

Synthesis of EP-POSS Mixture and the Properties of EP-POSS/Epoxy, SiO₂/Epoxy, and SiO₂/EP-POSS/Epoxy Nanocomposite

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ABSTRACT: The hybrid material of EP-POSS mixture was synthesized by the hydrolysis and condensation of (γ -glycidoxypropyl) trimethoxysilane. A series of binary systems of EP-POSS/epoxy blends, epoxy resin modified by silica nanoparticles (SiO₂/epoxy), and ternary system of SiO₂/EP-POSS/epoxy nanocomposite were prepared. The dispersion of SiO₂ in the matrices was evidenced by transmission electron micrograph, and the mechanical properties, that is, flexural strength, flexural modulus, and impact strength were examined for EP-POSS/epoxy blends, SiO₂/epoxy, and SiO₂/EP-POSS/epoxy, respectively. The fractured surface of the impact samples was observed by scanning electron micrograph. Thermogravimetry analysis were applied to investigate the different thermal stabilities of the binary system and ternary system by introducing EP-POSS and SiO₂ to epoxy resin. The results showed that the impact strength, flexural strength, and modulus of the SiO₂/EP-POSS/epoxy system increased around by 57.9, 14.1, and 44.0% compared with the pure epoxy resin, T_g , T_{max} and the residues of the ternary system were 387°C, 426°C, and 25.2%, increased remarkably by 20°C, 11°C and 101.6% in contrast to the pure epoxy resin, which was also higher than the binary systems. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 810–819, 2013.

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INTRODUCTION

In recent years, organic-inorganic hybrid materials have been regarded as a new generation of the high performance materials because of combining the advantages of both inorganic materials (rigidity and high stability) and organic polymers¹ (flexibility, ductility, and processability). Hence, this method has been an important approach to preparing the high-performance and functional materials.^{2,3} Polyhedral oligomeric silsesquioxanes (POSS) as shown in Figure 1 are a class of intramolecular organic-inorganic hybrid materials with a three-dimensional cage-like network structure, which contain a thermally stable inorganic Si[—O—]₃Si core surrounded by substituent R where R could be hydrogen, alkyl, epoxy group, arylene groups, or other organic functional derivatives.^{4,5} Generally, POSS could be incorporated into polymers via chemical grafting and copolymerization methods when R is active group, while the POSS will be introduced into the polymer matrix by physical blending methods^{6–8} when R is inert group. Nanda et al.⁹ studied the aqueous polyurethane dispersions grafted by amino-POSS via homogeneous solution polymerization, and the results showed that the storage modulus, T_g , complex viscosity, and surface hydrophobicity displayed prominent changes.

Butola, et al.¹⁰ prepared the Octamethyl-POSS and Octaphenyl-POSS reinforced polypropylene nanocomposite by melt blending route, and the results showed that mechanical as well as thermal properties were enhanced largely.

Epoxy resins are one of the most important thermosetting materials that are widely used in many fields such as aviation, aerospace, mechanics, electronics, transportation, and so on.¹¹ However, the thermal and mechanical properties of the cured resins are restricted due to crosslinking network structure.¹² Many types of epoxy-filler composites have been developed to overcome these drawbacks. As expected, the epoxy resins filled with nanoparticles have exhibited some improvements in many properties including good mechanical properties, excellent thermal stability, lower dielectric permittivity, and lower surface energy. Some researchers studied the epoxy resin/silica hybrid materials and found that the mechanical properties and thermal stability of hybrid materials were improved because of the high modulus and large surface area of nanoparticles.^{13–15} The nanosilica could be homogenous dispersed in the epoxy resin composites, resulting in the mechanical and thermal properties improvement when adding the proper content of nanosilica, but

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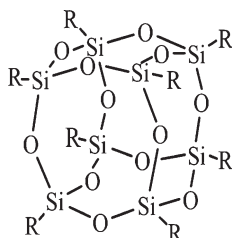


Figure 1. Structure of polyhedral oligomeric silsesquioxane.

there may be agglomerates and unevenly scattered.¹⁶ In addition, the cubic cage structure of POSS combines related properties of conventional organic and inorganic components, and provides an important method to modify the epoxy resin to improve the mechanical properties and thermal stability of epoxy matrix. Nagendiran et al.¹⁷ investigated the aminophenylsilsesquioxane-reinforced DGEBA and TGDDM epoxy nanocomposites, and the results showed that the glass transition temperatures and thermal stability were improved. Chiu et al.¹⁸ synthesized the side-chain POSS-type epoxy hybrid material, which modified the diglycidyl ether of bisphenol A and concluded that the introduction of the POSS could improve the thermal degradation activation energies. Moreover, the char yield was enhanced from 14.48 to 19.21% in the nitrogen atmosphere and the mechanical properties were increased when the contents of the side-chain POSS-type epoxy were ~50 wt %.

We synthesized the epoxide POSS (EP-POSS) via the hydrolysis and condensation of (γ -glycidoxypropyl)trimethoxysilane

(GPMS) in this work. The EP-POSS had good compatibility with the epoxy resin, and the EP-POSS had the similar Si[O Si] structure with the silica. Therefore, the silica had good compatibility with epoxy resin with the action of the EP-POSS. The influence of addition of EP-POSS as well as SiO_2 on the mechanical properties and thermal stability of 4,4'-diaminodiphenylsulfone (DDS)-cured epoxy blends were revealed, respectively. Furthermore, the ternary system of SiO_2 /EP-POSS/epoxy nanocomposite with proper content of modifiers was prepared. Mechanical properties and thermogravimetric analysis (TGA) were also tested.

EXPERIMENTAL

Materials

GPMS, a colorless-clarity liquid, with a purity of 98%, was supplied by Shandong Jinan Duoweiqiao Organic Silicon Plant (Jinan, China). Anhydrous methanol, analytical reagent, was purchased from Tianjin Fuchen Chemical Reagent Plant (Tianjin, China). Anhydrous ethanol, analytical reagent, was supplied by Xi'an Sanpu Chemical Reagent Crop (Xi'an, China). Concentrated hydrochloric acid, analytical reagent, Beijing Chemical Plant (Beijing, China). Distilled water, was made by our laboratory. The Bisphenol A epoxy resins (E-51, epoxy value = 0.51) were obtained from Wuxi Resin Plant (Wuxi, China). DDS, a solid powder, used as curing reagent and purchased from Shanghai Third Chemical Plant (Shanghai, China). Nanosilica, were supplied by Zhoushan Mingri nano-materials Corp (Zhoushan, China). The chemical structures of main raw materials were shown in Figure 2.

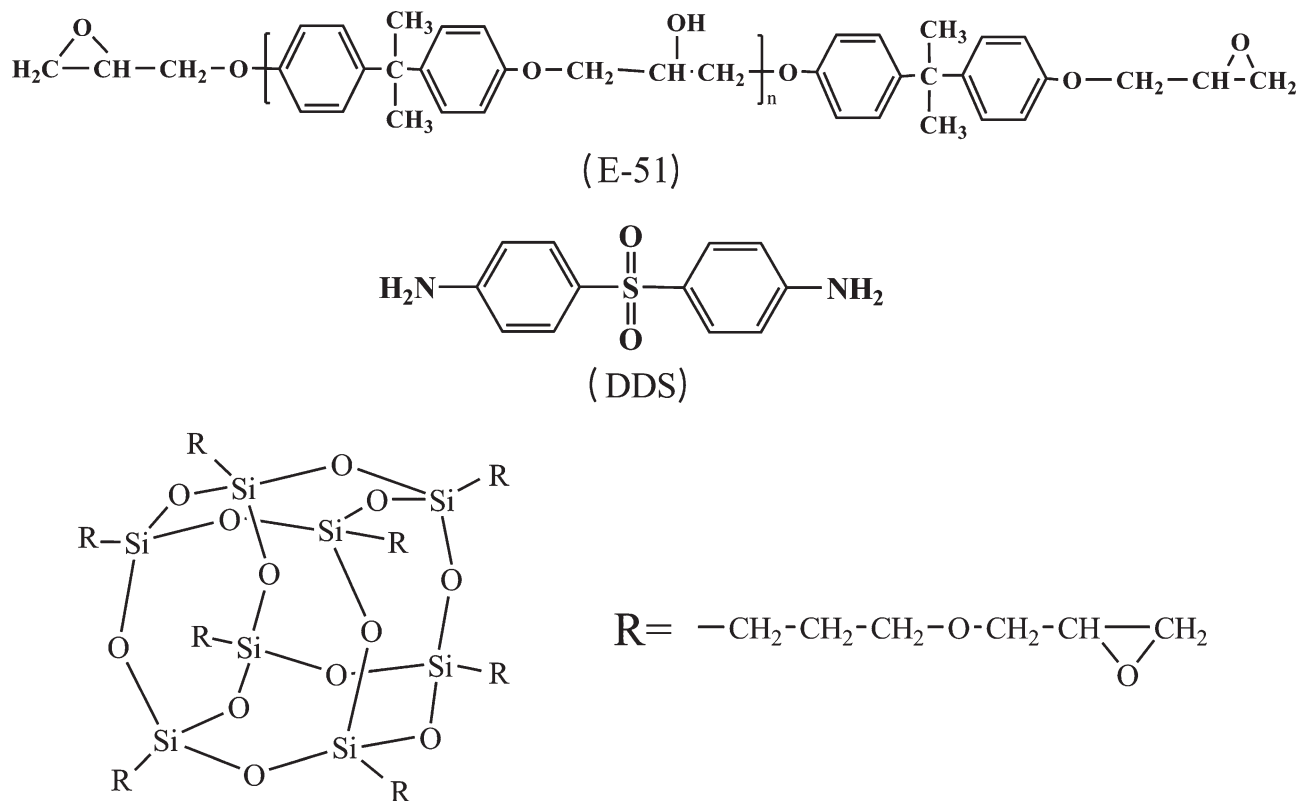


Figure 2. The chemical structures of raw materials.

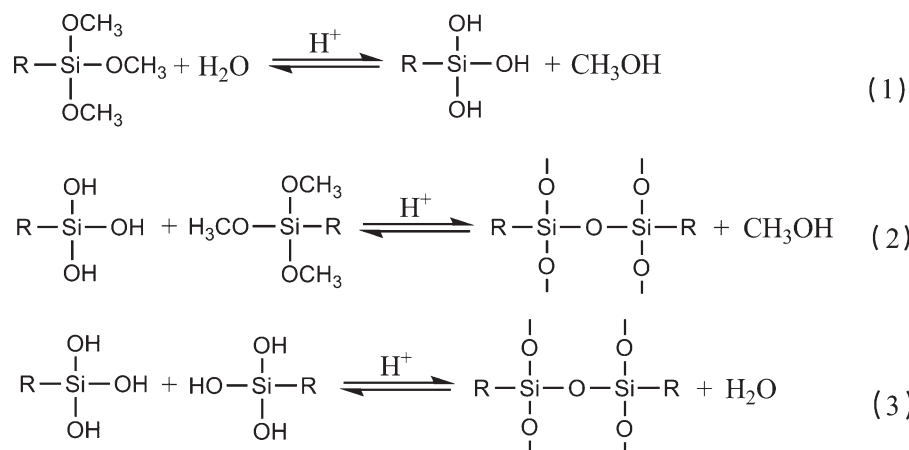


Figure 3. Mechanism of the hydrolysis and condensation of GPMS.

Preparation of EP-POSS Mixture. The GPMS, anhydrous methanol, anhydrous ethanol, deionized water, and concentrated hydrochloric acid in certain proportion were placed in a 500 mL round-three neck flask and stirred for six hours using a mechanical stirrer and temperature was maintained at 37–39°C. The crude product was obtained after removing the solvent, and the viscosity was 4500 mpa s and epoxy value was 0.32.

Preparation of the EP-POSS/Epoxy Blends. Typically, the blends consisting of 100 g epoxy resin and a certain amount of EP-POSS were stirred in a beaker at 60–70°C and formed a homogeneous solution, and the mixture was dispersed by a uniform shear blender. Then, 31.09 g DDS (The DDS and epoxy resin were reacted with each other by 1 : 4 mole ratio according to the active hydrogen. That was to say, the amount of the DDS was $0.51 \times M_{\text{DDS}}/4$ g) was added to the mixture and stirred vigorously at 125°C for 1 h to obtain a viscous and homogeneous transparent mixture. The prepolymer was dumped into the preheated mold, and degassed in a vacuum for 45 min at 130°C. Lastly, the cured resin system was adopted the following curing conditions: 140°C/2 h, 200°C/2 h, and 220°C/4 h when downing to room temperature. The EP-POSS mass ratio in the resultant polymer network was 0, 5, 10, 15, and 20 wt %. For the SiO₂/epoxy system, the SiO₂ content was 0, 1, 3, and 5 wt %, and the reaction was performed under the identical conditions.

Preparation of the SiO₂/EP-POSS/Epoxy Nanocomposite. The EP-POSS and SiO₂ were simultaneously added into the 100 g epoxy resin, and the mixture obtained was heated to 60–70°C for 40 min with continuous stirring to form a homogenous mixture. Then, the mixture was dispersed by a uniform shear blender. At last, the 31.09 g DDS was added to the mixture and stirred continuously at 125°C for 1 h. The mixture was poured into the preheated mold, and degassed in a vacuum for 45 min at 130°C. The curing conditions were performed in accordance with the above conditions, in this case, the corresponding content of EP-POSS was 10 wt % and the SiO₂ was 3 wt %.

Analysis methods

The Fourier transform infrared (FTIR) analysis of the EP-POSS was measured on a WQF-310 FTIR spectrometer (Beijing

Optical Instrument, China). Nuclear magnetic resonance (NMR) spectral analysis was acquired with an Inova 400 spectrometer at about 20°C, and the ¹H NMR spectrum was recorded in a CDCl₃ solution at 399.8 MHz. The morphology of the fractured surface of the materials was investigated by scanning electron micrograph (SEM) on a HITACHI S-570 SEM (fractured surfaces of the specimens were coated with gold), and the dispersion of nanosilica in the epoxy matrix was examined by transmission electron micrograph (TEM), which performed on a Hitachi H-7650 TEM by ultrathin section samples at an accelerating voltage of 80 kV. Impact strength was tested by XCL-40 with the samples of dimensions 80 × 10 × 4 mm³ according to the GB2570-08 Standard of China. Flexural strength and modulus were carried out by ZMGIZ250 with the samples of dimensions 80 × 15 × 4 mm³ following the GB2570-81 Standard of China. Thermogravimetry analysis was conducted by USA TGA Q50 from room temperature to 800°C at a heating rate of 20°C/min under the nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of EP-POSS Mixture

The synthesis of EP-POSS was conducted via the hydrolysis and condensation of GPMS referring to the hydrolytic condensation of EP-POSS.¹⁹ The reaction mechanism of the hydrolysis and condensation of GPMS was listed in Figure 3. The Si[sbond]OCH₃ bonds were not stable in H₂O medium and easily to produce the hydrolysis reaction under catalyst of acid or alkali as shown in Figure 3(a). The Si[sbond]OH groups of hydrolysis products could develop polysiloxane through the condensation reaction with GPMS or self-condensation under certain conditions as shown in Figure 3(b,c). The polysiloxane could continue to condense repeatedly and some possible structures could be produced as shown in Figure 4, which included ladder structure, random structure, incompletely condensation structure, and cubic cage structure.

The FTIR spectrum for EP-POSS was shown in Figure 5. The peaks at 910 and 1255 cm⁻¹ wavenumbers, which belonged to the epoxy group and the Si[sbond]C stretching vibration, respectively. The peaks at 2933, 2870, and 1199 cm⁻¹ were attributed to C[sbond]H stretching vibration (former two) and

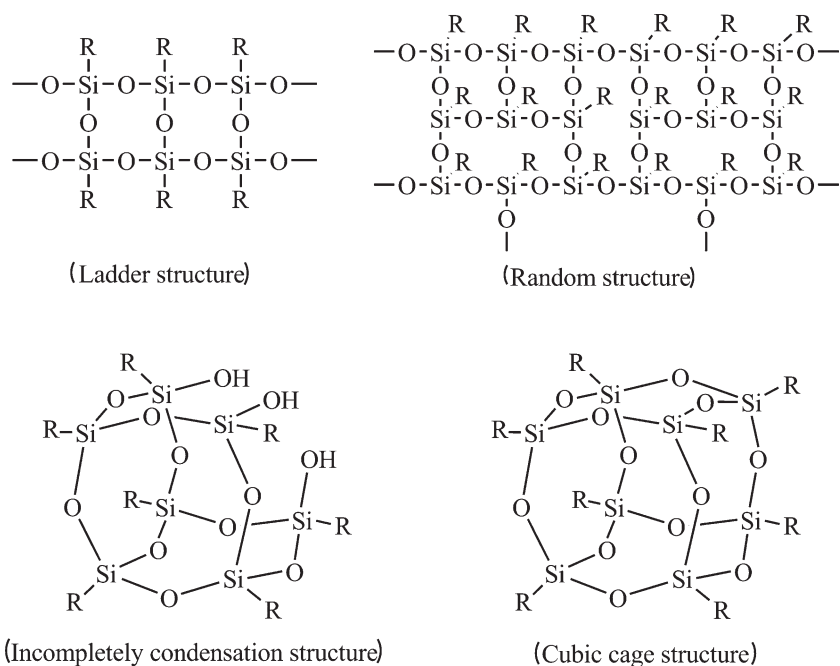


Figure 4. Structures of EP-POSS mixture.

C[Si-O-Si]C stretching vibration, respectively. The distinct Si[Si-O-Si]Si absorption peak at 1125 cm^{-1} could be observed, and the generation of the 3450 cm^{-1} was assigned to OH groups from Si[Si-OH] and the diol formed through epoxy ring hydrolysis.²⁰ Therefore, it was clearly indicated that the EP-POSS was an incompletely condensation mixture of cage-like sisesquioxanes with other various silsesquioxanes²¹ as shown in Figure 4.

The ^1H NMR spectrum of the EP-POSS was shown in Figure 6. The chemical shift δ at 0.062 and 7.287 ppm with the sharp peaks belonged to TMS and CDCl_3 , respectively, and the chemical shift of ^1H was moved to the low field at 0.651 ppm due to the ^1H linked with Si. The peak at 1.681 ppm belonged to ^2H and δ of ^3H was splitted into two peaks at 3.461 and 3.731

ppm by the influence of C[Si-O-Si]C bond. The δ at 3.520, 3.171, 2.780, and 2.605 ppm were attributed to 4H, 5H, and 6H (latter two), respectively. The weak peak at 4.863 ppm was caused by the H of Si[Si-OH],²² and the δ at 3.202–3.387 ppm could be ascribed to 5H and 6H as a result of the epoxy ring opening reaction.²³ As a consequence, the structure of EP-POSS was not completely cage-like.

Morphology Analysis of Nanocomposites

The size and the dispersion of the nanoparticles in polymer matrices largely influenced the properties of the nanocomposites. Therefore, the dispersion and distribution of the SiO_2 in pure epoxy as well as epoxy with EP-POSS blends were observed by TEM as shown in Figure 7. It was showed that SiO_2 could

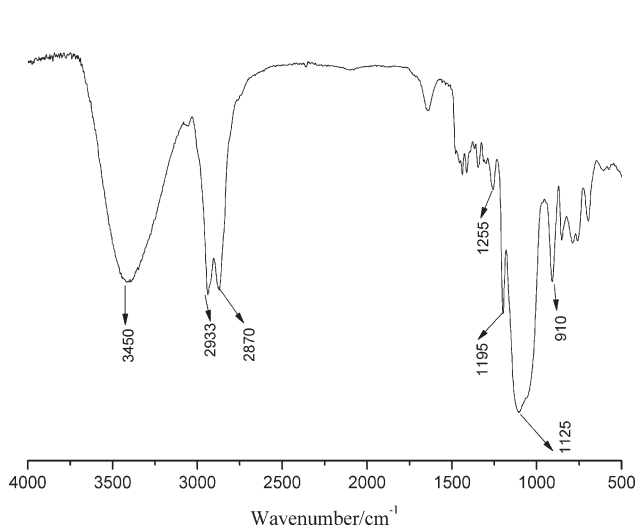


Figure 5. FTIR spectrum of EP-POSS mixture.

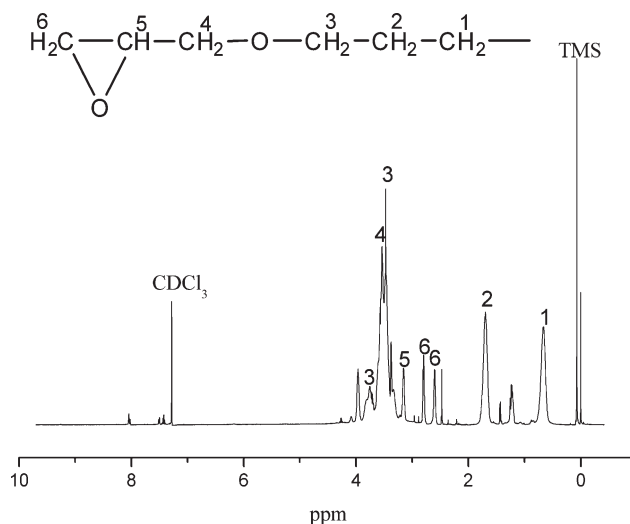


Figure 6. ^1H NMR spectrum of EP-POSS mixture.

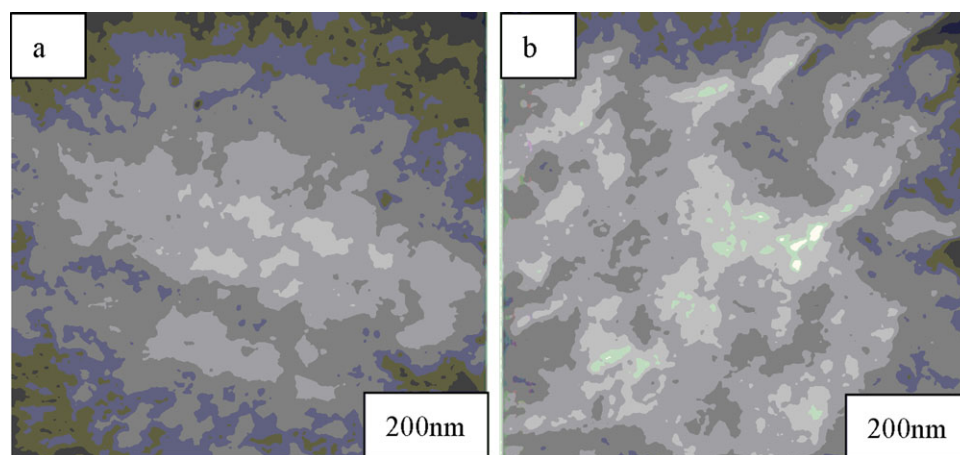


Figure 7. TEM of (a) SiO₂/epoxy and (b) SiO₂/EP-POSS/epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be dispersed in the entire matrix with obvious interface between nanoparticles and polymer in pure epoxy as shown in Figure 7(a). In contrast, it was found that the nanoparticles of SiO₂ dispersed very well in blends of EP-POSS/epoxy and the interface of nanoparticles with blends was a bit of vague. The structure of POSS core composed with Si[---]O[---]Si on EP-POSS was similar to the structure of SiO₂ nanoparticles, and epoxy groups on EP-POSS mixture were affinity with epoxy, which could promote the compatibility of inorganic particles SiO₂ with polymer blends of EP-POSS/epoxy, influencing the morphologies of ternary systems, consequently, and enhancing the interface adhesive.

Mechanical Properties

The influence of EP-POSS and SiO₂ on mechanical properties of epoxy resins, including impact strength, flexural strength, and flexural modulus, were tested and summarized in Figures 8–10, and the optimized data were listed in Table I. The impact strength, flexural strength and modulus of EP-POSS/epoxy

blends were presented as green column in these three figures. It could be seen that these three properties (impact strength, flexural strength, and modulus) of the EP-POSS/epoxy system increased with the addition of EP-POSS at lower content, and decreased gradually when the EP-POSS content exceeding 10%, and the properties at 10 wt % of EP-POSS achieved the maximum value. The impact strength, flexural strength, and modulus of the EP-POSS/epoxy system increased around by 37.2, 4.6, and 39.4%, respectively, when the content of EP-POSS was 10%, which implied that the proper incorporation of EP-POSS could effectively enhance toughness and rigidity of epoxy. It was probably due to the peculiar cage-like structure with reactive epoxy group on EP-POSS, and the epoxy group could react with DDS, forming the cured network and also emerging the POSS core into epoxy matrix, leading to the flexural strength and modulus improvement. For these reasons, the impact strength of EP-POSS/epoxy blends was higher than that of pure epoxy at all range of addition, which meant that EP-POSS could modify the toughness of epoxy resin. The fractured

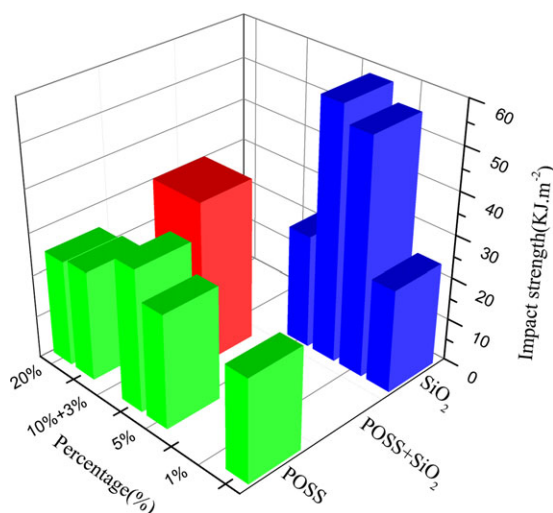


Figure 8. Impact strength of different materials systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

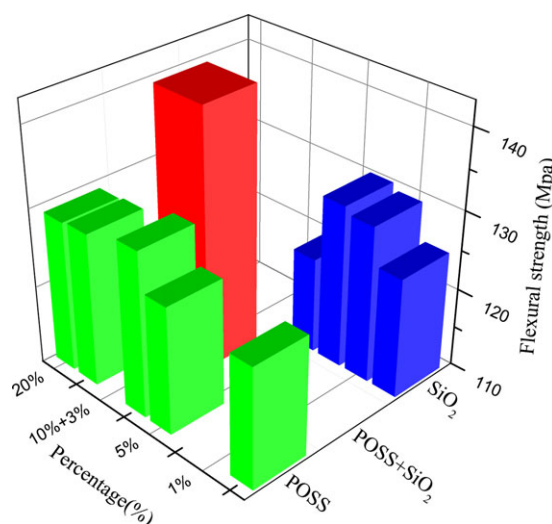


Figure 9. Flexural strength of different materials systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

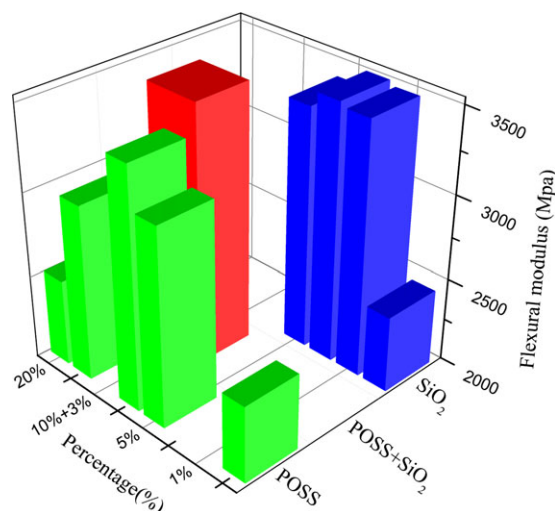


Figure 10. Flexural modulus of different materials systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface of modified system as well as pure epoxy resin matrix was shown in Figure 11. It was found that the fractured surface morphology of pure epoxy was relatively smooth and homogeneous, while the surface morphology of EP-POSS/epoxy blends system had some wrinkles and a few toughening whorls, which implied that the much more fracture energies were absorbed when the blend samples were being destroyed, which would hinder the further damaged of samples.²⁴

As for the SiO₂/epoxy system with blue column display in the three figures as well as Table I, the mechanical properties mentioned in previous increased with the increasing of SiO₂ content, while the mechanical properties decreased when the SiO₂ content was >3%. Therefore, the optimum SiO₂ content was found to be 3%. The mechanical properties were correspondingly increased maximumly with the 3% SiO₂ content. In reality, some particles could aggregate when the addition of SiO₂ was >3%, and these aggregates might be broken easily by stress, which aggravates the interface defects and weaken the interfacial effect. These restrictions resulted in the decline of the mechanical properties eventually.^{25,26} However, with the proper addition of SiO₂, the SiO₂ may act as physical cross-linking reagent by the Si[---]O[---]Si bond in the matrix, which would improve the stress-strain behavior of the materials system¹⁸ and uniformly distributing the stress to enhance the flexural strength and modulus. Moreover, nanoparticles play an important effect on the impact strength. First, the addition of nanoparticles could scatter the extension of impact cracks and produce the fracture modes of multiple cracks. Second, it could hinder the progress of the cracks in the direction of the cracks

fracture. As a result, the impact strength of SiO₂/epoxy system was enhanced. The SiO₂ (3%) nanoparticles were well uniformly dispersed in the epoxy matrix from the Figure 7(a), which could develop special interface layer and restrained the extension of the crack, and more fracture energies were needed if the crack were broken completely.^{27,28} Besides, there were more wrinkles, toughening whorls, and white zones of toughening as shown in the Figure 11. The wrinkles, toughening whorls, and white zones of toughening could absorb large numbers of impact energies when the fracture happened, leading to the impact strength improved.²⁴

Based on the results as above mentioned analysis, the SiO₂/EP-POSS/epoxy ternary nanocomposite system was prepared by adding 10% EP-POSS and 3% SiO₂. The mechanical properties as shown in the three figures with red column as well as Table I. The impact strength, flexural strength, and modulus of the SiO₂/EP-POSS/epoxy system increased around by 57.9, 14.1, and 44.0% compared with the pure epoxy resin, respectively. Notably, the ternary system had the higher flexural strength and modulus than that of the EP-POSS/epoxy and SiO₂/epoxy systems as a result of the EP-POSS and SiO₂ synergistic effect according to the above mentioned analysis. Because the silica had good compatibility with the epoxy resin due to the existence of EP-POSS wherein both EP-POSS and silica had the Si[---]O[---]Si structure, and SiO₂ could form the cross-link with the epoxy resin. However, the impact strength of the ternary system was not the optimal in the three materials systems. It may because of the difference of toughening mechanism due to EP-POSS and SiO₂. In another respect, we did not have a plausible explanation for this behavior based on these data alone, and more complicated reasons needed to be further explored. The toughening whorls and white zones of toughening decreased in the SiO₂/EP-POSS/epoxy system in contrast to the SiO₂/epoxy system while was more than that of the EP-POSS/epoxy system observed by SEM from the Figure 11. The wrinkles, toughening whorls, and white zones of toughening could absorb large numbers of impact energies when damages occur, which will reinforce the impact strength.²⁴

Thermal Stability

The thermogravimetry analysis was used to measure the thermal stability of the materials system when heated at a controlled rate and in a certain environment as shown in Figure 12 and Table II. The bond energy²⁹ of the Si[---]O structure was higher than other bond energy of the POSS, which could improve the initial decomposition temperature and residue, retarding the rate of the decomposition. T_b , T_{max} , and the residues of EP-POSS (10%)/epoxy blends showed an increase from 367°C, 415°C and 12.5% to 385°C, 423°C, and 24.3% compared

Table I. The Data of Mechanical Properties

	Epoxy resin	EP-POSS(10%)/epoxy	SiO ₂ (3%)/epoxy	SiO ₂ /EP-POSS/epoxy
Impact strength (kJ m ⁻²)	24.2	33.2 (37.2%)	59.1 (144.2%)	38.2 (57.9%)
Flexural strength (MPa)	125.2	130.9 (4.6%)	130.7 (4.4%)	142.8 (14.1%)
Flexural modulus (MPa)	2451.7	3418.6 (39.4%)	3523.1 (43.7%)	3530.2 (44.0%)

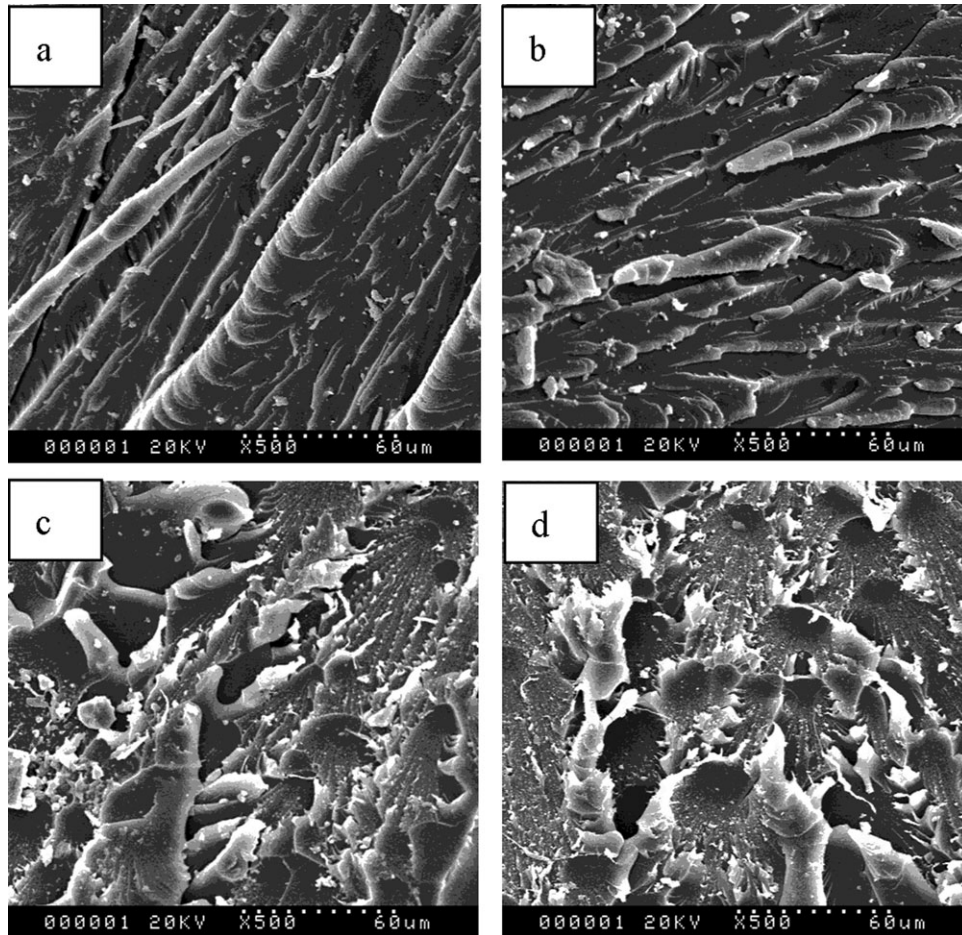


Figure 11. Fractured surface of the materials by SEM: (a) Epoxy resin, (b) EP-POSS/epoxy, (c) SiO₂/epoxy, and (d) SiO₂/EP-POSS/epoxy nanocomposites.

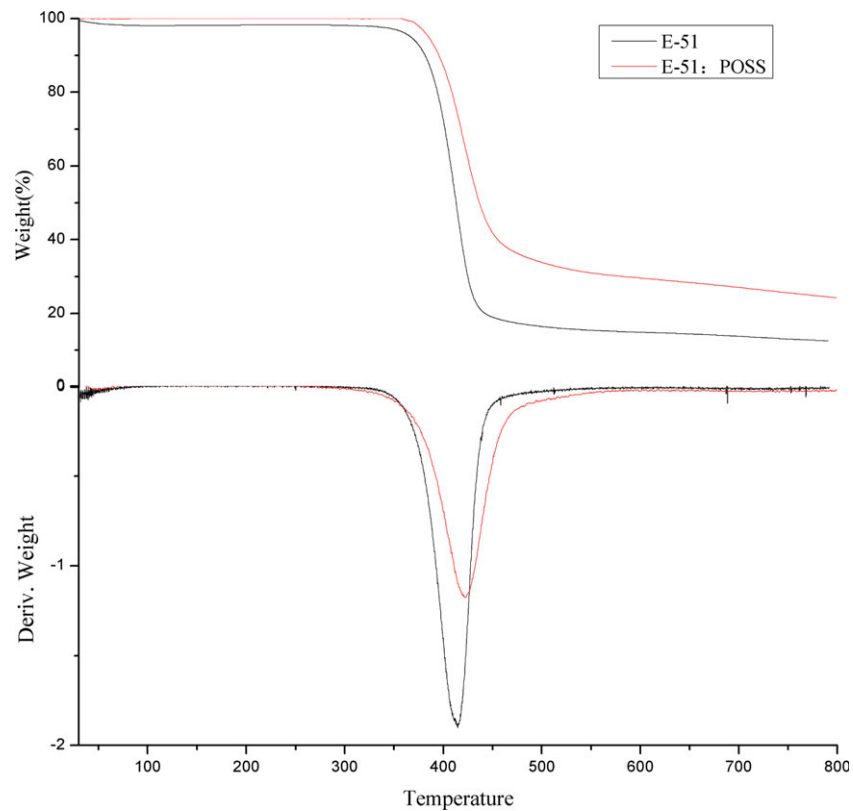


Figure 12. TGA and DTG curves of EP-POSS/epoxy blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. The Data of Thermal Properties

System	T_i (°C)	T_{max} (°C)	Residues (%)
Epoxy resin	367	415	12.5
EP-POSS(10%)/epoxy	385	423	24.3
SiO ₂ (3%)/epoxy	380	415	12.5
SiO ₂ /EP-POSS/epoxy	387	426	25.2

with the neat epoxy matrix, respectively, which implied that the incorporation of EP-POSS into epoxy networks could improve the thermal decomposition temperature and retard loss mass rate, leading to a higher residue at same temperature. However, improvement of the thermal stability is due to the difference of bond energies of hybrid structural (i.e., Si[sbond]O, Si[sbond]C, C[sbond]C, and C[sbond]O is 422.5, 242.7–334.7, 344.0, and 344.4 kJ/mol, respectively), and higher bond will lead to higher thermal decomposition. The Si[sbond]O bonds are the majority bonds in EP-POSS structure. Therefore, the incorporation of EP-POSS into epoxy producing an increase the proportion of the Si[sbond]O bond in the system, which was not easy to be destroyed unless the more energy was added. Therefore, the T_i and T_{max} were increased. However, the core of the EP-POSS was the stable Si[sbond]O[sbond]Si inorganic structure, which retarded the decomposition of blends and much residues remained at the high temperature.²⁴

For the SiO₂/epoxy system as shown in the Figure 13 and Table II, T_i of SiO₂/epoxy system was 380°C, increased by 13°C compared with the pure epoxy resin, while T_{max} and residues remained to be stable with the SiO₂ content at 3%. The SiO₂ could be uniformly distributed according to the TEM from Figure 7(a) and improved the thermal stability effectively,²⁶ and the stable Si[sbond]O[sbond]Si bond was uniformly distributed in the epoxy matrix network. The SiO₂/epoxy system became protected and decomposed in a slower rate because of the silica layer, which largely increased the thermal stability.

Considering the abovementioned analysis, we studied the thermal stability of SiO₂/EP-POSS/epoxy nanocomposite. T_i , T_{max} , and the residues of the ternary system were 387°C, 426°C, and 25.2%, increased remarkably by 20°C, 11°C, and 101.6% in contrast to the pure epoxy resin as shown in Figure 14 and Table II, respectively. The thermal stability of the ternary system furtherly exceeded that of the EP-POSS/epoxy and SiO₂/epoxy systems, because there were much more stable Si[sbond]O[sbond]Si bonds that slowed down the decomposition and enhanced the residues greatly than that of EP-POSS/epoxy and SiO₂/epoxy systems. It was the result of EP-POSS and SiO₂ synergistic effect. The properties of the ternary system were more superior to the binary system, and it owned the two effects by the EP-POSS and silica, which could acquire the optimal effect when the EP-POSS and SiO₂ were added into the system simultaneously.

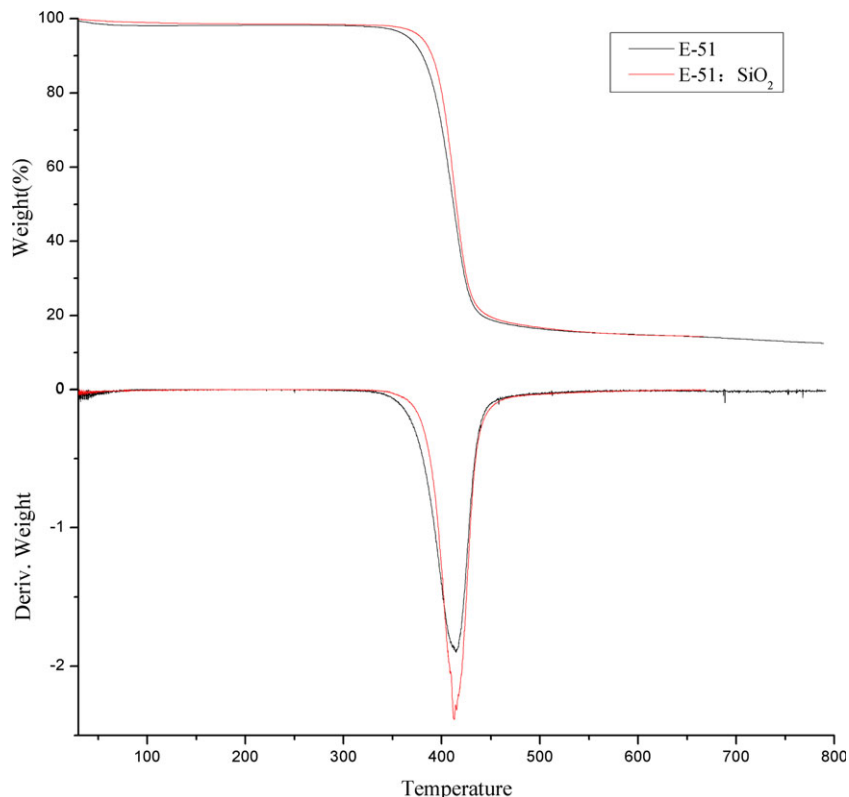


Figure 13. TGA and DTG curves of SiO₂/epoxy nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

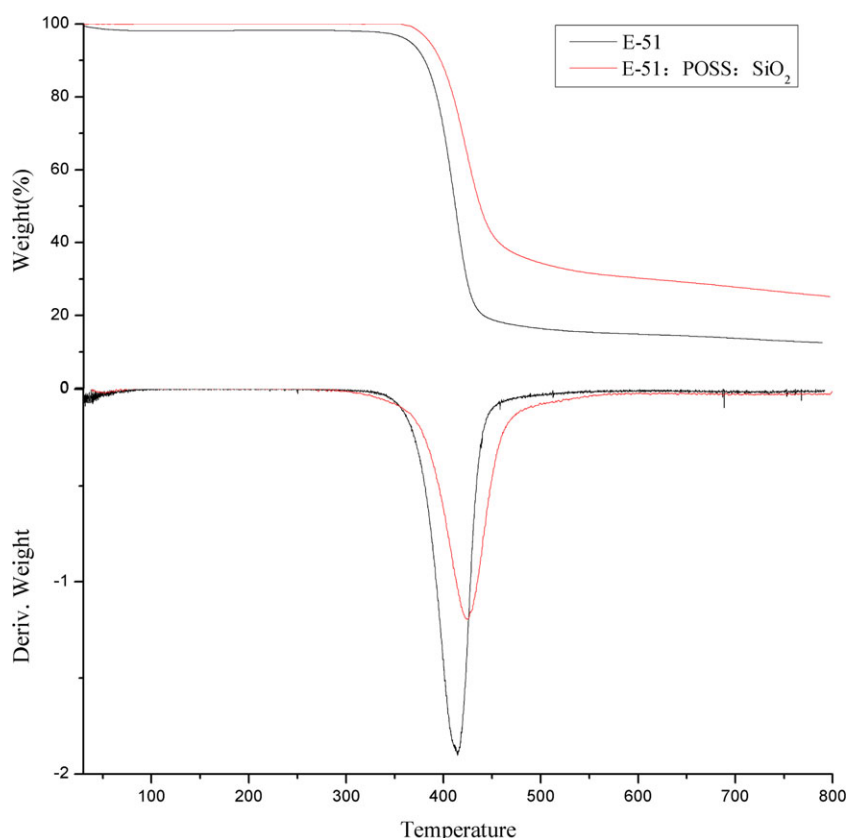


Figure 14. TGA and DTG curves of SiO₂/EP-POSS/epoxy nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

A series of EP-POSS/epoxy blends and SiO₂/epoxy nanocomposite were prepared wherein EP-POSS was synthesized via the hydrolysis and condensation of GPMS. EP-POSS and SiO₂ could improve the mechanical properties of binary systems with the corresponding addition of 10% EP-POSS and 3% SiO₂, respectively. It was clearly shown that the SiO₂/EP-POSS/epoxy ternary nanocomposite system displayed the optimum flexural strength and modulus with the addition of 10% EP-POSS and 3% SiO₂ compared with the binary systems and pure epoxy matrix. TGA and DTG analysis results showed that T_b , T_{max} , and residues of EP-POSS (10%)/epoxy, and especially for the SiO₂/EP-POSS/epoxy system were improved significantly compared with the pure epoxy resins. T_i of SiO₂ (3%)/epoxy system was increased slightly higher than the neat epoxy resin matrix, wherein the thermal stability of the ternary system was higher than the binary systems and the pure epoxy matrix. It was concluded that the properties of SiO₂/EP-POSS/epoxy system was the optimal system among the three systems. These improvements were attributed to the peculiar EP-POSS, excellent dispersion, and interface effect of the SiO₂.

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