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ORIGINAL PAPER

Hybrid cationic ring-opening polymerization of epoxy resin/glycidyloxypropyl-polyhedral oligomeric silsesquioxane nanocomposites and dynamic mechanical properties

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Abstract Glycidyloxypropyl-polyhedral oligomeric silsesquioxanes (G-POSS) were prepared from 3-glycidyloxypropyl-trimethoxysilane (GTMS) by hydrolytic condensation. The hybrid cationic thermal polymerization of G-POSS with bisphenol A epoxy resin (E-51) using diphenyliodonium fluoride borate (DPI·BF4) as a cationic initiator and benzoyl peroxide (BPO) as a co-initiator was investigated by DSC and FTIR. The structure of G-POSS was characterized by liquid chromatography–mass spectrometry (LC/MSD), FTIR and NMR. The effect of BPO content on reaction system, the distribution of G-POSS in the curing system, curing reaction activation energy E_a and dynamic mechanical properties of the E51/G-POSS nanocomposites were characterized. The results showed that octa(3-glycidyloxypropyl)-POSS (G-POSS) had been synthesized and displayed uniform dispersion in E51/G-POSS curing system. The DPI·BF_4, which was capable to initiate the thermal ring-opening curing of epoxy resin, showed an initial curing temperature of epoxy resin decreased by 54.7 °C when the added amount of BPO was 2 wt%. The reaction process was well accorded with Kissinger's kinetics model, and the average curing reaction activation energy E_a was increased as the content of G-POSS increased. The T_g and storage modulus of the E-51/G-POSS nanocomposites reached its optimum when the content of G-POSS was 2 wt%. The T_g of nanocomposite was 8.3 °C higher than that of the pure epoxy resin. The T_g and storage modulus decreased with the further increasing of G-POSS content.

Keywords Epoxy resin · Hybrid composites · Cationic ring-opening polymerization · Silsesquioxanes · Thermomechanical properties

Introduction

Epoxy resins have been widely used as adhesives, coatings, laminates, casting materials, and a matrix resin for composites due to their excellent mechanical properties, low price, good adhesion and chemical stability [1]. To achieve well-balanced ultimate properties, uncured epoxy resins must be converted into a crosslinked macromolecule under optimal curing and processing conditions [2]. All the commercialized curing agents of epoxy resins can be divided into three basic categories: amine type (especially aromatic and aliphatic amines), anhydride type and polymeric type (polyamide, polyurethane and phenol resin, etc.,) [3, 4]. However, these conventional curing agents have some disadvantages, especially the amine type, which will significantly decrease the thermal properties of the materials. The pure epoxy-opening polymer has many advantages as high toughness, etc. To obtain pure polymer of the epoxy resin, the cationic ring-opening polymerization is an available method, and resulting polymeric materials exhibit excellent adhesion, abrasion resistance, chemical resistance and lower shrinkage. Therefore, it has been regarded as a new method to obtain high-performance materials.

Diaromatic iodonium salt is a kind of highly efficient cationic photoinitiator, which was first reported by Crivello and Lam [5]. After that the cationic polymerization

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was intensified by the development of diaryliodonium and triarylsulfonium salts [6]. Abu-Abdoun has reported the photoinitiated cationic polymerization of epoxide and vinyl monomers by *p*-trimethoxytrityl salts [7]. Oxman, et al. has reported free radical/cationic hybrid photopolymerizations [8, 9]. In these reactions, the onium salts are used to generate very strong Brônsted acids. Usually cationic species or Brônsted acids are generated by the interaction of the UV light with a certain wavelength and UV reagent, which will induce the polymerization of the monomers and oligomers.

UV radiation curing has become a well-accepted technology because it is an environmentally friendly, efficient and less consuming energy method and has a mild reaction condition [10, 11], however, some unreacted regions exist in shadow areas, such as in electronic printed circuit boards, where the UV radiation cannot reach. For these reasons, the other curing mechanisms, such as dual curing technology, typically UV/thermal [12], UV/moisture [13] or only thermal curing [14] system have been developed. The thermal cationic curing process of epoxy resin is one of the most suitable industrial technologies. But the report for the thermal cationic polymerization initiated with phenyliodonium salt is fewer than others. The thermal cationic polymerizations of cyclohexene oxide, tetrahydrofuran, and s-trioxane using the diaryliodonium salt/ascorbate redox couple as initiator were studied by Crivello et al. [15]. We have already studied the hybrid free radical-cationic thermal polymerization of methylacryloylpropyl-POSS/epoxy resin nanocomposites [16].

Epoxy resin is usually limited in many high-performance application fields because of its brittleness and low thermal deformation temperature. Organic–inorganic hybrid materials have been regarded as a new generation of high-performance materials; they combine the advantages of both inorganic materials (rigidity, high thermal stability) and organic polymers (flexibility, electric insulation properties, ductility and processibility). There are many reports on the epoxy resin modified by nanomaterials; Shokrieh et al. [17] have reported carbon fiber-reinforced epoxy composite. Wang et al. [18] have reported the preparation and properties of organic rectorite/epoxy resin nanocomposites.

Polyhedral oligomeric silsesquioxanes (POSS) are a relatively new type of organic–inorganic hybrid molecules. POSS has great potential in the synthesis of organic–inorganic nanocomposites. POSS has a –Si–O–Si– nanostructured inorganic framework as the core and reactive or non-reactive functional groups around the framework. The reactive functional groups on POSS not only can further form homopolymers of the POSS, but also can react or copolymerize with other reactants. Polymer/POSS nanocomposites often have higher anti-oxidation ability, thermal properties, mechanical properties and flame resistance than the pure polymer. These enhancements have been shown to apply to both thermoplastic and thermosetting systems. The amide-containing POSS such as *N*-aminoethyl-γ-aminopropyl-POSS, aminophenyl-POSS and aminopropyl-POSS are used as curing agents of epoxy resin. The preparation of epoxy resin/POSS nanocomposites, cured with the amide-containing POSS, has been reported in the past [19, 20]. The co-curing nanocomposites of epoxy-containing POSS with epoxy resins in the presence of curing agent have also been reported. Pistor et al. [21] has reported the dynamic mechanical characterization of epoxy/epoxycyclohexyl-POSS nanocomposites. Choi J et al. [22] have reported the organic/inorganic hybrid composites from the cubic silsesquioxane epoxy resins of octa(dimethylsiloxyethyl cyclohexylepoxide) silsesquioxane. We have reported the curing kinetics, thermal, mechanical, and dielectric properties for *o*-cresol formaldehyde epoxy resin with polyhedral oligomeric (*N*-aminoethyl-*g*-aminopropyl) silsesquioxane [23].

To the best of our knowledge, there is no precedent report on the thermal cationic ring-opening co-polymerizations of epoxy resin with glycidyl-containing POSS epoxy resin with BPO as a co-initiator. In this work, considering the deficiency of the photoinitiator system, a thermal cationic initiator of diaryliodonium fluoride borate (DPI·BF4) was synthesized, and a radical/cationic thermal hybrid curing initiator system was formed using DPI·BF4 and benzoyl peroxide (BPO) as initiator. The thermal cationic ring-opening copolymerization of the epoxy resin with 3-glycidyloxypropyl-POSS (G-POSS) was investigated, and the dynamic mechanical property of the nanocomposites was determined.

Experimental

Materials

Bisphenol A epoxy resin (E-51, 0.51 mol/100 g), technical grade, supplied by Yueyang Petrochemical Plant, China. 3-Glycidyloxypropyl-trimethoxysilane (GTMS) was purchased from Shenda Chemical Co. China. Tetramethylammonium hydroxide (TMAH), isopropyl alcohol, toluene, benzoyl peroxide (BPO), potassium iodate (KIO_3), HBF_4, $AgNO_3$, NH_4Cl, benzene, petroleum ether, diethyl ether, sodium bisulfite ($NaHSO_3$), hexafluorophosphate and other reagents were all analytically pure, and supplied by Tianjin Chem Co. China. Diaryliodonium fluoride-borate (DPI·BF4) was synthesized according to the literature source [24] and it was used to generate the protonic acid, which could initiate the cationic ring-opening polymerization of the epoxy monomers. The melting point of DPI·BF4 was determined by the DSC method at a heating rate of 10 °C/min showing 139 °C. The nuclear resonance spectrograph (NMR, 400 k, Bruker Co. Switzerland) and Fourier transform infrared spectroscopy (FTIR, 600-IR, Varian Co. USA) were used to determine the structure of DPI·BF4.

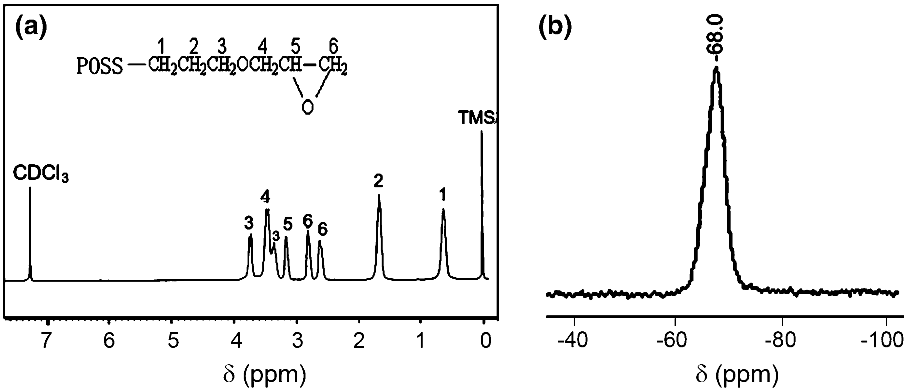
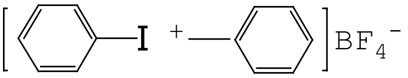


Fig. 1 ^{1}H NMR spectra (**a**) and ^{29}Si NMR spectra (**b**) of G-POSS

FTIR: Ar–H, 3042.72 cm^{-1}; AR, 1604.6 cm^{-1}, 1464.6 cm^{-1}; Ar–I, 1083.9 cm^{-1}.

NMR: ‘H $\delta = 7.38$–7.98 (2H). The molecular structure of DPI·BF4 is as follows:



3-Glycidyloxypropyl-containing polyhedral oligomeric silsesquioxane epoxy resin (G-POSS) was prepared and analyzed according to the literature [25]. 120 mL of isopropyl alcohol and 3 g 10 % TMAH aqueous solution were added into a four-necked flask. Then the mixture of 40 g GTMS and 30 mL isopropyl alcohol was dropped into the foregoing system. After the reaction mixture was stirred for 6 h at 25 °C, the water and isopropyl alcohol were removed in a vacuum. Then, the hydrolytic product was dissolved by adding 110 mL toluene and refluxed for 4 h, during which the Si–O–Si bonds were formed through the reaction of cyclizations of Si–OH groups. Finally, a pellucid and viscous liquid was obtained after water and toluene were removed under vacuum. The yield was 82 % and the epoxy value was 0.50 mol/100 g. Nuclear resonance spectrograph (NMR) and liquid chromatography–mass spectrometer (LC/MSD, 1100 type, Agilent, USA) were used for determination of the POSS components and detailed structure.

Sample preparation and characterization

G-POSS and epoxy resin (E-51) were mixed in acetone according to G-POSS mass content ratio of 0, 1, 2, 4, 6, 8 wt%, (based on the amount of E-51 resin), and were labeled samples No. 0, No. 1, No. 2, No. 4, No. 6 and No. 8, respectively, then added DPI·BF4 and BPO as initiator. The reaction process was tracked by FTIR with KBr tablet method. The sample was dissolved in acetone and coated on the KBr tablet, and after the solvent was removed under vacuum, the changes in the groups were determined. The distribution of G-POSS in the curing system was characterized by energy disperse spectroscopy (EDS). The resin was prepared into a 1.0-mm-thick film, and then the energy dispersion was determined by transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, USA) using an acceleration voltage of 60–200 kV and a resolution of 0.24 nm.

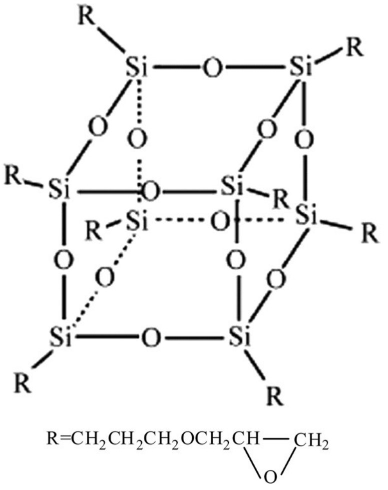
The curing reactions of E-51/DPI·BF4/BPO with different contents of G-POSS were carried out in a differential scanning calorimeter (DSC, Diamond, Perkin-Elmer Co., USA) calibrated with high-purity indium and operated under 20 mL/min nitrogen flow rate. About 5 mg specimen was placed in a sealed aluminum sample pan. Dynamic scans were conducted from 30 to 250 °C at heating rates (β) of 5, 10, 15, 20 and 25 °C/min.

The specimens were all cured under the 170 °C/2 h, and post-cured for 2 h at 80 °C for measuring the dynamic mechanical properties. The dynamic mechanical behavior of the materials was characterized by a dynamic mechanical analyzer (DMA, Q8000, Perkin-Elmer Co. USA). The stripes of 25 × 6 × 1 mm were prepared for DMA measurements. In the DMA analysis, the samples were heated from 25 to 250 °C at a heating rate of 2 °C/min, the single revolving method and frequency of 2 Hz were used.

Results and discussion

Characterization of G-POSS

The structure of G-POSS was analyzed by ^{1}H NMR (CDCl$_3$) and ^{29}Si NMR. The ^{1}H NMR and ^{29}Si NMR spectra are shown in Fig. 1. The ^{1}H NMR spectrum (Fig. 1a) displays the sharp single peaks at chemical shift of 0.018 and 7.286 ppm, which may correspond to TMS and solvent CDCl$_3$, respectively. In addition to the absorption peak of TMS and CDCl$_3$, the integral area respective for 8 peaks from left to right are 0.925, 1.982, 1, 0.989, 0.998, 0.901, 1.947 and 1.927 ppm, the ratio of the integral area was about 1:2:1:1:1:1:2:2. According to the label of absorption peaks in Fig. 1a, ^{1}H NMR (CDCl$_3$, δppm) 1: δ 0.644 ppm (2H, H of 3-glycidypropyl), the δ shifts to lower value, since the CH$_2$ connected with the Si directly, 2: δ 1.680 ppm (2H), 3: δ 3.460 ppm and 3.731 ppm (2H of



Scheme 1 Molecular structure of the G-POSS

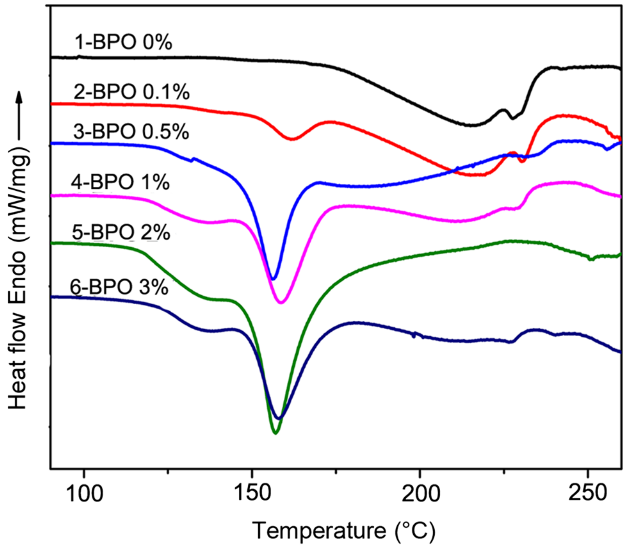


Fig. 2 Thermal curing DSC curves of E-51 resin with 3 wt% DPI·BF_4 and different contents of BPO

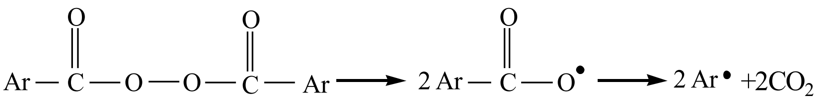
3-glycidypropyl), because it suffers the effect of ether bond, chemical shifts move toward high direction, and split into two peaks. 4: δ 3.466 ppm (2H), 5: δ 3.172 ppm (1H); 6: δ 2.629 ppm and 2.813 ppm (2H). There is no hydroxyl hydrogen chemical shifts appearance in the ^{1}H-NMR spectrum. It is illustrated that hydroxyl almost entirely participates in the closed loop reaction. The structure of synthesized G-POSS is consistent with the theory.

To further identify G-POSS structure, ^{29}Si NMR was used to detect the structures. Figure 1b shows the ^{29}Si NMR spectrum of G-POSS. The ^{29}Si NMR analysis shows that the G-POSS synthesized from 3-glycidyloxypropyltrimethoxysilane (GTMS) by hydrolytic condensation has only a Si–O–Si chemisorption peak at 68.0 ppm. The LC/MSD results showed that the M/Z appeared on the 1432.3, corresponds to a molecular weight of octamer, so, that it is a T_8. The result showed that the octa(3-glycidyloxypropyl)-POSS (G-POSS) has been synthesized. The molecular structure of G-POSS is shown in Scheme 1.

The effect of BPO content on thermal polymerization

Figure 2 shows the curing behavior of E-51 with 3 wt% DPI·BF4 and different amounts of BPO (based on the amount of E51 resin) at the heating rate of 10 °C/min. As seen from Fig. 2, for the E-51/DPI·BF_4 curing system, the curing peak is very wide and usually takes on the double exothermic peaks; moreover, it has a high initial curing temperature T_{ci} (175 °C). This may illustrate that the thermal initiating rate of DPI·BF_4 for the epoxy resin is slow, and needs a high reaction temperature. When BPO was added into the curing system, the initial curing temperature T_{ci} decreased, and a new exothermic peak independently (about 150 °C) appeared at low-temperature region. The heat of curing reaction at low-temperature region increased gradually as the BPO content increased, and the curing peak in the high-temperature region decreased gradually. At 2 wt% BPO content the curing peak disappeared at high-temperature region, and the initial curing temperature dropped to about 54.7 °C compared to the pure E-51/DPI·BF_4 system. But in further increase in BPO content, the DSC curves show only a little change, considering the BPO can also induce the free radical decomposition reaction of polymers. Therefore, the optimal additive amount of BPO is 2 wt% in this work.

It is known that the DPI·BF_4/BPO initiator system makes the reaction to form a free radical-cationic dual reaction system, in which the free radical produced from BPO can accelerate cationic ring-opening reaction and plays a coordination role for cationic reaction, because it plays an indirect role in the electron transfer of the iodonium salt [13–15]. The free radical is produced through the thermal decomposition of BPO at about 80 °C, which could act as the reducing agent of onium salts, and induce DPI·BF_4 to generate cationic active state. Then, the radical and the cationic active center exist simultaneously in the system and a free radical-cationic hybrid initiating system is formed [12]. It is coincident with the thermal initiating curing mechanism of epoxy resin/onium salt system proposed by Crivello and Pappas et al. [5, 12]. The possible reaction mechanism of DPI·BF_4/BPO initiator system is as follows:



$$Ar-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-Ar \longrightarrow 2\,Ar-\overset{\overset{O}{\|}}{C}-O^{\bullet} \longrightarrow 2\,Ar^{\bullet}+2CO_2$$

$$\mathrm{Ar}\cdot + \mathrm{Ar_2I^+BF_4^-} \rightarrow \mathrm{Ar_2I}\cdot + \mathrm{Ar^+} + \mathrm{BF_4^-}$$

$$\mathrm{Ar_2I}\cdot \rightarrow \mathrm{ArI} + \mathrm{Ar}\cdot$$

$$\mathrm{Ar}\cdot + \mathrm{RH} \rightarrow \mathrm{Ar-H} + \mathrm{R}\cdot$$

$$\mathrm{Ar_2I^+X^-} + \mathrm{R}\cdot \rightarrow \mathrm{Ar_2I}\cdot + \mathrm{R^+} + \mathrm{X^-} \rightarrow \text{etc.}$$

Curing reaction of the E-51/G-POSS system

The FTIR spectra of the sample No. 8 are shown in Fig. 3. The absorption peak at 1608, 1510 and 829 $\mathrm{cm^{-1}}$ was associated with the bisphenol A skeleton. The absorption peak of Si–O–Si belongs to G-POSS at the range about 1000–1100 $\mathrm{cm^{-1}}$. After curing for 60 min at 170 °C, the epoxy group characteristic peak of the system without BPO at 913 and 970 $\mathrm{cm^{-1}}$ shows a slight decrease (Fig. 3, curve 3). The characteristic peak at 913 $\mathrm{cm^{-1}}$ is decreased and 970 $\mathrm{cm^{-1}}$ seems disappeared for the system with DPI·BF4 and BPO (Fig. 3, curve 4). The feature absorption peaks belong to the epoxy group of the system (which contain only BPO as initiator) and have not changed before and after curing (curve 2). This indicates that the opening ring reaction of epoxy group has occurred in the presence of initiator DPI·BF4, and BPO has promoted the reaction of epoxy group at an ever faster rate; with the DPI·BF4/BPO forming free radical/cationic hybrid initiation system in the heating process. The ring-opening reaction of epoxy group has been unable just to carry out in the presence of BPO.

The thermal ring-opening curing behavior of the E-51/G-POSS using 3 wt% DPI·BF4 and 2 wt% BPO as co-initiator was determined by a non-isothermal DSC method at the heating rates of 10 °C/min, as the reaction mechanism has not changed after adding G-POSS. Moreover, the epoxy resin is the main component, so that, the No. 0, No. 2, No. 4 and No. 8 are listed in Fig. 4 as representatives in the kinetics study. For the purpose of comparison, the curing curve of the pure G-POSS is also listed in Fig. 4. Figure 4 depicts that all the DSC curves have an obvious continuous bi-exothermic peak except G-POSS. The initial curing temperature of the pure G-POSS is at 90.1 °C, and has only a very sharp curing exothermic peak between 90 and 150 °C. A continuous curing peak appears in the E-51/G-POSS system between 112 and 179 °C, and the heat release of exothermal peak between 145 and 179 °C is obviously higher than the peak at 112–145 °C. This result indicates that the curing system is a complex exothermic process, which is caused by the initiator of onium salts.

The initiating characteristic of onium salt is first activated to an excited state, and then a series of the decomposition reaction occurs and produces the strong acids of Brönsted and Lewis acids. The pyrolysis mechanism of $\mathrm{DPI{\cdot}BF_4}$ is as follows [13, 14, 16]:

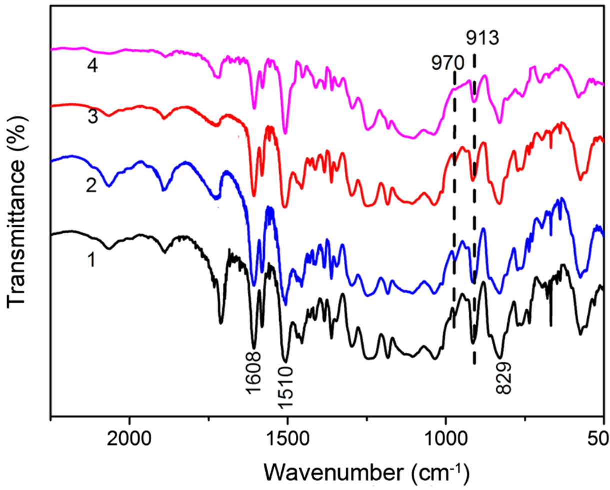


Fig. 3 FTIR spectra of sample No. 8 cured for 60 min at 170 °C. *1—uncured*, *2—cured* with 2 wt% BPO, *3—cured* with 3 wt% DPI·BF4, *4—cured* with 3 wt% DPI·BF4 and 2 wt% BPO

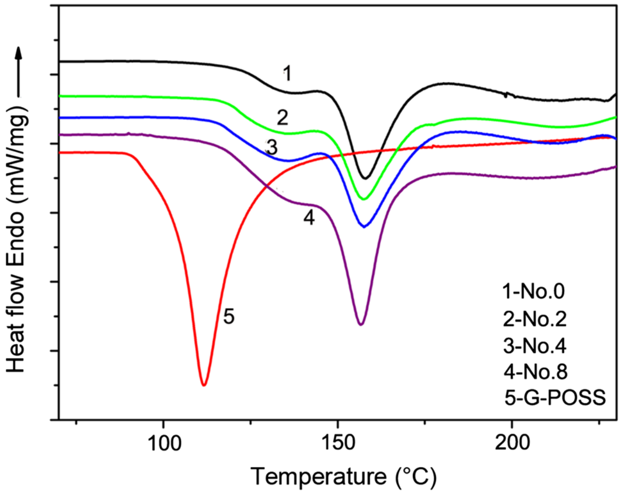


Fig. 4 DSC curves of some samples

First step:

$$\mathrm{Ar_2I^+BF_4^-} \rightarrow [\mathrm{Ar_2I^+BF_4^-}]^*$$

$$[\mathrm{Ar_2I^+BF_4^-}]^* \rightarrow \mathrm{ArI}\cdot^+\,\mathrm{BF_4^-} + \mathrm{Ar}\cdot$$

Second step:

$$\mathrm{RH} + \mathrm{ArI}\cdot^+\,\mathrm{BF_4^-} \rightarrow \mathrm{ArI} + \mathrm{R}\cdot + \mathrm{H^+BF_4^-}$$

$$\mathrm{Ar}\cdot + \mathrm{RH} \rightarrow \mathrm{ArH} + \mathrm{R}\cdot$$

$$\mathrm{H^+BF_4^-} + \mathrm{M} \rightarrow \mathrm{H-M^+BF_4^-}$$

Generally, Lewis acid ($\mathrm{ArI^+BF_4^-}$) is produced directly through the decomposition of onium salt. The proton acid

Table 1 Curing parameters of curing system in relation to different G-POSS contents

Curing system	No. 0	No. 1	No. 2	No. 4	No. 6	No. 8	G-POSS
T_{ci} (°C)	119.5	117.0	116.3	114.9	114.0	112.4	90.1
T_{cp} (°C)	157.8	157.0	157.6	157.6	157.6	156.7	111.5
T_{cf} (°C)	177.5	176.3	178.6	179.1	178.9	175.3	154.6
ΔH ($J \cdot g^{-1}$)	81.6	86.7	92.4	93.6	99.8	99.2	292.3

($H^+BF_4^-$) is an indirect product of the reaction between Lewis acid (or the decomposition reaction of carbocation) and alcohol which contains activated hydrogen substances. The reason for complex exothermal peaks in the curing process can be explained as the reaction of epoxy resin and onium salts including the following process: first, the reaction takes place between onium salt and hydroxyl groups of epoxy resin, because hydroxyl has a higher activity than ring-opening reaction, and this reaction corresponds to a small peak in the front, and the main exothermic peak at 145–179 °C which corresponds to the ring-opening reaction of epoxy group. G-POSS does not contain hydroxyl and, moreover, each POSS contains eight active epoxy groups, so the curing peak has only a sharp exothermic peak.

Figure 4 also shows that the initial curing temperature (T_{ci}) displays a slight declining trend after adding G-POSS. It is because the G-POSS structure is a regular hexahedron, and the nano-sized core is surrounded by eight epoxy groups having high reactivity, so the initial curing temperature decreases with the G-POSS content increasing. The final temperature (T_{cf}) and the peak temperature T_{cp} have not obviously changed. But the final temperature T_{cf} has increased first and then decreased with the addition of G-POSS. This is mainly due to the viscosity and the crosslink degree of the system increasing in the later stage of the reaction, which has an inhibitory role for the diffusion motion of molecular chains. These may cause the curing reaction shift to a higher temperature in the final curing stage. The exothermic enthalpy ΔH increases with the G-POSS content increasing. This is because the addition of G-POSS can increase functionality and the degree of crosslinking, so that curing heat release is increased, but with further increases in G-POSS content, the cage structure of the POSS has also a large steric hindrance for movement of the molecules or chain segment, which will inhibit the diffusion motion of molecules, and make the crosslinked network not perfectly, so the curing system is not changed much in exothermic enthalpy ΔH. G-POSS contains 8 epoxy groups, so it has a high cross-linking degree and maximum value of enthalpy. The curing temperature parameters and exothermic enthalpy (ΔH) of the different systems are listed in Table 1.

The activation energy of curing reaction

Curing of E-51/G-POSS is accompanied by a significant heat release that can be conveniently measured by differential scanning calorimetry (DSC), and the reaction kinetics are almost universally described by the basic rate equation [26].

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{1}$$

where $f(\alpha)$ is the reaction model related to the mechanism. For non-isothermal conditions of linear heating, Eq. (1) is modified as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{2}$$

where $\beta = dT/dt$ is the heating rate, T is the absolute temperature (K), A is the pre-exponential factor of the Arrhenius equation, R is the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), and E_a is the activation energy of curing reaction.

For the non-isothermal curing process, the Eq. (2) for the isoconversional method can be expressed in several ways. Perhaps the simplest and most popular representative of multiple heating rate methods is the method of Kissinger Eq. (3) [27, 28], which can be applied to different conversions α of the curing process [28].

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{R} \cdot \frac{1}{T} \tag{3}$$

If α is the conversion rate of epoxy group, the T in the Eq. (3) is defined as T_α, which is the temperature when the conversion rate of curing reaction is α. From the plots of $-\ln(\beta/T_\alpha^2)$ vs. $1/T_\alpha$, we can obtain E_α at each α value. Figure 5 shows the curves of E_α vs. α for samples No. 0, No. 2, No. 4, No. 8 and G-POSS, which are obtained from the DSC curing curves at the heating rates of 5, 10, 15, 20 and 25 °C/min, respectively. Their linear correlation coefficients are all between 0.9882 and 0.9966, and the average E_α of No. 0, No. 2, No. 4, No. 8 and G-POSS are 96.53, 101.18, 106.39, 114.92 and 122.44 kJ/mol, respectively.

As seen from Fig. 5, the result shows that the reaction process is in accordance with Kissinger's kinetics model. The E_α values of the pure epoxy resin are lower than other samples, and almost not changed on the whole or have only slightly decreased with the reaction progressing, because it has a lower crosslink density than other samples. E_α of the E-51/G-POSS samples increases with the increases in G-POSS content. E_α is just slightly changed between the interval of $0.3 < \alpha < 0.8$, this is because the

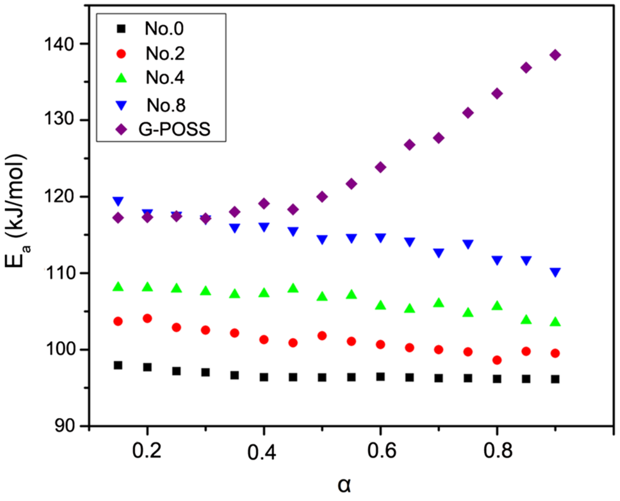


Fig. 5 E_a-α curves of samples No. 0, No. 2, No. 4, No. 8 and G-POSS

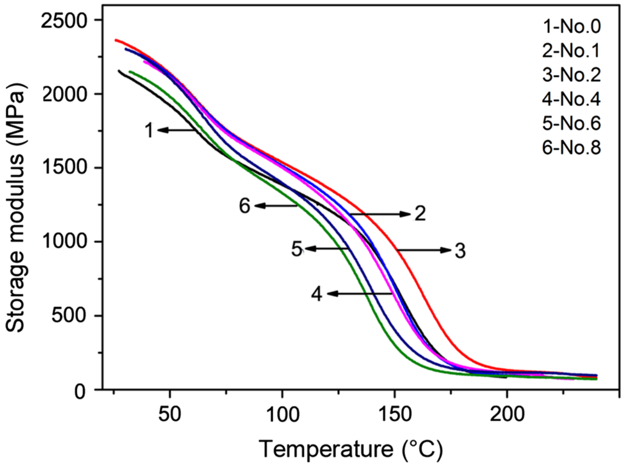


Fig. 6 Storage modulus curves of cured E-51/G-POSS composites

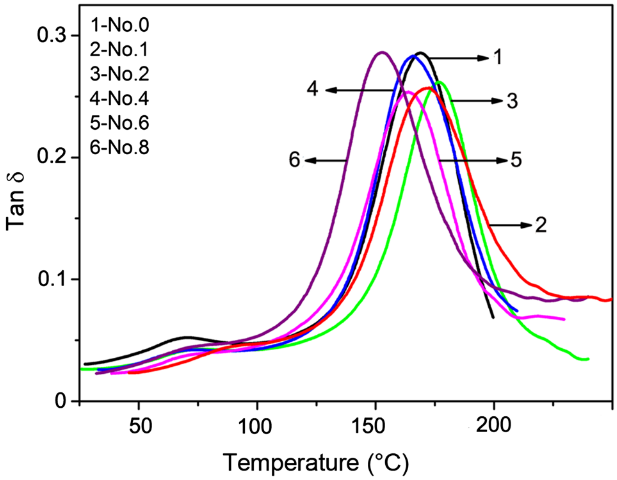


Fig. 7 Mechanical loss curves of cured E-51/G-POSS system

surroundings of the proton acid and free radical have been formed and have a stable concentration at that time. But in the interval of $0.8 < \alpha < 1.0$, E_α is little decreased, which suggests that a diffusion control becomes operative and controls the curing process [29]. The E_α values of pure G-POSS is the highest (122.44 kJ/mol) and increases as the reaction progresses. This is because the G-POSS structure is a regular hexahedron, and is surrounded by epoxy groups, the viscosity and cross-linking degree of reaction system increase quickly with the reaction process. The cage structure of the POSS has also a large steric hindrance for movement of the molecules or chain segment, which will further inhibit the diffusion motion of molecules, so it needs a relatively higher E_α to complete the curing reaction.

Dynamic mechanical analysis

DMA was used to investigate the effect of G-POSS content on the T_g and modulus of the E51 epoxy matrix. In the DMA technology, two different moduli are determined as a function of temperature, the storage modulus reveals the amount of elastic energy stored in the composite. Figure 6 shows the change in storage modulus along with the content of G-POSS. The pure resin system (No. 0) has the lowest storage modulus at the temperature below 75 °C. In this case, the storage modulus is enhanced with increases in G-POSS content, due to the cage structure of G-POSS which may provide large spaces and multiple end groups on G-POSS to react with epoxy group of the E-51 resin. This increases chemical cross-linking, as a result of which the segmental motion of the molecules becomes more restricted leading to greater rigidity of the materials. When G-POSS contents increase continually, the storage modulus of the composites will decrease. Moreover, the storage modulus shows a platform at temperature 75–120 °C. This may be due to the perfect cross-linking network of epoxy resin formed by a curing agent such as $DPI{\cdot}BF_4$. At higher temperature, when the content of G-POSS is over 4 wt%, G-POSS molecules will aggregate and decrease the cross-link density of materials, so that, the E-51/G-POSS system will have a lower storage modulus than the E-51 resin at temperature of above 130 °C.

The glass transition temperature (T_g) may be used as a heat distortion parameter of the polymeric materials and is also a conversion parameter in the analysis of the reaction kinetics of thermosetting polymers, which depends on the curing conditions, molecular structure, cross-linking degree, curing temperature and time. The dynamic mechanical loss peak (tan δ) temperature T_p reflects the

Table 2 T_p of the samples with different G-POSS contents

Samples	No. 0	No. 1	No. 2	No. 4	No. 6	No. 8
T_g (°C)	169.5	171.3	177.8	169.3	163.7	152.6

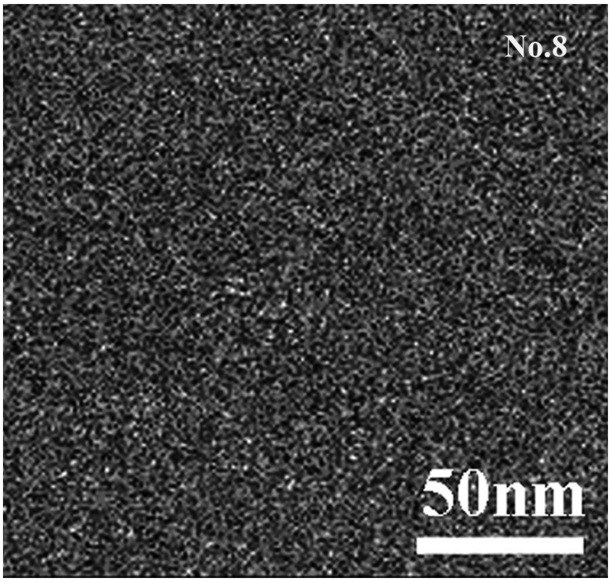


Fig. 8 Distribution of G-POSS in the curing system by TEM method

onset micro-Brownian movement of the macromolecular chain segments, i.e., the glass transition temperature (T_g) [30, 31].

Figure 7 shows the tan *δ* curves of cured E-51/G-POSS samples. The mechanical loss tan *δ* peak temperatures (T_p) of the E-51/G-POSS are listed in Table 2. The T_p of cured pure E-51 sample is 169.5 °C, with the content of G-POSS increasing, the T_p increases at first and then slowly decreases. When the content of G-POSS is 2 wt% the T_p is increased to 8.3 °C (177.8 °C). This is because the rigid cage structure is connected to the segment of E-51 epoxy resin through co-curing reaction. The nanometer size effect and high functionality of the G-POSS will lead the curing system to form a cross-linking network with the G-POSS as the center and increase the cross-linking density. In Fig. 8, the distribution of G-POSS in the curing system shows that the G-POSS is uniformly dispersed in the curing system. Figure 9 is the schematic representation of the E-51/G-POSS nanocomposites. These factors would hinder the thermal motion of the chain segment and raise the T_g. However, when the G-POSS content continues increasing, the T_g and storage modulus would be decreased. This is due to the introduction of much more flexible glycidyloxypropyl groups on POSS cages and that a part of glycidyloxypropyl group cannot fully participate in cross-linking reaction, because of the increasing viscosity of the curing system. Then the G-POSS, which fails to complete the cross-linking reaction, has a large space volume, and it will also reduce the molecules arranged closely and increase the free volume of molecular movement. These factors would cause the negative effects to increase the T_g and storage modulus of curing system.

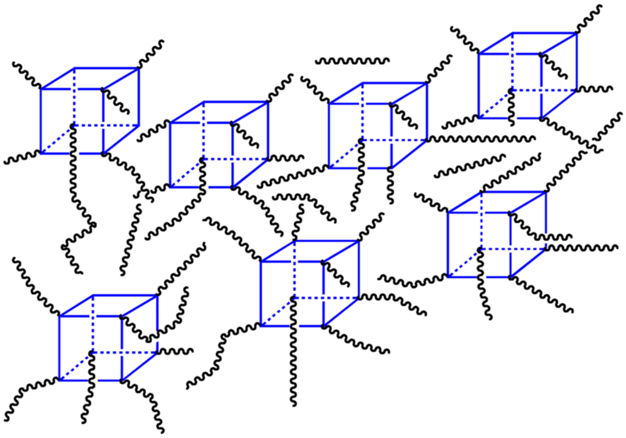


Fig. 9 Schematic representation of E-51/G-POSS nanocomposites

Conclusions

Polyhedral oligomeric silsesquioxanes epoxy resin (G-POSS) with bisphenol A epoxy resin can co-cure by thermal cationic opening ring polymerization using diphenyliodonium fluoride-borate (DPI·BF_4) as initiator and benzoyl peroxide as co-initiator. As a free radical initiator, BPO has played an indirect role in electron transfer to the onium salt. When the content of BPO is 2 wt%, the initial curing temperature of E-51 decreases to 54.7 °C, more than that of the pure DPI·BF_4 curing system.

The initial curing temperature of E-51 system displays a declining trend, but the final temperature, curing exothermic enthalpy (ΔH) and the average reaction activation energy E_a increase with the addition of G-POSS. The glass transition temperature T_g and the storage modulus of the E51/G-POSS composites increased first and then decreased with G-POSS higher content. When 2 wt% G-POSS was added and co-cured with E-51, the material with the highest storage modulus was obtained and its mechanical loss tan *δ* peak temperature (177.8 °C) was improved by 8.3 °C compared to pure E-51 resin.

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