, China).

**Synthesis of GO and GO/POSS**

GO was prepared from graphite using Hummers’ method (25). GO (20 mg) was suspended in THF (50 mg) under sonication for 30 min, then POSS (200 mg), DCC (200 mg), and DMAP (80 mg) were added into the suspension under sonication for another 20 min. Then, the mixture was introduced into a 250 ml three-neck flask with stirring. The mixture was heated to 60°C and refluxed for 24 h under nitrogen atmosphere. Every 6 h, the stirring was stopped and the suspension was sonicated for 15 min. After the reaction was stopped, the mixture was separated by centrifuge and washed by THF to remove the residual POSS. The product was freeze dried to remove the solvent.

**Synthesis of silicone resin with epoxy group**

Dimethyldiethoxysilane, A1871, ethanol, deionized water, and HCl (36.5%) were mixed together (molar ratio: 1:2.3:10:6.6:0.3), the solution was heated to 60°C and refluxed for 6 h. After the reaction, solution pH is controlled to 7 via ammonium hydroxide. Then the solution was distilled to remove water and ethanol to obtain the target product by rotary evaporators. The prepared 30 wt% of silicone resin solution with anhydrous alcohol was used in below experiment.

**Preparation of GO/POSS/silicone composites**

Prepared silicone resin (3.33 g) and GO/POSS (10 mg) were mixed together under sonication for 40 min, and the mixture was heated to 60°C to remove the solvent. For comparison, pure POSS and ethylenediamine modified GO were also added into the resin. All the samples were cured at 80°C for 2 h, 100°C for 2 h, 120°C for 2 h, 150°C for 2 h, and 180°C for 2 h. GO/POSS/epoxy–silicone samples were prepared via above method.

**Characterization**

Transmission electron microscopy (TEM) analysis was conducted by JEM-2100 instrument with an acceleration voltage of 100 kV to get image of pure GO, POSS, and GO/POSS. X-ray photoelectron spectroscopy (XPS) was carried out with a VG Escalab Mark II spectrometer (Thermo-VG Scientific Ltd., Silchester, UK), using Al Ka excitation radiation (hν = 1253.6 eV) to analyze the chemical elements. Fourier transform infrared (FT-IR, 4000–400 cm⁻¹) spectra were recorded using a Nicolet 6700 spectrophotometer using KBr pellets to analyze the typical chemical bond. Thermogravimetric analysis (TGA)
was performed by a Q5000 thermal analyzer (ZRY-2P, Shanghai precision instruments Co., Ltd, Shanghai, China) at a heating rate of 10°C/min in nitrogen atmosphere; scanning electron microscopy (SEM; JSM-6700F, Tokyo, Japan) was adopted to analyze the fracture morphology of different silicone samples at an activation voltage of 15.0 kV.

Results and discussion

GO/POSS

The amino POSS was grafted onto the surface of GO, this process is shown in Scheme 1. Pure GO and GO/POSS were dispersed in the tetrahydrofuran, and color change and picture were provided in Supporting Information 3.1 and Fig S1 (in the online supplementary information). The morphological information of POSS, GO, and GO/POSS is shown in Fig. 1. POSS is a spherical particle with a diameter of about tens of nanometers. After GO grafted POSS, it can be observed that there are many black spots in GO surface, because POSS particle affected the result (Fig 1c). The distribution is effectively determined by the carboxyl and epoxy groups on the GO sheets. From FT-IR spectra of GO and GO/POSS (Fig S2), the new band at 1347 cm\(^{-1}\) is corresponding to the stretching vibrations of the C–N group via the amidation of amino group and carboxyl/epoxy groups for GO/POSS. The amido bonds imply that POSS was successfully grafted to GO.

GO/POSS grafting process is further confirmed by C\(_{1s}\) and O\(_{1s}\) XPS peaks in Fig. 2. The new peak of Si\(_{1s}\), Si\(_{2p}\), and N\(_{1s}\) is observed from GO/POSS.

Nitrogen and silicon are derived from the amino POSS. Three peak positions of 284.8, 288.4, and 286.8 eV represent C–C bond, the epoxy/ether bond, and the carbonyl structure (Fig 2c), respectively. In Fig 2(d), a new peak at 285.6 eV can be seen which represents C–N bond via the amidation between the amino and carboxyl/epoxy. As a comparison, in Fig 2(d) C–O peak intensity is much lower than in Fig 2(c), this result implies that POSS was successfully grafted onto the surface of the graphene oxide via amidation, the oxygen functional groups on GO surface were partly reduced by POSS. The decrease in the amount of oxygen functional groups can increase the heat resistance of GO.

TG curves for GO and GO/POSS are shown in Fig. 3. The initial thermal decomposition temperature of pure GO is about 80.3°C in nitrogen due to water; small molecular decomposition of oxygen-containing functional groups in a low temperature, the major mass loss occurs around 200–250°C. For GO/POSS, the initial decomposition temperature increased to 287.2°C due to the decrease of oxygen-containing functional groups. The major mass loss occurs around 250–300°C. At 300–750°C, GO and GO/POSS exhibit the similar thermal gravimetric behavior; at 750–850°C, GO/POSS presents mass loss because of the destruction of the cage structure of POSS which was turned to stable \(\text{SiO}_2\) molecular structure, and the mass loss of GO can be explained with that the GO gradually turned into carbon powder. The different weight loss of pure GO and GO/POSS between 300°C and 750°C corresponds to the weight of POSS nano-particle on GO sheets.

![Scheme 1. Synthesis of GO/POSS.](Image)
Figure 1. (a) TEM of POSS, (b) GO, and (c) GO/POSS.

Figure 2. XPS spectra of (a) GO and (b) GO/POSS, and higher resolution C\textsubscript{1s} spectra of (c) GO, and (d) GO/POSS.
Microstructure and molecular feature of the modified silicone resin

Microstructure of the silicone resin containing GO/POSS nano-composites is shown in Fig. 4. The fracture surface of pure silicone resin is smooth; when lamellar structure of GO was added into silicone resin, the surface appears rough and wrinkled in composite system. Fig 4(c) presents that the little particles representing the POSS have grown on the surface of the silicone composites, and as a result of micro-size compared with silicone macromolecule, the picture shown in Fig 4(c) is not very clear. Whereas in comparison with POSS nano-particle in the silicone resin matrix, the GO platelets show a non-uniform distribution. Functional GO/POSS was incorporated into the epoxy–silicone resin via amide bonds, large regions of the pure epoxy–silicone matrix remained visible and the GO/POSS nano-structure did not completely occupy the entire composite volume after being modified. The image shows the GO/POSS nano-composite particle morphology incorporating the epoxy–silicone matrix. The lamellar graphene was observed and the POSS nano-particle playing a role of linkage was covered with GO platelets. As shown in Fig 4(d), the functional GO/POSS was thoroughly dispersed in the epoxy–silicone matrix.

As chemical modification, FT-IR was employed to analyze the typical bonds of pure epoxy–silicone and GO/POSS/epoxy–silicone, the result is shown in Fig. 5. The absorption of pure epoxy–silicone at around 1105 cm\(^{-1}\) is attributed to the Si–O group, and the band at around 915 cm\(^{-1}\) is corresponding to the epoxy group. After the GO/POSS was incorporated into the resin matrix, the new band at 1367 cm\(^{-1}\) corresponds to the stretching vibrations of the C–N group, which indicates the GO/POSS can cross-link the molecular chain of polysiloxane. These results further confirm that the functional GO/POSS was chemically incorporated into the epoxy–silicone resin.

Figure 3. TG curves of GO and GO/POSS.

Figure 4. SEM images of (a) pure silicone resin, (b) GO/silicone resin, (c) POSS/silicone resin, and (d) GO/POSS/silicone /rein.
Heat resistance of the modified silicone resin

TG evaluated to the heat resistance of the GO/POSS/silicone resin (Fig. 6). Nano-particle influences the initial thermal decomposition temperature ($T_{IDT}$) of epoxy–silicone resin: 253.5°C, 314.5°C, 274.1°C, 330.7°C, for pure silicone resin, POSS/silicone resin, GO/silicone resin, and GO/POSS/silicone resin, respectively. As a comparison, epoxy–silicone resin, GO/POSS modified epoxy–silicone resin $T_{IDT}$ increased to 77.2°C.

Due to the stable cage structure of POSS, big size steric effect can limit the movement of the polysiloxane molecular chain to enhance the heat property (Fig. 7). In addition, the excellent compatibility of the homologous of nano-scale structure can enhance to the initial decomposition temperature. Nanoscale GO sheet layer can be well dispersed in resin matrix to prevent heat and mass transfer between the polysiloxane chain and the sheets. The synergistic effect of GO/POSS nano-particles can limit the movement of the polysiloxane molecular chain and enhances the heat resistance of silicone matrix.

The chemical grafting is prominent than physical blending at heat resistance. Due to the redundant –NH$_2$ cross-linking of the molecular chain, the movement of the silicone molecular chain was profoundly limited by GO/POSS. At high temperature, the cage structure of POSS will be destroyed and turn to SiO$_2$, which is a much stable structure with excellent heat resistance property. Effect of homologous of nanocomposites prevented further degradation of the silicone resin at high temperature.

Thermal decomposition activation energy of silicone with epoxy group

Ozawa method was developed to calculate the thermal decomposition activation energy of silicone with epoxy group. The values of activation energy were determined from plots of $\ln (b \,(dX/dT))$ against $1/T$, obtained from each thermogram at constant values of $X$.
1 - \alpha = \frac{m_t - m_f}{m_0 - m_f} \tag{1}

\log \nu = \log \frac{AE}{RF(\alpha)} - 2.315 - \frac{0.4567E}{RT} \tag{2}

E = -k \times \frac{R}{0.4567} \tag{3}

where \(\alpha\) is decomposition degree, \(m_t\) is the mass of \(t\) moment in the process of decomposition, \(m_f\) is the residual mass at the end of decomposition, \(m_0\) is the mass before decomposition, \(\nu\) is heating rate, \(E\) is thermal decomposition activation energy of silicone resin, \(T\) corresponds to the temperature of different \(\alpha\). The heating rates are 5, 10, 20, and 50°C/min, \(\log \nu \sim 1000/T\) curve is made by choosing \(\alpha = 0.1–0.9\) steps and the slope of each straight line is the different values of \(k\). The calculated results are illustrated in Fig. 8.

It can be observed from Fig. 9 and Table S1, when the degree of decomposition increases, the activation energy of thermal decomposition has an increasing trend and caused the difficult decomposition. When GO/POSS was incorporated into the silicone matrix, the activation energy has the similar trend and increased at each degree of decomposition than that of pure silicone resin, which means the thermal decomposition of modified silicone with epoxy group requires more energy, as the heat resistance was enhanced.

Curves of the pure epoxy–silicone resin are shown in Fig. S3. Homologous effect of GO/POSS on silicone resin molecular structure is shown in Fig. 10.

**Mechanism of the thermal decomposition of the modified silicone resin based on effect of homologous**

The above-described analytical results imply that the thermal decomposition temperature of the modified silicone resin was improved. The thermal depolymerization
and thermal oxidative degradation of the composite were reduced due to the incorporation of the nano-composite particles. The mechanism of thermal decomposition was analyzed via steric hindrance, the isolation of oxygen, and small activated molecules based on homologous nano-composites structure.

The degradation of the silicone resin occurred in two different steps: unzip degradation and rearrangement degradation. The unzip degradation can be interpreted as follows. The first step of degradation of the polymer occurs between 250°C and 500°C, the polymer’s maximum degradation temperature influenced by the nanoparticle contents present in the nano-composite as the back-biting reaction of terminal hydroxyl groups which generated cyclic siloxane (26). The rearrangement degradation was caused by the heterolytic cleavage and rearrangement of Si–O–Si bonds in the main chain, generating low-molecular-weight cyclic siloxanes. The steric hindrance was an important factor. The homologous nano-composites were occupied by the molecular chain of the silicone resin. Thus, the activation of the molecular chain was difficult, and the thermally activated transport of small molecules was ceased. To enhance the capacity for molecular motion, energy was provided by increasing the temperature. The initial decomposition temperature increased for the modified silicone resin. This process is illustrated in Fig 10(b).

Second, oxygen atoms and small activated molecules were isolated. The Si–O bonds of the silicone resin have a partial ionic character. The external oxygen atom and activated molecules attack the silicon atoms of the silicone at high temperatures, resulting in the dissociation of the Si–O bond. Because the silicone resin was surrounded by nano-composites, the molecular structure of the silicone was protected. Nano-composites formed a thermally protective and stable structure, and the resulting system thus exhibited excellent thermal and oxidative stability.

**Conclusions**

Polymer resin matrix reinforced by nano-particles are the heart of key important energy for heat-resistant silicone resin. Despite tremendous efforts, developing heat-resistant silicone resin at high temperature is a great challenge. Herein, we developed a strategy to enhance the initial decomposition temperature of silicone resin based on homologous of nano-composites effect. The initial decomposition temperature of the epoxy–silicone resin is improved by 77.2°C via grafting modification. The developed strategy has significance for homologous effect on the polymer molecular structure. This study directs the developments for novel heat-resisting polymer.

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**References**

1. Lei, X.F., Chen, Y.H., Qiao, M.T., Tian, L.D., and Zhang, Q.Y. (2016) Hyperbranched polysiloxane
(HBPSi)-based polyimide films with ultralow dielectric permittivity, desirable mechanical and thermal properties. *Journal of Materials Chemistry C*, 4:2134–2146.

2. Kim, Y.H., Lim, Y.W., Kim, Y.H., and Bae, B.S. (2016) Thermally stable siloxane hybrid matrix with low dielectric loss for copper-clad laminates for high-frequency applications. *ACS Applied Materials Interfaces*, 8:8335–8340.

3. Anderson, S.E., Mitchell, C., Haddad, T.S., Vij, A., Schwab, J.J., and Bowers, M.T. (2006) Structural characterization of POSS siloxane dimer and trimer. *Chemistry of Materials*, 18(6):1490–1497.

4. Iso, Y., Takeshita, S., and Iseobe, T. (2014) Electrophoretic deposition and characterization of transparent nanocomposite films of YVO4: Bi3+, Eu3+ nanophosphor and silicone-modified acrylic resin. *Langmuir*, 30(5):1465–1471.

5. Yoon, C., Kim, T., Shin, M.H., Song, Y.G., Shin, K., Kim, Y.J., et al. (2015) Highly luminescent and stable white light-emitting diodes created by direct incorporation of Cd-free quantum dots in silicone resin using the thiol group. *Journal of Material Chemistry C*, 3:6908–6915.

6. Gan, L., Shang, S.M., Yuen, C.W.M., Jiang, S.X., and Mai, Y.W. (2010) Novel ultraviolet-opaque, visible-transparent and light-emitting ZnO-QD/silicone composites with tunable luminescence colors. *Polymer*, 51(12):2755–2762.

7. Pradhan, B., Roy, S., Srivastava, S.K., and Saxena, A. (2015) Synergistic effect of carbon nanotubes and clay platelets in reinforcing properties of silicone rubber nanocomposites. *Journal of Applied Polymer Science*, 132(15):3–11.

8. Schubert, U.S. (2003) Electronic properties of POSS: Synthesis and applications in low-dielectric epoxy composites. *Composites Science and Technology*, 63(13):2864–2876.

9. Liao, W.H., Yang, S.Y., Hsiao, S.T., Wang, Y.S., Li, S.M., Ma, C.C.M., et al. (2014) Effect of octa (aminophenyl) polyhedral oligomeric silsesquioxanes on graphene oxide sheets immobilized onto an amino-silane modified silicon surface. *Journal of Materials Chemistry C*, 2(13):6213–6217.

10. K. (2014) A graphene hybrid material functionalized with POSS: Synthesis and applications in low-dielectric epoxy composites. *Composites Science and Technology*, 92:112–119.

11. Liao, W.H., Yang, S.Y., Hsiao, S.T., Wang, Y.S., Li, S.M., Ma, C.C.M., et al. (2014) Effect of octa (aminophenyl) polyhedral oligomeric silsesquioxane functionalized grahpe-ne oxide on the mechanical and dielectric properties of polyimide composites. *ACS Applied Material Interfaces*, 6(18):15802–15812.

12. Huang W.S., and Offerman R.E. (1958) Preparation of graphitic oxide. *Journal of the American Chemical Society*, 80:1339–1339.

13. Matins, P., Costa, M., Benelmekki, M., Botelho, G., and Lanceros-Méndez, S. (2013) Interface characterization and thermal degradation of ferrite/poly (vinylie fluoride) multiferroic nanocomposites. *Journal of Materials Science*, 48:2681–2689.