



Investigation of Thermostability of Modified Graphene Oxide/Methylsilicone Resin Nanocomposites

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To promote the thermostability of methylsilicone resin, toluene-2,4-diisocyanate (TDI) modified graphene oxide (GO) was grafted on silicone resin. Fourier-transformed infrared (FT-IR) spectra suggested that modified GO was grafted on silicone resin successfully. Thermogravimetric analysis (TGA) curves showed the initial decomposition temperature of modified methylsilicone resin increased from 391.2 °C to 427.0 °C, maximum weight loss rate temperature increased from 423.5 °C to 542.5 °C, indicated that the incorporation of modified GO could obviously improve the thermostability of methylsilicone resin. The effects of GO on the methylsilicone resin were also characterized to assess the degradation behavior of methylsilicone resin. Furthermore, the mechanism of improving the thermostability of methylsilicone resin by modified GO was also discussed: Reducing remaining Si-OH in the curing process of silicone resin; isolating oxygen atoms and other substances, hindering the thermal movement of the silicone resin chain can effectively improve the thermostability of the silicone resin.

Keywords: Graphene oxide; Silicone resin; Modification

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1 Introduction

Methylsilicone resin is a kind of material between organic and inorganic material with highly cross-linked siloxane backbone.¹ Owing to the much higher binding energy of the silicon-oxygen bond (460.5 kJ/mol) than the carbon-oxygen bond (358.0 kJ/mol) or carbon-carbon bond (304 kJ/mol),² the thermostability of methylsilicone resin is better than the conventional organic polymer. Therefore, methylsilicone resins with high-temperature resistance,³ good electric insulation, chemical resistance⁴ and excellent weather resistance⁵ as a candidate for alternative organic materials are widely used in chemical, aerospace⁶ and other fields. However, especially in the practical application of aerospace, the service temperature of composites is usually about 200 °C, and even the peak temperature reaches more than 300 °C.⁷ Hence, it is necessary to further improve the heat resistance of methylsilicone resins. In general, the thermal oxidation of silicone resin consists of three parts: terminal hydroxyl groups react forward along Si-O segments forming low molecular weight cyclic siloxanes; thermal oxidative degradation of the

side group; reactions occurs on the backbone of the siloxane molecule, causing the molecular chain to break and form small molecule siloxanes.

For this reason, many modification methods have been developed to prepare methylsilicone resins with higher thermostability. For the heat-resistance modification of silicone resin, there are usually the following three ideas: (1) Modifying the structures of the main chain. Commonly, the method of modifying the main chain structure to increase the heat resistance is by adding rigid segments. Such as carboranes,⁸⁻¹⁰ arylene,¹¹ the mechanism of this method is by incorporating bulky segment to increase the rigidity of main chain, disturbing the folding of siloxane, and then delay the degradation speed. (2) Modifying the structure of the side groups. There are two methods for changing the structure of the side groups. Cross-linkable groups are introduced into the sidechains for improving the crosslinking density of silicone resin greatly.¹² Hence the thermostability of silicone resin is improved. The other method is replacing the methyl side groups with better thermostability groups, such as phenyl, to help improve the thermostability of methyl silicone resins. (3) Adding high temperature resistant fillers. Incorporating inorganic fillers are utilized to improve the thermostability of silicone resin, such as polyhedral oligomeric silsesquioxane,^{7,13} ferric oxide,¹⁴ zinc oxide^{15,16} and any other metal-oxide. In recent years, lamellar fillers are also widely used in the heat-resistant modification of composite materials, such as layered nano-clay system,¹⁷⁻¹⁹ graphite based system.^{20,21}

Graphene—a single atomic plane of graphite²² — which has excellent optical, electrical and mechanical properties, is considered to be a revolutionary material in the future.²³ Graphene has lots of important applications in the field of material science, micro or nano processing,

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energy, biomedicine and drug delivery. Since the pioneering study of graphene as a new member of carbon nanostructures by Novoselov et al.,²⁴ graphene has been extensively investigated, especially in the fields of nanoscience and nanotechnology.²⁵⁻²⁷ So far, there are various articles on the heat-resistant modification of methylsilicone resin by graphene. Jiang²⁸ et al. reported a method of incorporating Co_3O_4 nanoparticles and nitrogen-doped graphene oxide into silicone resins to increase the activation energy in order to decrease the thermal degradation of the composite. It is still necessary to carry out research on a more rapid and effective heat-resistant modification method for methyl silicone resin.

The purpose of this study is to help improve the thermostability of methyl silicone resin by incorporating chemically modified graphite. The mechanism of thermostability of graphene modified methyl silicone resin has also been analyzed. At the same time, the possibility of using modified graphene oxide instead of conventional fillers to improve the thermostability of silicone has been discussed in the aerospace field.

2 Experimental

2.1 Main Materials

Methylsilicone resin (SAR-2) was purchased from Ningbo Kele New Material Co., Ltd., China. Toluene-2,4-diisocyanate (TDI), Polyethylene glycol 600 (PEG600) were purchased from Tianjin Tianli Chemical Reagent Co., Ltd., China. Flake graphite was purchased from Qingdao Baichuan graphite Co., Ltd., China.

2.2 Preparation of modified GO

The method of preparing GO is given in *supporting material*.

The modified GO was prepared according to the method of Voronov et al.²⁹ and Xu et al.³⁰ The amphiphilic oligoester was esterified in toluene solution with a molecular weight of 600 polyethylene glycol and sebacic acid using a trace amount of sulfuric acid as a catalyst. GO and toluene-2,4-diisocyanate (TDI) at a mass ratio of 1 : 0.03 were blended, then added to toluene solution of oligoester, and stirred at 80 °C for 8 hours under a nitrogen atmosphere. The product was centrifuged and dried under vacuum at 60 °C to constant weight, marked as modified GO.

2.3 Preparation of modified GO/methylsilicone resin composite

The incorporation content of the modified GO was 0.5 wt% in the methylsilicone matrix. Then pour the mixture into a Teflon mold and heat for 1 hour at 80 °C, 100 °C, 120 °C, 150 °C. After the above heat curing step, a graphene oxide/methylsilicone resin composite was obtained. In order to compare the dispersion of modified GO and pure graphite in methylsilicone resin matrix, the same content (0.5 wt%) of graphite was added to methyl silicone resin to prepare graphite/methylsilicone resin composite. The method for preparing the graphite/methylsilicone resin composite is the same as the method of modified GO/methylsilicone resin composite.

2.4 Instrumental Characterization

Fourier transform infrared (FT-IR) spectra was obtained from 400 to 4000 cm^{-1} using a FT-IR spectrophotometer (Nicolet 670, USA). Scanning electron microscopy (SEM) was used to examine the dispersion of graphene in methylsilicone resin of the samples by using a Quanta 200F scanning electron microscopy, USA. The surface of composites was coated with a gold layer before examination. The X-ray diffraction pattern (XRD) was collected through a X-ray diffractometer (Shimadzu, Japan) from 3° to 50°. TGA of composites samples (about 10mg) were dried at 120 °C for 4 h to remove the residual water in the samples. TG analysis was performed on a NETZSCH thermoanalyzer (STA449C,

Germany) and the range of scanning temperature was from 30 °C to 1000 °C under nitrogen atmosphere at a heating rate of 10 °C/min. The XPS spectra of the samples of methylsilicone resin and GO modified methylsilicone resin were operated by a VG electron spectrometer (ESCALAB Mk II, UK).

3. Results and Discussion

The mechanism of thermal oxidation of the methylsilicone resin consists of three parts: Thermal oxidative degradation of the side methyl group on the siloxane backbone, leading to molecular chains break and forming small molecular weight siloxanes. Terminal hydroxyl groups react forward along Si-O segments forming low molecular weight cyclic siloxanes; with further heating, backbone of siloxanes occurs rearrangement. For the purpose of further investigate the effect of modified graphene oxide on the thermal degradation mechanism of methylsilicone resin, the following tests were performed.

3.1 Results analysis of the modified GO/methylsilicone resin

In accordance with the procedure shown in Fig. 1, the modified GO is successfully grafted onto the methylsilicone resin segment.

Fig. 2a is a SEM image of graphite/methylsilicone resin composite. Among them, it can be seen that the white graphite layer is in the form of a dispersed phase in the dark methylsilicone resin. This indicated that there is poor dispersion and phase separation between the graphite sheet and the methylsilicone resin.

As shown in Fig. 2b, a large area of methylsilicone resin can be seen without any significant phase separation. This indicates that a certain polymerization reaction between modified GO and methylsilicone occurred. This also has a clear relationship with the delamination and exfoliation of graphite after modification. The better compatibility between Modified GO and methylsilicone resin reduces the agglomeration of the graphite sheet itself and improves the dispersion

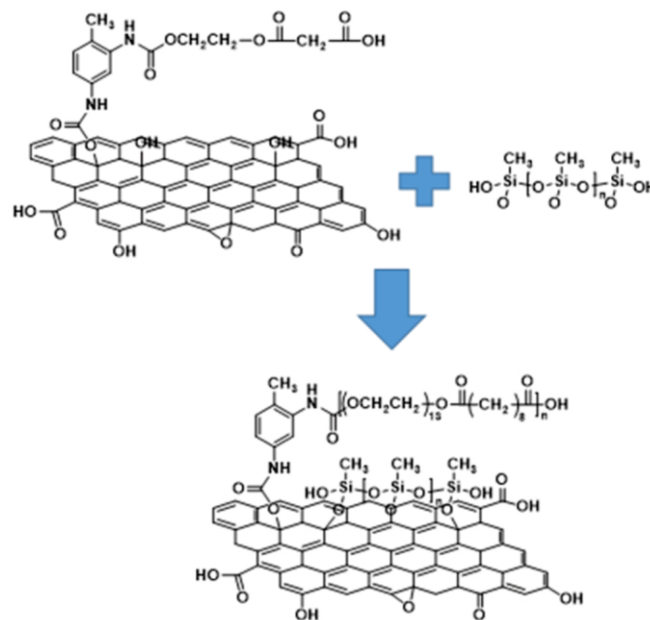


Fig. 1 Preparation of modified GO/methylsilicone resin nanocomposite.

of Modified GO in methylsilicone resin. This also helps to further improve the thermostability of the composite at a certain degree.

Because of the native graphite has been exfoliated, X-ray diffraction (XRD) spectra (Fig. 3) of the modified GO/methylsilicone resin composite

shows no diffraction peak of GO (XRD of graphite and GO is shown in *supporting material*), except for methylsilicone resin-polymer matrix. Methylsilicone resin is an amorphous polymer without crystalline regions. Therefore, the peaks of the XRD pattern do not represent a crystal face. The XRD pattern of methylsilicone resin revealed two peaks, 2θ at 10.8° and 22.8° reveals interpretation for the existence of two peaks is that the silicone resins contain an amorphous phase. After modification, the characteristic diffraction peak of the methylsilicone resin has moved forward indicating that the structure of the methylsilicone resin has been destroyed. It proved that graphene oxide was successfully polymerized on methylsilicone resin molecules. At the same time, there are no characteristic peaks of graphite and graphene oxide in the composite spectrum, indicating that the modified GO and methylsilicone resin are successfully polymerized.

X-ray photoelectron spectroscopy (XPS) showed distinct silicon peaks in the determination of chemical composition and functional groups of the methylsilicone resin surfaces, representing the major constituents of the methylsilicone resin investigated. As shown in Fig. 4, for two cases of methylsilicone and modified GO reinforced methylsilicone resin, remarkable difference can be seen between the distribution of the silicone components of the degraded surfaces. It could observe that the relative amounts of C-Si-O increased and Si-OH decreased for modified GO/methylsilicone resin. The results of these analyses indicated that the modified GO was successfully grafted onto methylsilicone resin molecules. Poorly thermally stable Si-OH groups are selectively react with modified GO. At the same time, the graphite layer forms a

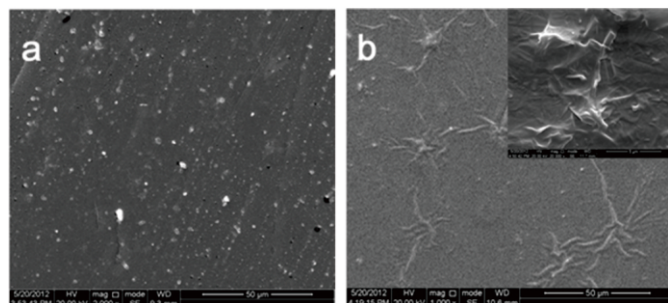


Fig. 2 SEM images of thin sections: (a) Graphite/methylsilicone resin composite; (b) Modified GO/methylsilicone resin composite.

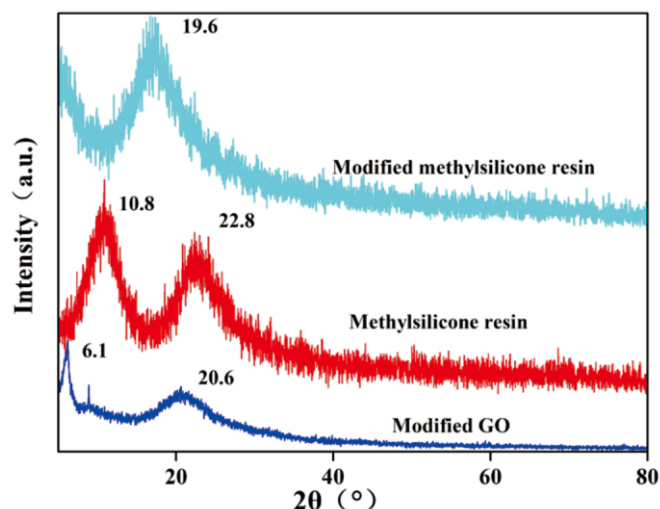


Fig. 3 XRD patterns of modified GO, methylsilicone and modified methylsilicone resin.

protective barrier on the surface of the modified methylsilicone resin, preventing further degradation of the siloxane chain.

Fig. 5 shows the Fourier transform infrared spectroscopy (FT-IR) pattern of methylsilicone and modified GO/methylsilicone resin. Among them, 3500 cm^{-1} and $1130\text{--}1000\text{ cm}^{-1}$ are characteristic absorption peaks of Si-OH and Si-O-Si, respectively.

After modification with modified GO, the characteristic peak of the conforming material at 3500 cm^{-1} was significantly reduced, indicating that Si-OH has been implicated in the reaction. At the same time, the broad peak at $1130\text{--}1000\text{ cm}^{-1}$ is the characteristic peak of methylsilicone resin. The intensity of the Si-O-Si absorption band increased with the incorporation of modified GO. Meanwhile, 1705 cm^{-1} and 1598 cm^{-1} are C=O and C-N absorption peak for modified methylsilicone resin. These

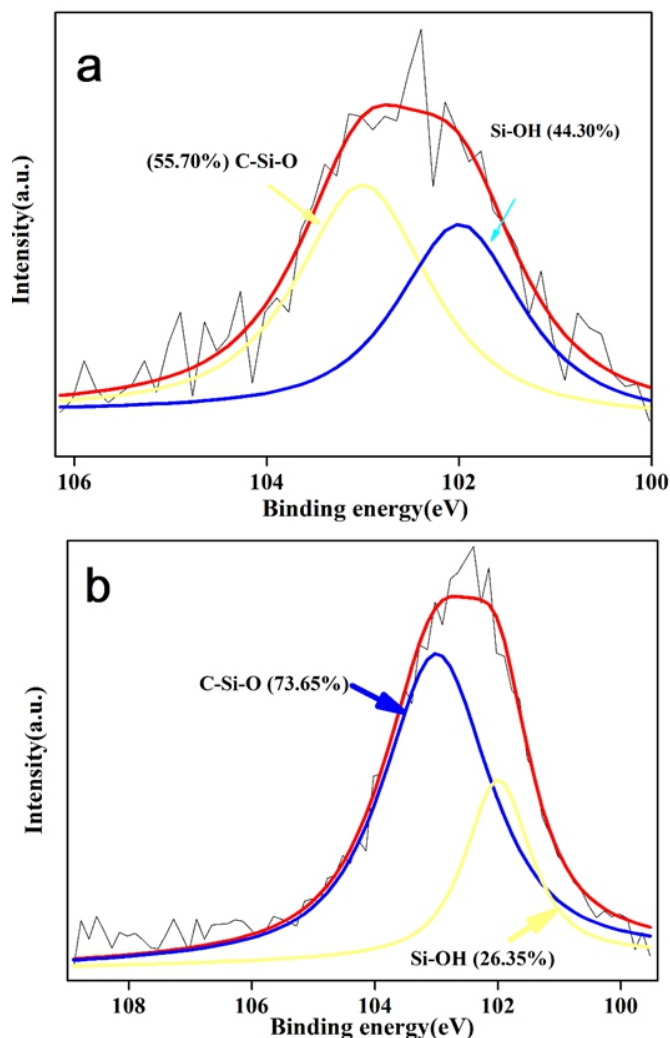


Fig. 4 Si_{2p} XPS of the (a) methylsilicone and (b) modified GO/methylsilicone resin.

results indicated that modified GO was successfully grafted to methylsilicone resin rather than just as a filler. Moreover, the decrease of the thermostability of the Si-OH peak indicated that the Si-OH group content significantly reduced, further improved the thermostability of the composite.

After curing the composite of the methylsilicone resin and modified GO/methylsilicone resin, it was placed at room temperature, 450°C and 550°C 1 h. The methylsilicone resin has been cracked and powdered at

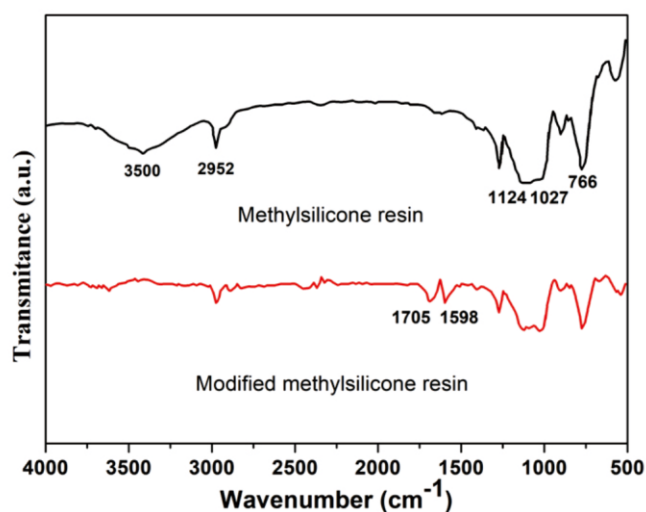


Fig. 5 FT-IR spectra: methylsilicone and modified methylsilicone resin.

450 °C and 550 °C. However, the modified methylsilicone resin has been fractured only at 550 °C. The morphology change of the samples is given in Fig. 6a. Fig. 6b indicates the weight loss at different temperature 1 h. The weight loss of the methylsilicone resin significantly increased. Fig. 6c shows the TGA curves of methylsilicone and modified GO/methylsilicone. As the curve shows, the decomposition process of methylsilicone and modified GO/methylsilicone resin is started from the temperature 391 °C and 427 °C. The cross point of two tangents is the initial decomposition temperature, it has been marked in Fig. 6c, respectively. The weight loss of the methylsilicone resin at 391 °C and 427 °C were 9.53 % and 11.55 %, respectively; the weight loss of modified methyl silicone resin was 1.48 % and 2.17 % at 391 °C and 427 °C, respectively. This phase is mainly the condensation reaction and the 'back-biting' reaction of terminal hydroxyl groups for the methylsilicone and modified methylsilicone. Losing weight mainly is the generated H₂O and small molecules. After modification of methylsilicone resin with modified GO, the maximum thermal decomposition rate temperature increased from 423.5 °C to 542.5 °C. This stage is mainly due to the oxidative degradation caused by the formation of free radicals by the Si-CH₃ cleavage of the methylsilicone and modified methylsilicone resin. Losing weight mainly is the generated CO₂ and H₂O.

3.2 The mechanism analysis of thermostability of the modified GO/methylsilicone resin

In summary, due to the addition of modified GO, pyrolysis and thermal oxidative degradation is inhibited, and the thermostability of the methylsilicone resin is improved. Judging from the above experimental results, the mechanism of thermostability of composites can be analyzed from steric hindrance and hydroxyl reduction.

Firstly, the content of activated Si-OH is decreased. The degradation process of methylsilicone resin is divided into two stages: unzipping degradation and rearrangement degradation.³¹ Unzipping degradation is the process of dehydroxylation of terminal hydroxyl groups of methylsilicone chain forming cyclic siloxanes under thermal degradation conditions. Rearrangement degradation is a process that the siloxane backbone Si-O-Si rearranges forming cyclic siloxane under thermal degradation conditions. The modified GO was added the methylsilicone resin, this result cause that Si-OH decreased. Therefore, the hydroxyl content of the modified methyl silicone resin decreases, and the initial decomposition temperature and the maximum decomposition temperature of the composite material increase.

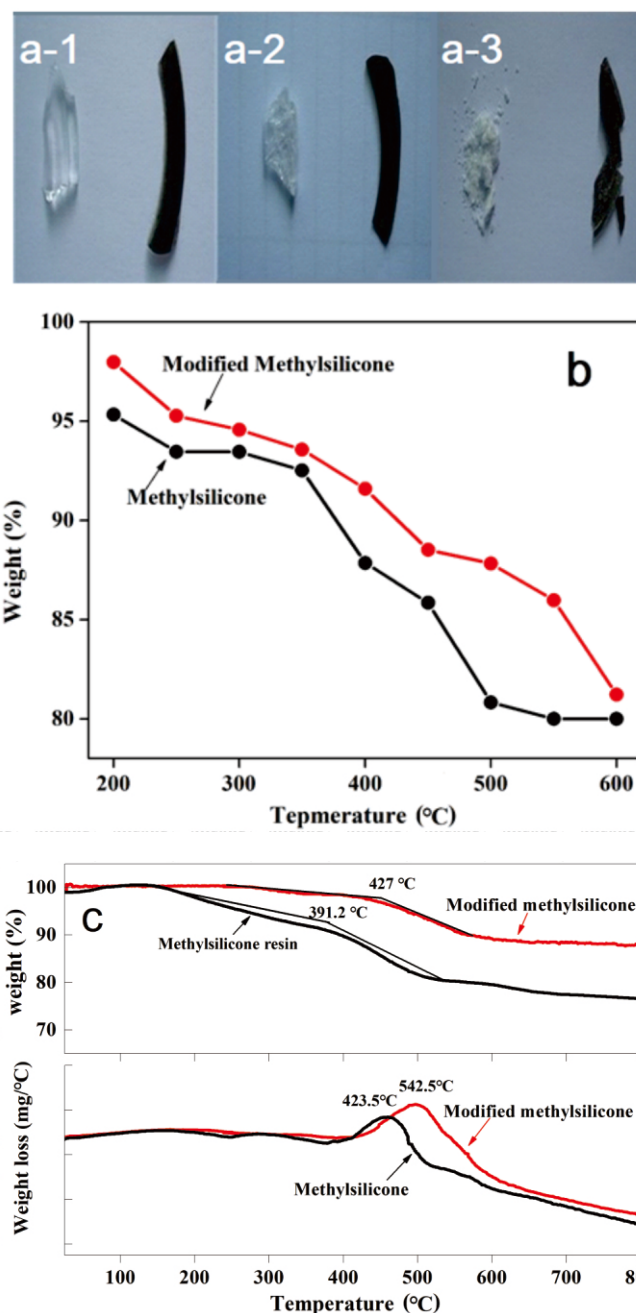


Fig. 6 Thermostability of the methylsilicone and modified methylsilicone resin.

- (a) Picture of the sample after being placed at different temperatures for 1 h: (a-1) Room temperature, (a-2) 450 °C, (a-3) 550 °C;
 (b) Weight of the sample after being placed at different temperatures for 1 h;
 (c) TG and DTG curves.

Secondly, steric hindrance increased. Rigid graphene oxide is grafted onto the methylsilicone resin molecular segment, increasing the rigidity of the methylsilicone resin. In this case, which improves the difficulty of thermal movement of molecular segments. Therefore, in order to destroy the structure of the molecule, higher energy is required, means higher temperature. This process is illustrated in Fig. 7a.

At the same time, GO is evenly dispersed in the methyl silicone resin matrix to act as a barrier to oxygen and heat, illustrated in Fig. 7b, and it can also improve the thermostability of the composite material. On the

other hand, the nanoscopic size and composition of GO nanostructured chemicals deter the formation of appreciable vapor pressure, and hence, the system is inherently of the excellent thermal and oxidative stability.

4. Conclusion

In summary, we have reported an efficient method to enhance the thermostability of the methylsilicone resins via the modified GO. The results showed that the thermostability of the modified methylsilicone resin was greatly improved. Compared to unmodified methylsilicone resin, the initial decomposition temperature of the modified material is increased by 9.2% and the maximum weight loss rate temperature increased by 28.1%. Moreover, the compatibility of modified GO in methylsilicone resin played a great role in isolating small molecules such as oxygen from entering the composite material.

In conclusion, the modified heat-resistant methylsilicone resin was prepared by adding modified GO. The modified methylsilicone resin has higher initial decomposition temperature and maximum decomposition temperature. The advantageous properties of such heat resistant silicone resins bode well for their application in high temperature environments

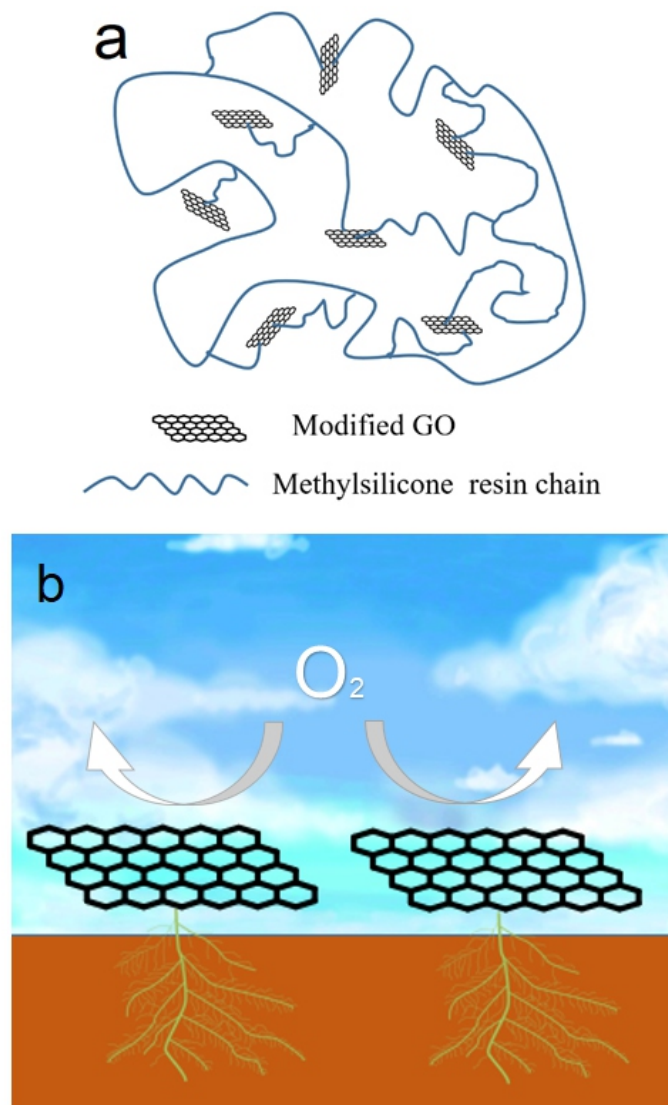


Fig. 7 Schematic of steric hindrance and interrupted the activated Si-OH in modified methylsilicone resin.

such as aerospace, for example in high speed aircraft, for which keeping the structural integrity is necessary for short periods of high heat.

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