

Curing Octaepoxysilsesquioxane with Different Curing Agents

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Received 5 May 2011; accepted 5 November 2011

DOI 10.1002/app.36452

Published online 20 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Octaepoxysilsesquioxane (POSS-Ep) was first synthesized by the hydrolysis and condensation of γ -[(2,3)-epoxypropoxy]propyltrimethoxysilane (KH-560) with the presence of ethanol and HCl at 55°C for 72 h. Then, it was cured with 4,4'-diaminodiphenylsulfone (DDS) and methyl nadic anhydride (MNA), respectively. The curing reactions between POSS-Ep and DDS or MNA were investigated by FTIR. Thermal stability of the cured nanocomposites was studied by TGA. The micromorphologies of the obtained hybrids were observed by SEM. FTIR results show that POSS-Ep can be cured completely with DDS or MNA to obtain the final organic-inorganic (O-I) hybrids after the same experimental curing cycle: 120°C/2

h + 140°C/2 h + 160°C/2 h + 180°C/2 h + 200°C/2 h. TGA results show that POSS-Ep/DDS hybrid displays better thermal stability than that of POSS-Ep/MNA hybrid. Initial thermal degradation temperature (T_{di}) of POSS-Ep/DDS hybrid is 420°C, 195°C higher than that of POSS-Ep/MNA (225°C). SEM images of the fracture surfaces of the hybrids suggest the cured POSS-Ep possesses good mechanical properties. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2281–2288, 2012

Key words: polyhedral oligomeric silsesquioxane; curing reaction; nanocomposites; 4,4'-diaminodiphenylsulfone; methyl nadic anhydride

INTRODUCTION

Organic-inorganic (O-I) nanocomposite materials have been regarded as a new generation of high performance materials since they combine the advantages of the inorganic materials (rigidity and high stability) and the organic polymers (flexibility, dielectric, ductility, and processibility).^{1,2} Polyhedral Oligomeric Silsesquioxane (POSS) emerges as one of the most important organic-inorganic hybrid materials owing to its excellent mechanical, electrical, and thermal properties. It consists of inorganic siloxane (Si-O-Si) core surrounded by organic groups that

could be modified in various functionalities.¹⁻³ Depending upon the characteristics of the groups connected with the vertexes of the POSS cage, it can be divided into two categories, functional and non-functional. The functional POSSs are very attractive because the nanostructured materials can be thought of as the smallest particles of silica. They are not only compatible with polymers or monomers but also can be incorporated into various polymers through chemical reaction to produce the organic-inorganic hybrids, in which organic (polymer matrix) and inorganic parts (Si-O-Si core) are connected through covalent bonding.⁴ They may contain various kinds of functional groups, such as epoxy,^{5,6} amino,⁷ vinyl groups,⁸ etc. Now, many POSS derivatives functionalized with different groups have been synthesized and characterized. For example, octa(aminophenyl)silsesquioxane(OAPS), an aromatic amine-functionalized silsesquioxane, was synthesized in two steps by nitration of octaphenylsilsesquioxane (OPS) in fuming nitric acid.⁹ Poly(ethylene oxide) (PEO) chains were grafted onto octahydro-silsesquioxane ($Q_8M_8^H$) to obtain the PEO-functionalized silsesquioxanes.¹⁰ The first representatives of alkoxy-zircono-silsesquioxane compounds have been prepared with quantitative yield by interaction of

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Contract grant sponsor: China Postdoctoral Science Foundation; contract grant numbers: 20090450102, 201003661.

Contract grant sponsor: Basic Research Support Project of Chang'an University; contract grant number: CHD2012JC025.

Contract grant sponsor: Key Program of Shaanxi Natural Science Foundation for Basic Research Plan; contract grant number: 2010JZ009.

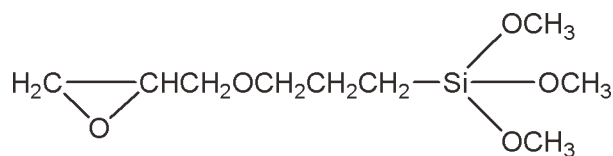
Journal of Applied Polymer Science, Vol. 125, 2281–2288 (2012)
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the corresponding zirconium alkoxides with the cycloalkyl-substituted cage silsesquioxanes in hexane.¹¹ POSSs have been added to different kinds of polymers to form the POSS containing O-I hybrids. These polymers include polyethylene,¹² polypropylene,^{13–15} polysilicone,¹⁶ epoxy,^{17–19} cyanate ester,²⁰ polyurethane,^{21–23} polyimide,²⁴ polycarbonate,²⁵ etc. The POSS containing polymers displayed enhanced mechanical, thermal, dielectrical properties, etc. Recently, metal-functionalized POSSs were used as fire retardants for polypropylene.^{14,15} It is reported that a series of iron (III) containing POSS compounds showed potential as catalysts for aerobic oxidation of tetrahydrofuran (THF).²⁶ The ordinary way to obtain the POSS containing hybrids is the incorporation of POSS into polymers either by physical or chemical methods. Our group synthesized the epoxy-functionalized POSS monomer octaepoxysilsesquioxane (POSS-Ep) in the previous research.²⁷ Considering that the POSS-Ep monomer contains epoxy groups on the vertexes of the molecules, so it can be cured by various curing agents to obtain the POSS containing hybrid materials.

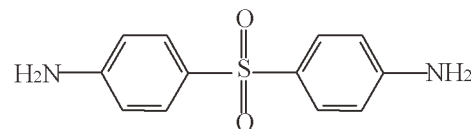
Various curing agents may cure epoxy resins. Aliphatic/aromatic amines and anhydrides are the two most important and commonly used ones. The amines include diaminodiphenylmethane (DDM), 4,4'-diaminodiphenyl sulfone (DDS), etc. Among them, DDS is a high-performance hardener in comparison with the other. The anhydride type curing agent often used is methyl nadic anhydride (MNA). So, POSS-Ep was cured by these two representative curing agents to obtain hybrid materials in this article. This study is helpful for understanding the curing characteristics of octaepoxysilsesquioxane. It is also instructive to obtain high-performance POSS containing hybrids by directly curing the functionalized POSS monomers. Cured POSS-Ep showed excellent thermal stability and mechanical properties. So, it is a potential candidate material that may be used in some severe conditions. For example, high degradation temperature and mechanical properties are desired for ablative materials in rocket, such as thermal resistant structural components, thermal protective coating, and inner insulating coating of rocket engine.

EXPERIMENTAL

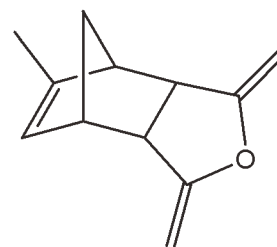
In this research, the POSS-Ep was cured by 4,4'-diaminodiphenylsulfone (DDS) and methyl nadic anhydride (MNA), respectively. The curing reactions of the two curing systems, POSS-Ep/DDS and POSS-Ep/MNA, were monitored by Fourier transforms infrared spectroscopy (FTIR). Their thermal properties were analyzed using thermogravimetric analysis (TGA). The micromorphologies of the obtained hybrids were studied by scanning electron micros-



KH560



4,4'-diaminodiphenyl sulfone (DDS)



Methylnadic anhydride (MNA)

Figure 1 Structures of KH560, DDS, and MNA.

copy (SEM). The structural, thermal, and morphological characterizations of POSS-Ep cured with different curing agent were performed.

Materials

γ -[(2,3)-epoxypropoxy]propyltrimethoxysilane (KH-560) (purity > 97%) was purchased from Jing Zhou Jiang Han Fine Chemical Co. (Hu Bei, China). 4,4'-diaminodiphenylsulfone (DDS), white crystalline solid (purity > 97%), was purchased from Suzhou Yinsheng Chemical Co. (Suzhou, China). Methyl nadic anhydride (MNA) (purity > 97%) is purchased from Aldrich (USA). The chemical structures of KH-560, DDS, and MNA are shown in Figure 1.

Synthesis and characterization of POSS-Ep

Octaepoxysilsesquioxane was synthesized in our laboratory in the light of the literature.²⁷ γ -[(2,3)-epoxypropoxy]propyltrimethoxysilane (KH-560) was hydrolyzed and condensed at 55°C for 72 h to synthesize POSS-Ep. Ethanol and HCl were used as the cosolvent and catalyst, respectively. The synthesis reaction of POSS-Ep is shown in Figure 2. The synthesized POSS-Ep is a transparent, viscous, and flowable liquid at room temperature.

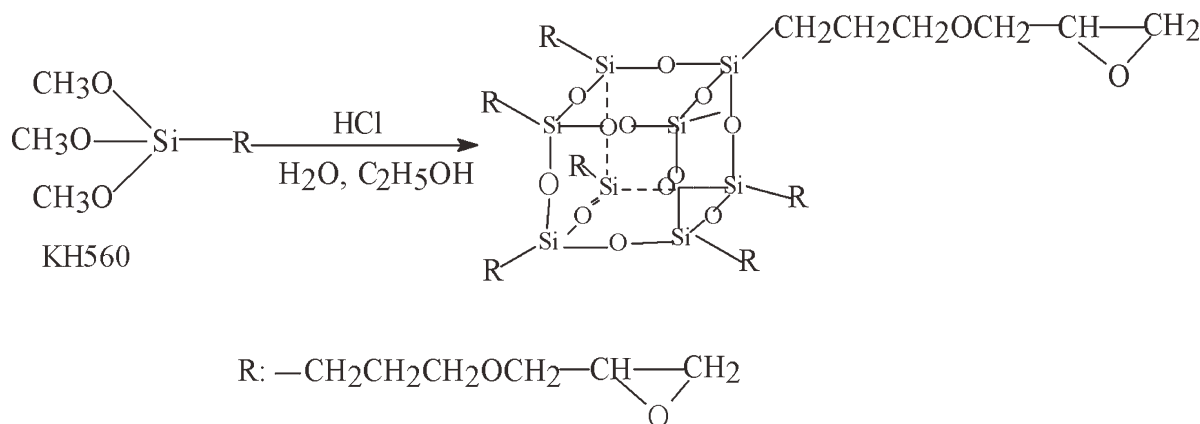


Figure 2 Synthesis reaction of POSS-Ep.

Curing procedure

POSS-Ep and equivalent amount of DDS (or MNA) were dissolved in acetone. The solvent was completely removed by placing the transparent solution in vacuum at 50°C for 24 h. As a result, the two resin systems (POSS-Ep/DDS and POSS-Ep/MNA) containing curing agents were obtained. They were cured according to this heating technique: 120°C/2 h + 140°C/2 h + 160°C/2 h + 180°C/2 h + 200°C/2 h. Finally, the materials were cooled to room temperature naturally.

Instruments

Fourier transforms infrared spectroscopy (FTIR) was conducted on an IBM instruments WQF-300IR spectrometer to study the cure reaction. Spectra were obtained in an optical range of 400–4000 cm^{-1} by averaging six scans at a resolution of 8 cm^{-1} to minimize the effects of dynamic scanning.

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA-7 microbalance coupled with a 1022 Perkin Elmer microprocessor. The microbalance was calibrated making use of the Curie points of perk alloy and nickel.

The micromorphology of the cured POSS-Ep was observed by HITACHI S-570 scanning electron microscopy (SEM). The fracture surface of the materials was sputtered with a thin layer (about 10 nm) of gold by vapor deposition on a stainless steel stub using a Polaron SC502 vacuum sputter coater before the SEM observation.

Determination of conversion of epoxy group

For system POSS-Ep/DDS, the peak of benzene ring at 1600 cm^{-1} was adopted as the internal standard to calculate the conversion of epoxy groups, since the content of benzene ring is invariant. As for POSS-Ep/MNA, the peak of $-\text{CH}$ at 2930 cm^{-1} is used as the internal standard. The conversion of epoxy groups for the two systems was calculated according to eqs. (1) and (2),^{28,29} respectively.

System POSS – EP/DDS :

$$\alpha(t) = 1 - \frac{h(t)_{915}/h(t)_{1600}}{h(0)_{915}/h(0)_{1600}} \times 100\% \quad (1)$$

System POSS – Ep/MNA :

$$\alpha(t) = \left[1 - \frac{h(t)_{915}/h(t)_{2930}}{h(0)_{915}/h(0)_{2930}} \right] \times 100\% \quad (2)$$

where $\alpha(t)$ is the conversion of epoxy groups at time t . $h(t)_{915}$, $h(t)_{1600}$, and $h(t)_{2930}$ are the heights of the absorption peaks of 915 cm^{-1} , 1600 cm^{-1} , and 2930 cm^{-1} at time t , respectively. While $h(t)_{915}$, $h(t)_{1600}$, and $h(t)_{2930}$ are the heights of the absorption peaks of 915 cm^{-1} , 1600 cm^{-1} , and 2930 cm^{-1} at time 0, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization of POSS-Ep

The synthesis reaction of POSS-Ep was monitored FTIR. The FTIR spectra of precursor KH560, the resultant at different reaction time, and POSS-Ep were shown in Figure 3. The main absorption peaks are

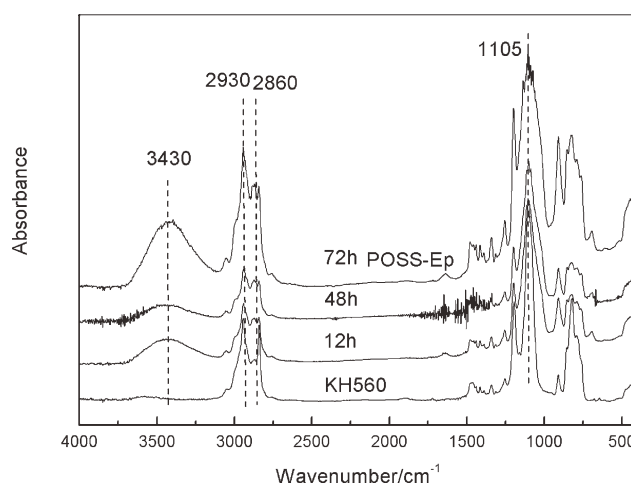


Figure 3 FTIR curves monitoring the synthesis of POSS-Ep.

TABLE I
Characteristic Absorption Peaks of POSS-Ep

Chemical group	-CH ₂	Si-O-Si	-OH	Si-C	Si-O-CH ₃	Benzene ring
Wavenumber/cm ⁻¹	2930, 2860	1200-1000	3430	1256, 760	750	1600

listed in Table I. The double peaks at 2930 cm⁻¹ and 2860 cm⁻¹ correspond to the absorption of C-H of CH₂. The bands at 1256 cm⁻¹ and 760 cm⁻¹ are due to the stretching and bending vibrations of Si-C bond, respectively. The strong and wide band in the range of 1200 cm⁻¹-1000 cm⁻¹ is caused by the stretching vibration of Si-O bond and the bending vibration of Si-O-H, Si-O-Si, and O-Si-O bonds. As far as POSS-Ep is concerned, this band is probably ascribed to the vibration of Si-O-Si inorganic cage.⁷ It can be seen from Figure 3 that the characteristic absorption of Si-O-CH₃ at 750 cm⁻¹ was disappeared after 72 h reaction, showing that the complete hydrolysis and condensation of Si-O-CH₃. The absorption peak of Si-OH at 3430 cm⁻¹ corresponds to the vibration of -OH bond, indicating that small amount of silanol groups still exist.

Besides, the synthesized POSS-Ep is also characterized by ¹³C NMR (Fig. 4). There are six signal peaks at different chemical shifts on the ¹³C NMR spectrum of POSS-Ep (73.00 ppm, 71.63 ppm, 50.49 ppm, 43.30 ppm, 29.20 ppm, and 22.84 ppm). They correspond to six C atoms at different chemical environments. As can be seen from Figure 4, the six resonance peaks accord well with the corresponding C atoms in the organic group on the vertex of POSS-Ep monomer. So, the cage structure of POSS-Ep is confirmed.

FTIR monitoring the curing reaction

POSS-Ep was cured by DDS and MNA, respectively, in this research. FTIR was used to monitor the curing

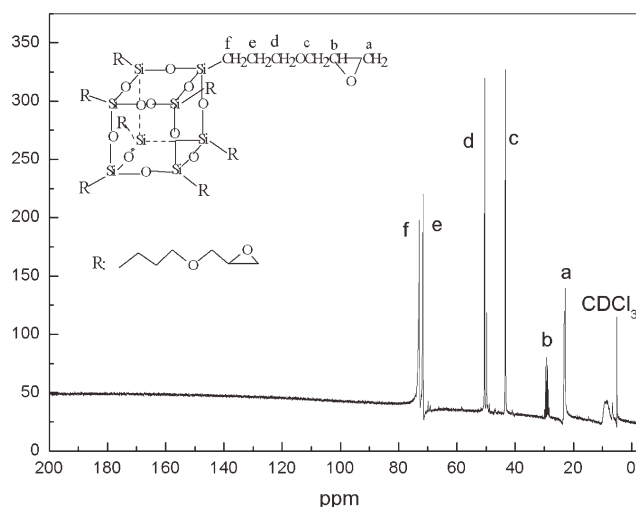


Figure 4 ¹³C-NMR spectrum of POSS-Ep.

reaction of POSS-Ep, as shown in Figure 5. The conversions of curing reaction (α) at different curing stages are also shown on the figure. It can be seen from the figures that epoxy groups (915 cm⁻¹) in both systems were disappeared at the end of the curing process. Although system POSS-Ep/MNA was cured faster at stage b and c than POSS-Ep/DDS, both curing systems were completely cured at the end of the curing cycle. So, the selected curing technique is suitable. As a result, POSS-Ep was cured by DDS or MNA to form the O-I hybrid network.

Curing mechanisms of POSS-Ep with different curing agents

As for the system POSS-Ep/DDS, the curing reaction is between the epoxy groups in POSS-Ep and the amino groups in DDS. The proposed reaction mechanism for this system is shown in Figure 6 according to the curing mechanisms of epoxy resin.⁹ Under

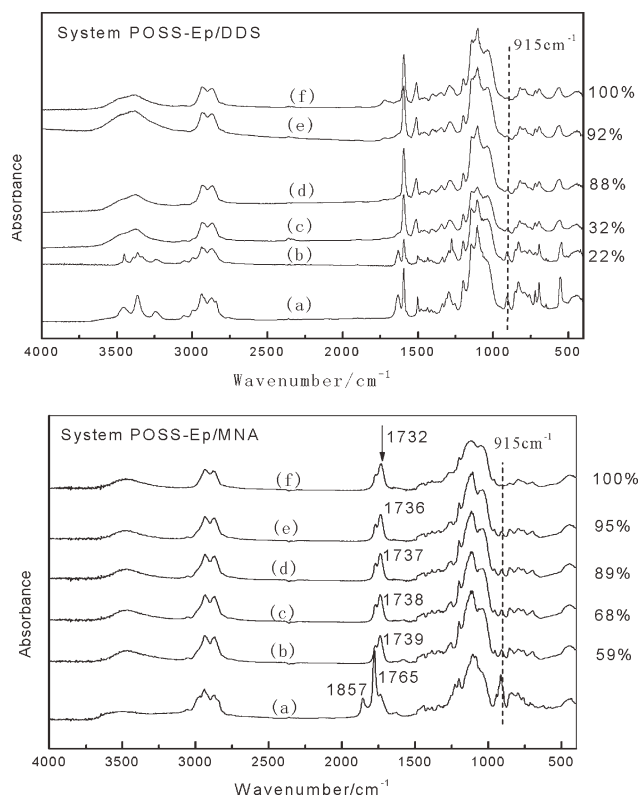


Figure 5 FTIR spectra of curing systems at different curing stages: (a) original; (b)120°C/2 h; (c)120°C/2 h + 140°C/2 h; (d)120°C/2 h + 140°C/2 h + 160°C/2 h; (e)120°C/2 h + 140°C/2 h + 160°C/2 h + 180°C/2 h; (f)120°C/2 h + 140°C/2 h + 160°C/2 h + 180°C/2 h + 200°C/2 h.

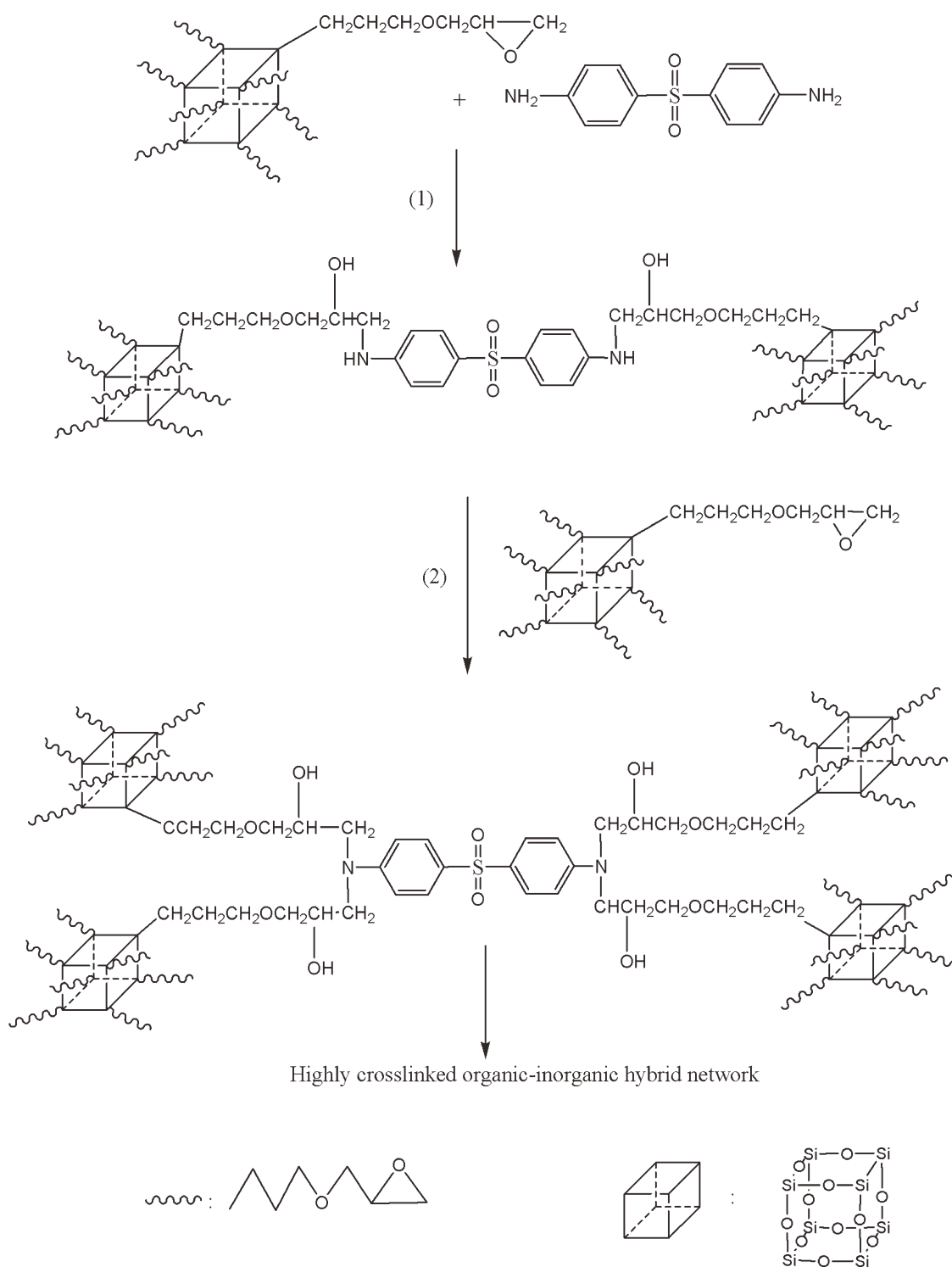


Figure 6 Reactions between POSS-Ep and DDS.

heating, the amine groups react with the epoxide groups to form a covalent bond. As can be seen, the curing mechanism for system POSS-Ep/DDS is a two-step reaction. The first step is the formation of -NH- and -OH . The second one is the formation of tertiary amine. The resultant polymer is heavily crosslinked and is thus rigid and strong. This mech-

anism is proved by the FTIR spectra in Figure 5. The absorption peaks of NH_2 correspond to $3457/3358\text{ cm}^{-1}$. They were generally diminished and finally disappeared, accompanying with the disappearance of epoxy groups (915 cm^{-1}).

When MNA is used as the curing agent for POSS-Ep, the curing reaction is different. The reactions

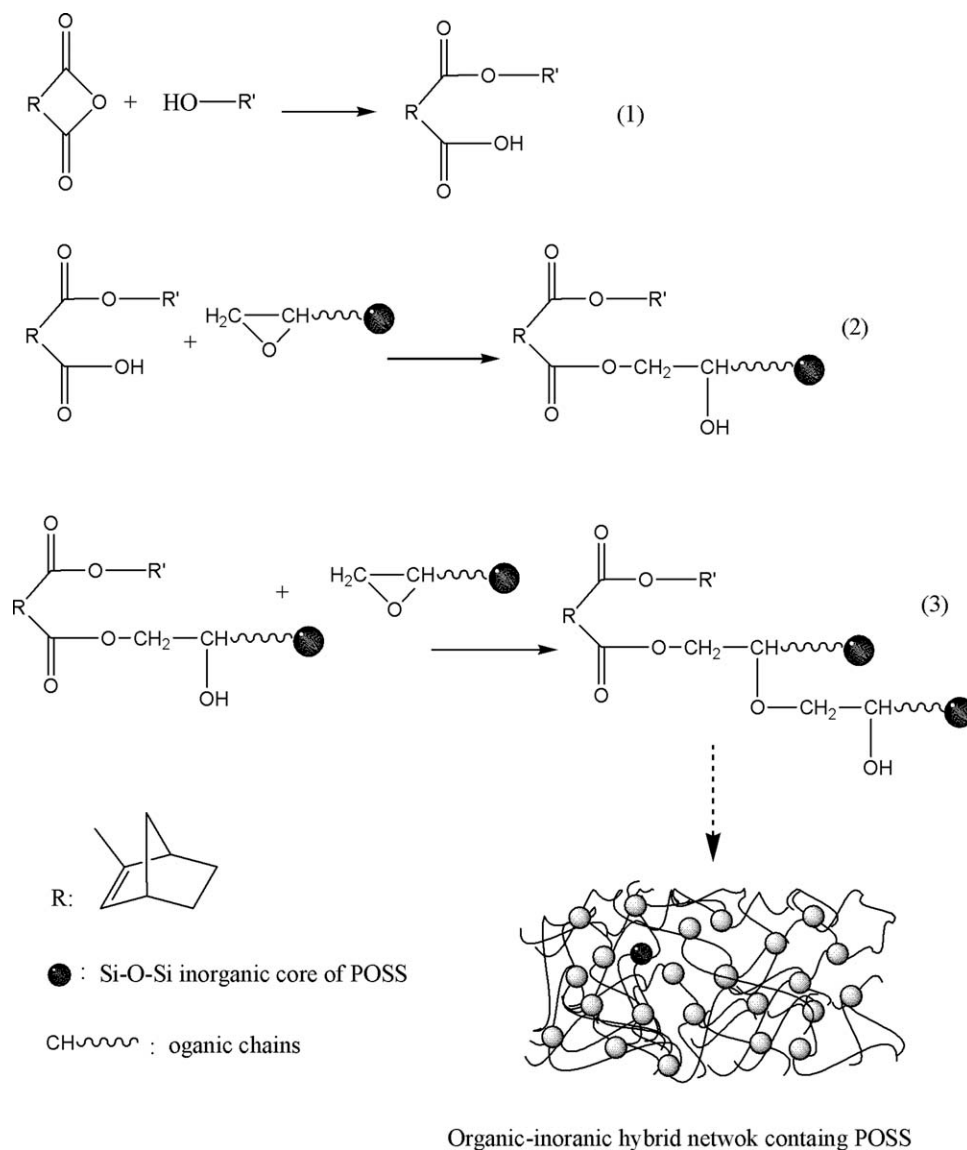


Figure 7 Reaction mechanisms between POSS-Ep and MNA.

between POSS-Ep and MNA are described in Figure 7.¹⁰ As can be seen, they consist of three steps. The first step is that —OH (very small amount of —OH exists in POSS-Ep) opens the anhydride ring to produce an ester containing carboxyl (1). Then, the carboxyl groups react with the epoxy ring of POSS-Ep to form the ester containing the second —OH group (2). The third step is that the second —OH group further reacts with the epoxy group to extend the polymer chain and form three-dimensional network structures. Figure 5 confirms this curing mechanism well. Along with the consumption of epoxy groups at 915 cm^{-1} , the change of the —C=O absorption can also be observed. The bands at $1857/1765\text{ cm}^{-1}$ are attributed to the —C=O of in anhydride. As the curing proceeds, red shift of the —C=O absorption occurs. The bands are reduced to 1732

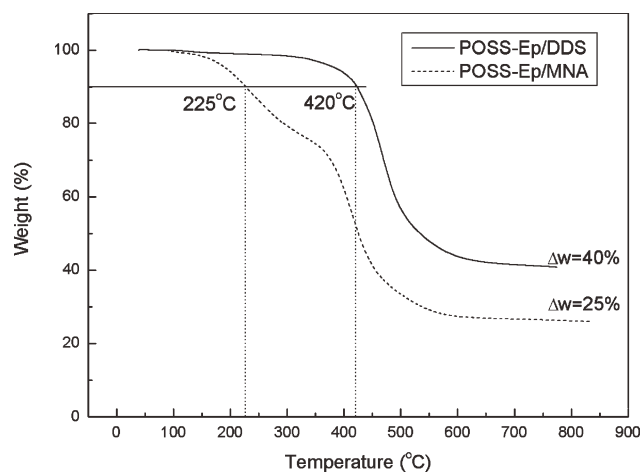


Figure 8 TGA curves of the two cured POSS-Ep systems.

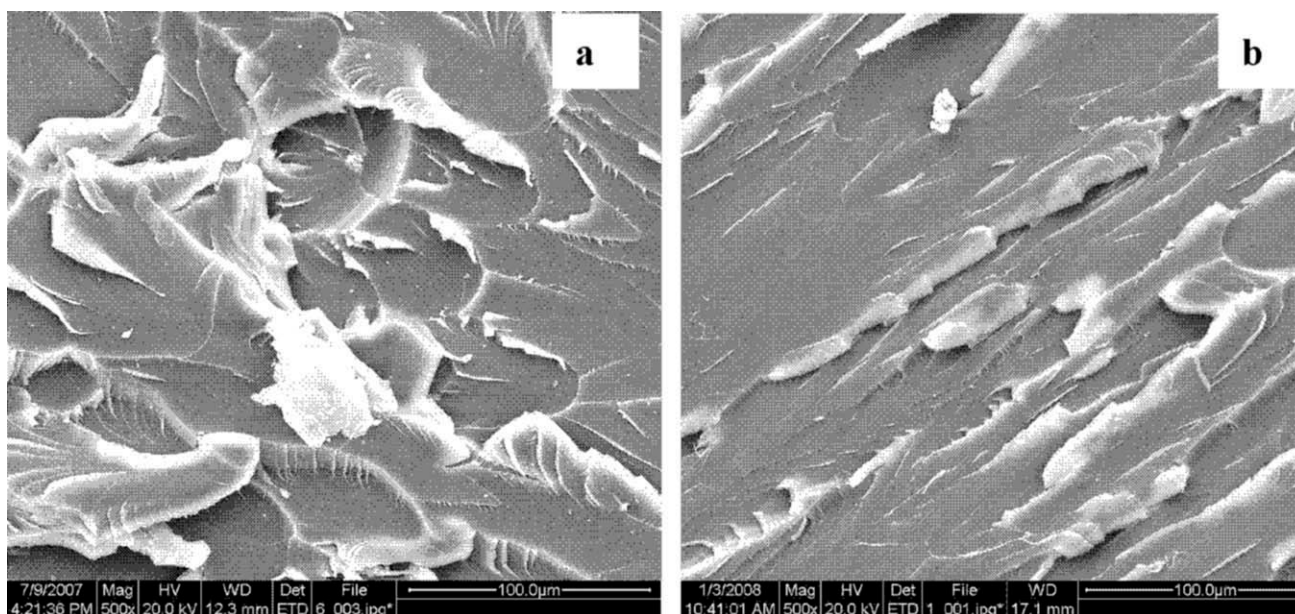


Figure 9 SEM images of the fracture surfaces of the cured hybrids: (a) POSS-Ep/DDS and (b) POSS-Ep/MNA.

cm^{-1} at the end of the curing. The reason is that anhydrides have been converted to the ester chains.

Thermal stability of the cured POSS-Ep hybrids

After the curing procedure, POSS-Ep was cured to be a transparent O-I hybrid material. Figure 8 is the TGA curves of the hybrids cured with DDS and MNA. Thermal stability of materials can be characterized by initial degradation temperature (T_{di}) and char yield (Δw), which can be obtained from the TGA curves. Here, T_{di} is defined to be the temperature to reach 10% weight loss. Δw is the char yield at 800°C. For POSS-Ep/DDS material, T_{di} is 420°C and Δw is 40%. On contrast, T_{di} of POSS-Ep/MNA is only 225°C, and the Δw is 25%. It shows that the thermal resistance of POSS-Ep/DDS hybrid is superior to that of POSS-Ep/MNA hybrid. This can be explained by the chemical structures of the two cured systems. The thermal degradation of materials is dependent on the bonding energies of the chemical bonds in the materials. The higher the bonding energy, the better the thermal resistance will be.³⁰ Figure 7 shows that the POSS-Ep/MNA hybrid contains large amount of C—O—C bonds, the bonding energy of which is only 330.22 kJ/mol. The existence of these weak bonds results in the lower T_{di} than POSS-Ep/DDS hybrid.

Micromorphologies of the cured hybrids

Figure 9 shows the SEM images of the fracture surface of the hybrids which were broken by impact strength testing. It can be seen that both images are similar to the micromorphologies of cured high-performance thermosetting polymers, such as epoxy,

Bismaleimids (BMI), and cyanate ester (CE) resins.^{31–33} For either cured hybrid, no phase separation or pores are observed, suggesting good mechanical properties. However, the SEM images of the two systems display different features. The fracture surface of cured POSS-Ep/DDS is coarse. A large number of tough whirls can be observed for the POSS-Ep/DDS hybrid [Fig. 9(a)]. The fracture surface of POSS-Ep/MNA is smooth and without tough whirls [Fig. 9(b)]. It suggests that POSS-Ep/DDS may possess better mechanical properties.

CONCLUSIONS

It is concluded that POSS-Ep can be cured to be a thermally stable, transparent hybrid materials with DDS or MNA as the curing agent. Although POSS-Ep/DDS and POSS-Ep/MNA are cured through different reaction mechanisms, both possess the organic-inorganic network structure. From the TGA results, it is concluded that the POSS-Ep/DDS hybrid displays superior thermal resistance than the POSS-Ep/MNA hybrid. SEM results suggest that POSS-Ep/DDS hybrid may possess better mechanical properties. So, POSS-Ep/DDS is a potential candidate material that may be used in some serious conditions, where excellent thermal resistance and mechanical properties are desired, such as high-performance materials in aviation and spaceflight.

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