

ORGANIC/INORGANIC HYBRID EPOXY NANOCOMPOSITES BASED ON OCTA(AMINOPHENYL)SILSESQUIOXANE

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Abstract Octa(aminophenyl)silsesquioxane (OAPS) was used as the curing agent of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin. A study on comparison of DGEBA/OAPS with DGEBA/4,4'-diaminodiphenyl sulfone (DDS) epoxy resins was achieved. Differential scanning calorimetry was used to investigate the curing reaction and its kinetics, and the glass transition of DGEBA/OAPS. Thermogravimetric analysis was used to investigate thermal decomposition of the two kinds of epoxy resins. The reactions between amino groups and epoxy groups were investigated using Fourier transform infrared spectroscopy. Scanning electron microscopy was used to observe morphology of the two epoxy resins. The results indicated that OAPS had very good compatibility with DGEBA in molecular level, and could form a transparent DGEBA/OAPS resin. The curing reaction of the DGEBA/OAPS prepolymer could occur under low temperatures compared with DGEBA/DDS. The DGEBA/OAPS resin didn't exhibit glass transition, but the DGEBA/DDS did, which meant that the large cage structure of OAPS limited the motion of chains between the cross-linking points. Measurements of the contact angle indicated that the DGEBA/OAPS showed larger angles with water than the DGEBA/DDS resin. Thermogravimetric analysis indicated that the incorporation of OAPS into epoxy system resulted in low mass loss rate and high char yield, but its initial decomposition temperature seemed to be lowered.

Keywords: Organic-inorganic hybrid composites; Nanostructures; Epoxy resin; Silsesquioxane; Curing kinetics.

INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) are a type of three-dimensional, structurally well-defined caged molecules with the general formula $(\text{RSiO}_{1.5})_n$. The inorganic silica-like core is surrounded by organic groups, and the cage size is about 1.5 nm^[1–4]. Typical POSS derivatives have the structure of a cube-octameric framework covalently bonded with eight organic groups, one or more of which is reactive or polymerizable. They have attracted considerable interest in recent years due to not only their high performance, which originates from the combination of advantages of the inorganic and organic components in these materials, but also the unique features derived from their nano-scale architecture^[5–8].

POSS cages can be incorporated into familiar polymers *via* co-polymerization^[9–12], grafting^[13, 14] or blending^[15–17]. New hybrid inorganic-organic thermoset^[18–21] and thermoplastic materials^[22, 23] were prepared with high use temperatures, oxidation resistance and mechanical properties. On the other hand, some POSS prepared *via* physical blending displayed immiscibility between the silsesquioxane and the organic polymer matrix^[15], an undesirable drawback. So the polymers comprising POSS skeletons *via* co-polymerization are becoming the focus of many studies^[24].

The application of epoxy resins is an obvious development since they are among the most successful commercial polymers known, and they have been widely used as coatings, adhesives, structural materials and

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electronic encapsulating materials due to their efficient bonding, high modulus and strength, excellent chemical resistance and simplicity in processing^[24]. Several reports of organic-inorganic nanocomposites involving epoxy resin and POSS have emerged, and POSS can endow the materials with improved thermo-mechanical and dielectric properties and flame retardance^[24–30].

There are two kinds of POSS applied in epoxy resin *via* co-polymerization, based on amino groups or epoxy groups. Octa(aminophenyl)silsesquioxane (OAPS) is the one owning eight amino groups. It can be used as curing agents for epoxy resins. Nagendiran *et al.*^[24] investigated the properties of thermal and thermo-mechanical properties of the diglycidyl ether bisphenol A (DGEBA)/4,4'-diaminodiphenyl sulfone (DDS)/OAPS system in which OAPS was used as an additive, instead of a curing agent. Laine *et al.*^[31, 32] investigated the modifications of epoxy resin by a series of octa- and polyfunctional silsesquioxanes with various R groups being aminophenyl and dimethylsiloxypolyglycidyl ether groups respectively, comparing the thermo-mechanical properties of DGEBA/OAPS and DGEBA/diaminodiphenylmethane (DDM).

In our previous study, OAPS could be prepared in tetrahydrofuran (THF) using hydrazine hydrate as reductant from octa(nitrophenyl)silsesquioxane (ONPS) in one hour on the 5% Pd/C-FeCl₃ catalyst^[33]. In the present work, OAPS is used as a curing agent for epoxy resin comparing with DDS. The investigations on them involve curing reaction, curing kinetics, surface hydrophobicity, thermal properties and morphology and so on.

EXPERIMENTAL

Materials

Octaphenylsilsesquioxane (OPS, Si₈O₁₂(C₆H₅)₈, *M* = 1033.2, 97%) was purchased from Hybrid Plastics Inc., America. Diglycidyl ether bisphenol A (DGEBA) with epoxy value of 0.51 was purchased from Wuxi Resin Plant, China. 4,4'-Diaminodiphenyl sulfone (DDS), white crystal with purity > 98%, and acetone were purchased from Beijing Chemical Reagent Company, China. All of the chemicals were analytically pure and were used as received.

Synthesis of OAPS

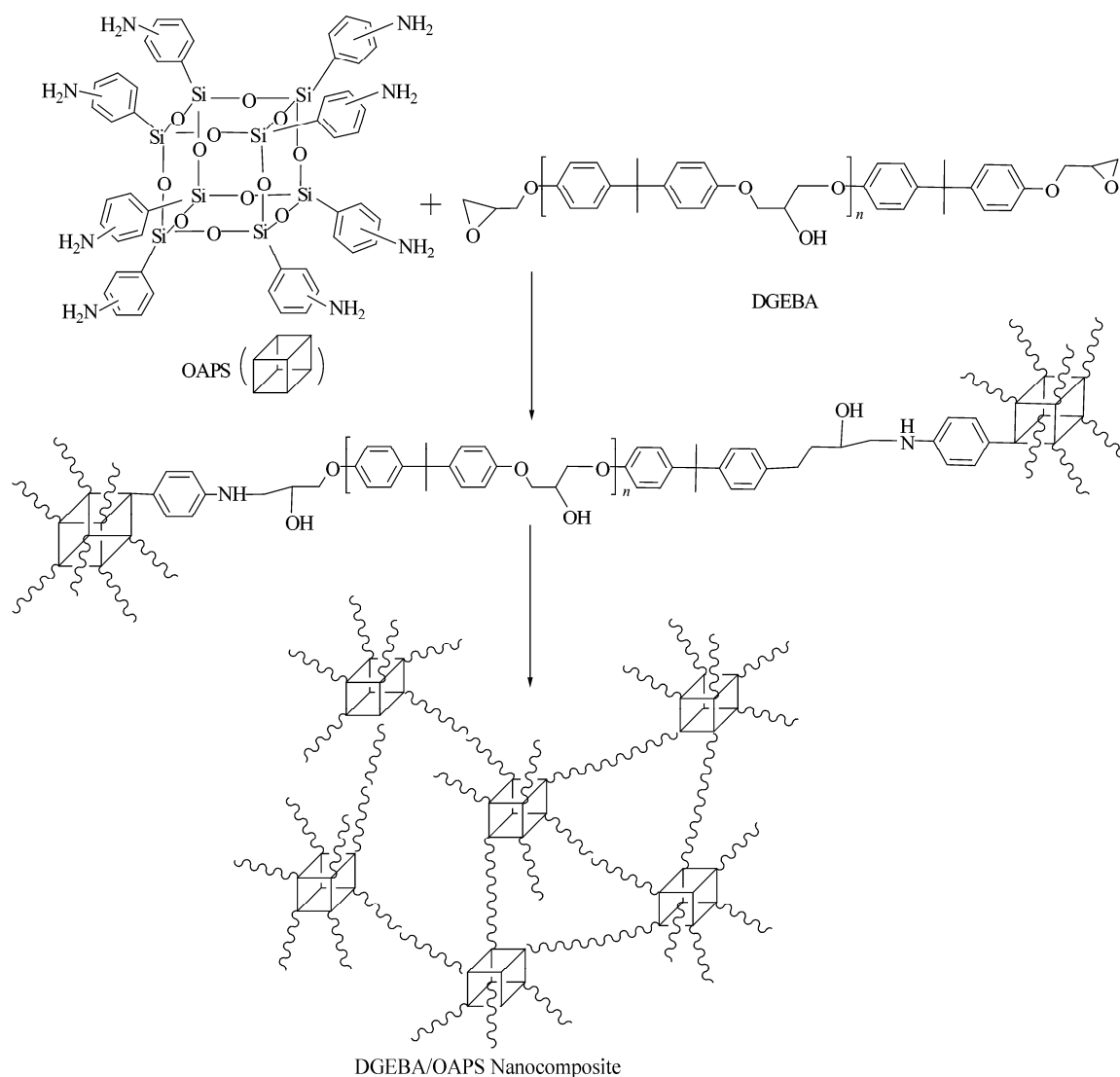
OAPS was synthesized from octaphenylsilsesquioxane (OPS) by following a literature method^[33]. OAPS: ¹H-NMR (DMSO-d₆, 500 MHz, δ): 7.7–6.2 (Ar, 2.0H), 5.4–4.5 (–NH₂, 1.0H); ²⁹Si solid NMR (500 MHz, δ): –68.3, –77.5; ¹³C-NMR (DMSO-d₆, 500 MHz, δ): 153.2, 147.9, 135.1, 131.4, 128.6, 121.2, 119.3, 116.4, 114.6, 113.3; FT-IR (KBr) ν : 3454 and 3350 (–NH₂), 1595 (C–H), 1078 (Si–O) cm^{–1}; Anal. calcd for OAPS: C 50.0, H 4.16, N 9.71; found C 48.9, H 4.38, N 9.31.

Preparation of DGEBA/OAPS Nanocomposites

In formulating OAPS-cured DGEBA nanocomposites (DGEBA/OAPS), *N* was defined as the molar ratio of –NH₂ (in OAPS) to epoxy groups (in DGEBA). A conventional stoichiometric ratio of 2 mol of epoxy to 1 mol of amine would occur at *N* = 0.5^[34]. OAPS powder (10.95 g) was weighed and dissolved in the smallest possible amount of acetone. DGEBA (30 g) was then added to the solution and the mixture was stirred to give a homogeneous solution at room temperature. The mixture obtained was heated to 40°C with continuous stirring to evaporate the majority of solvent and then degassed under vacuum at 40°C for 15 min to remove the residual solvent. The dark yellow, transparent solution was then transferred to a Teflon mould (90 mm × 50 mm × 5 mm) preheated at 50°C. The mixture was cured for 2 h at 80°C, 2 h at 100°C, 2 h at 120°C and finally 1 h at 140°C. The curing reaction is shown in Scheme 1.

Preparation of DGEBA/DDS Composites

For a comparison of the properties, DDS-cured DGEBA composites with *N* = 0.5 (DGEBA/DDS) were prepared. DGEBA (30 g) was added to a round-bottomed flask. Then, the stoichiometric amount of 4,4'-diaminodiphenyl sulfone (DDS, 9.50 g) was added into the molten epoxy at 130°C and stirred continuously until a homogeneous, transparent solution was formed. The light yellow, transparent solution was then transferred to a Teflon mould (90 mm × 50 mm × 5 mm) preheated at 80°C. The mixture was cured for 2 h at 140°C, 2 h at 160°C, and finally 2 h at 180°C.



Scheme 1 Preparation of DGEBA/OAPS nanocomposites

Preparation of DGEBA/DDS/OAPS and DGEBA/DDS/OPS Composites

DGEBA was added to a round-bottomed flask at 60°C. Then, OAPS or OPS in an amount of 3 wt% of DGEBA + DDS was added into the DGEBA (OAPS was dissolved in the smallest possible amount of acetone and then degassed under vacuum; OPS was added directly). Then, the stoichiometric amount of 4,4'-diaminodiphenyl sulfone (DDS) was added into the molten epoxy at 130°C and stirred continuously until a homogeneous, transparent solution was formed. The transparent solution was then transferred to a Teflon mould (90 mm × 50 mm × 4 mm) preheated at 80°C. The mixture was cured for 2 h at 140°C, 2 h at 160°C, and finally 2 h at 180°C.

Characterization

Fourier transform infrared spectroscopy (FTIR). FT-IR spectra were recorded on a Nicolet 6700 IR spectrometer. Potassium bromide (KBr) was used as the supporting medium. The spectra were collected in 32 scans with a spectral resolution of 4 cm⁻¹.

Differential scanning calorimetry (DSC). The calorimetry was performed on a Netzsch DSC 204 F1

instrument (Germany). Samples (7–10 mg) were weighed into small DSC aluminium pans, sealed with holed aluminium lids, and experiments were conducted under a nitrogen flow of 60 cm³/min. The DSC instrument was set for an appropriate temperature range. The heating rates of 2.5, 5, 10, and 12.5 K/min were chosen for the tests.

X-ray diffraction (XRD). The X-ray diffraction analysis was achieved using an XPERT-PRP diffractometer system; Cu K α radiation was used with a copper target over the 2θ range of 5°–60°.

Thermal gravimetric analysis (TGA). Thermal stability tests of materials under nitrogen or air were performed on a Netzsch 209 F1 thermal analyzer at a heating rate of 10 K/min, and in a temperature range from 40°C to 800°C. The initial thermal degradation temperature was taken as the temperature at which 5% mass loss occurred. The N₂ or air flow rate was 60 mL/min.

Contact angle measurements. The static contact angle measurements of the thermosets with deionized water were carried out with a JC2000C1 instrument (Shanghai Powereach Instruments Co., China) at room temperature.

Scanning electron microscopy (SEM). Scanning electron microscopy (BACPCS4800) was used to study the morphology of the samples at the gold coated cross-section area with accelerating voltage of 15.0 kV.

RESULTS AND DISCUSSION

Physical Properties: Appearance, Density and Surface Hydrophobicity

All the prepared DGEBA/DDS and DGEBA/OAPS exhibited good transparency. The appearances of DGEBA/DDS and DGEBA/OAPS are given in Fig. 1. Both of them are transparent, smooth and have few bubbles. DGEBA/OAPS is much yellower than DGEBA/DDS because OAPS is yellow. The density for DGEBA/OAPS (1.1523 g/cm³) measured by the density bottles is higher than that of DGEBA/DDS (1.1165 g/cm³).

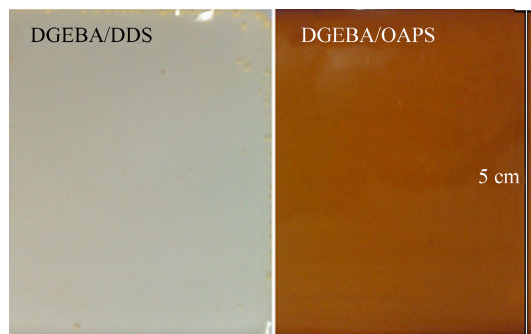


Fig. 1 Appearances of DGEBA/DDS and DGEBA/OAPS resins

It is known that organosilicon compounds are generally of low surface energy. In the present case, OAPS was covalently connected with DGEBA chains. The surface properties of two kinds of the epoxy resins were investigated in terms of the measurement of static contact angle. The contact angles were measured with water as probe liquid. The contact angle of DGEBA/DDS was estimated with water to be 54°. Replacing DDS by OAPS in the resin, the contact angle increased up to 64° (Fig. 2). This observation indicated that the epoxy resin has walked one step to hydrophobicity.

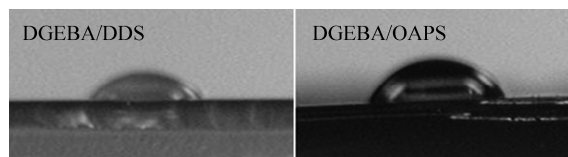


Fig. 2 Contact angles of DGEBA/DDS and DGEBA/OAPS with water

FTIR Spectral Analysis

Figure 3 shows the FTIR spectra of DGEBA/DDS and DGEBA/OAPS, from which it is clearly seen that absorbance of the epoxy group (913 cm^{-1}) is absent in both DGEBA/DDS and DGEBA/OAPS, indicating that complete curing was achieved in both systems. The appearance of Si—O—Si bands at 1103 cm^{-1} in DGEBA/OAPS nanocomposite is absent in DGEBA/DDS. The overlay of the O—H stretching region generated from the curing reaction of epoxy resin system is observed at $3250\text{--}3500\text{ cm}^{-1}$. The sharp —NH_2 stretching peaks in DDS or OAPS are absent in DGEBA/DDS or DGEBA/OAPS, clearly indicating that the amine is involved in the ring opening polymerization.

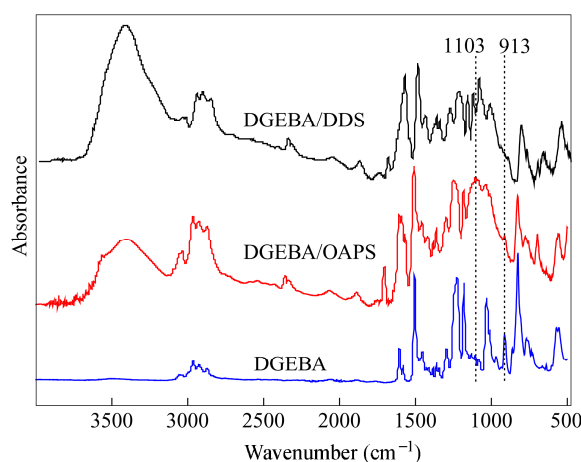


Fig. 3 FTIR spectra of DGEBA/DDS and DGEBA/OAPS

Investigation of Curing Kinetics

Figure 4 shows the comparison of DSC curves of DGEBA/DDS and DGEBA/OAPS prepolymers at the heating rate of 10 K/min . We could notice that the temperature range of the exothermic process of DGEBA/OAPS prepolymer is nearly 100 K lower than that of DGEBA/DDS prepolymer. It seems that DDS as aromatic amine curing agents is a high temperature curing agent for epoxy resin^[34], but OAPS is a low temperature curing agent. At the same time, the curing reaction heat of DGEBA/DDS prepolymer is 1.5 times as that of the DGEBA/OAPS prepolymer (Table 1). The results indicated that the reaction between OAPS and DGEBA was much easier than the reaction between DDS and DGEBA. One reason may be that the electron-withdrawing effect of the cage of OAPS enhanced the reactivity of the —NH_2 in OAPS.

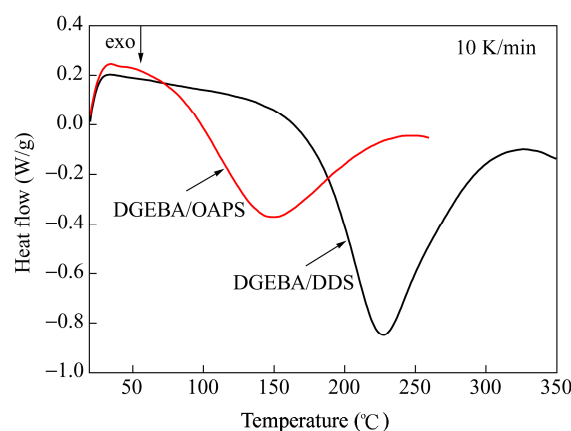


Fig. 4 DSC of DGEBA/DDS and DGEBA/OAPS prepolymers

Table 1 DSC analysis results at different heating rates

		Heating rate ϕ (K/min)			
		5	7.5	10	12.5
DGEBA/DDS prepolymer	ΔH (J/g)	398.9	377	364	342.8
	T_p ($^{\circ}\text{C}$)	207.3	219.2	227.3	233.7
	α_p	45.070	45.046	45.644	45.766
DGEBA/OAPS prepolymer	ΔH (J/g)	263.8	255.6	240.3	232.1
	T_p ($^{\circ}\text{C}$)	133.7	143.2	149.5	154.6
	α_p	49.47	50.53	50.63	49.23

The curing kinetics of DGEBA/DDS and DGEBA/OAPS prepolymers were investigated by dynamic DSC measurements for DGEBA/DDS or DGEBA/OAPS prepolymers performed in the range of 20–350 $^{\circ}\text{C}$ or 20–260 $^{\circ}\text{C}$ at the four heating rates of 5, 7.5, 10, and 12.5 K/min. Figure 5 shows the curves of heat flow versus the temperature at different heating rates for DGEBA/DDS and DGEBA/OAPS prepolymers. Exothermal peaks corresponding to the curing reactions at different heating rates could apparently be observed. The exothermal heat ΔH , curing peak temperature T_p and conversion α_p at T_p are listed in Table 1. As shown in Fig. 5, the heat flow curve shifts to higher temperatures with increasing the heating rate for the two systems. The T_p temperatures of DGEBA/OAPS prepolymer are at 133–155 $^{\circ}\text{C}$, lower than those of DGEBA/DDS prepolymer. The average curing reaction heat is 248.0 J/g for DGEBA/OAPS prepolymer, but 370.7 J/g for DGEBA/DDS prepolymer.

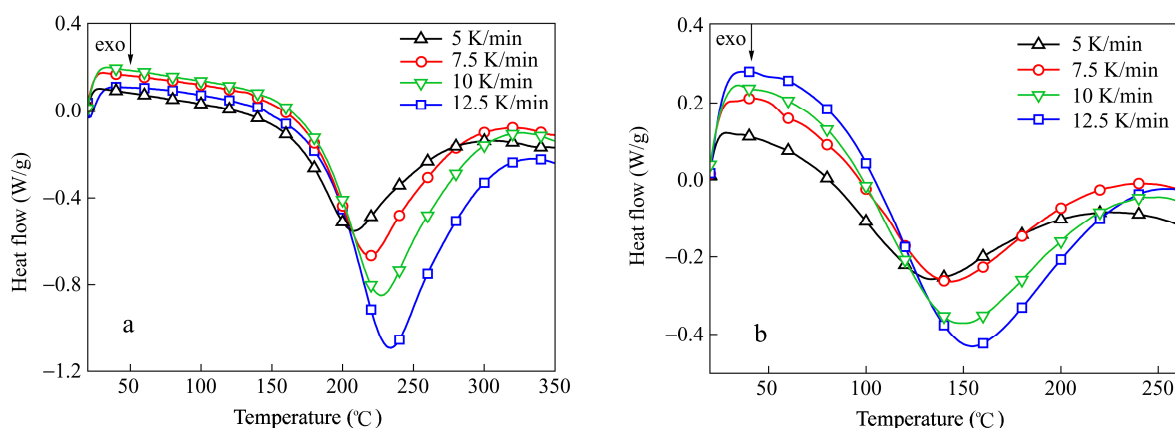


Fig. 5 Heat flow versus the temperature at different heating rates
(a) DGEBA/DDS prepolymer; (b) DGEBA/OAPS prepolymer

The multiple heating rate methods for non-isothermal analysis proposed by Kissinger and Flynn-Wall-Ozawa can be used to calculate the kinetic parameters of thermal curing reactions^[35–38], and they are shown in Table 2. The logarithmic plots of heating rate ϕ versus $1/T_p$ are given in Fig. 6. As shown, there is a good linear relationship between the logarithm of the heating rate and $1/T_p$. The values for E_a calculated according to the Kissinger or Flynn-Wall-Ozawa methods are 66.93 and 62.23 kJ/mol for DGEBA/DDS prepolymer, 60.32 and 56.55 kJ/mol for DGEBA/OAPS prepolymer, respectively. These computational results are agreed with the observation of the curing behaviors of DGEBA/OAPS prepolymer at low temperatures.

According to the Arrhenius equation: $k = A \cdot e^{-E_a/RT}$, where k was the chemical reaction rate constant and A was the frequency factor. According to Fig. 6, frequency factors A are 9.395×10^5 and $37.15 \times 10^5 \text{ min}^{-1}$ for DGEBA/DDS and DGEBA/OAPS prepolymers by the method of Kissinger^[21]. The calculated k of the DGEBA/OAPS prepolymer is higher than that of the DGEBA/DDS prepolymer at the same reaction temperature. For example, $k_{(\text{DGEBA/OAPS})}/k_{(\text{DGEBA/DDS})} = 3.963$ at the room temperature 25 $^{\circ}\text{C}$. And in our

experiment, the DGEBA/OAPS prepolymer lost fluidity after 2 days at the room temperature while the DGEBA/DDS prepolymer did after 8–10 days. At the same time, the curing reaction orders n for the two systems obtained by the Crane method are very close.

Table 2. Kinetic parameters of the thermal curing reaction.

		Methods		
		Flynn-Wall-Ozawa	Kissinger	Crane
DGEBA/DDS prepolymer	E_a (kJ/mol)	66.93	62.23	
	Correlation coefficient R^2	0.9997	0.9997	
	$A \times 10^{-5}$ (min $^{-1}$)		9.395	
	n			0.884
DGEBA/OAPS prepolymer	E_a (kJ/mol)	60.32	56.55	
	Correlation coefficient R^2	0.9996	0.9996	
	$A \times 10^{-5}$ (min $^{-1}$)		37.15	
	n			0.891

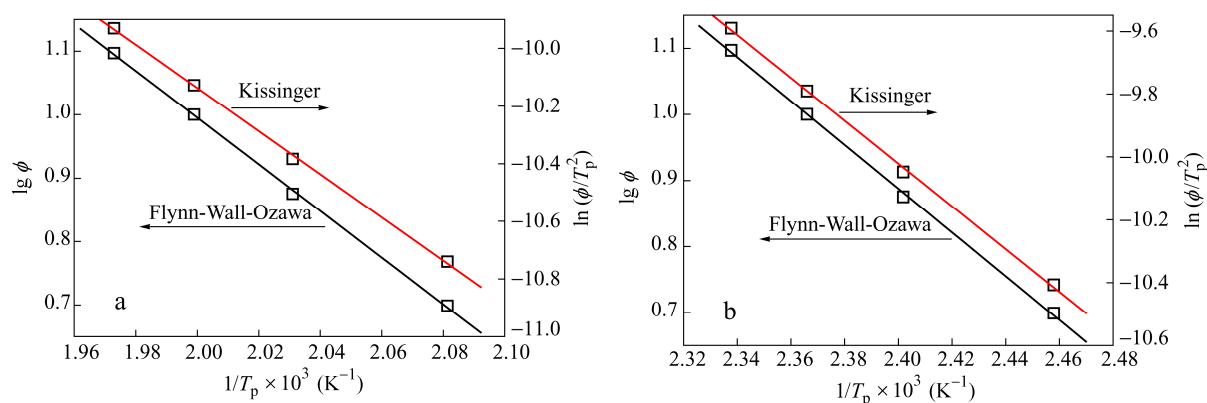


Fig. 6 $\lg \phi$ and $\ln(\phi/T_p^2)$ as a function of the inverse of absolute temperature for the thermal curing reaction (a) DGEBA/DDS prepolymer; (b) DGEBA/OAPS prepolymer

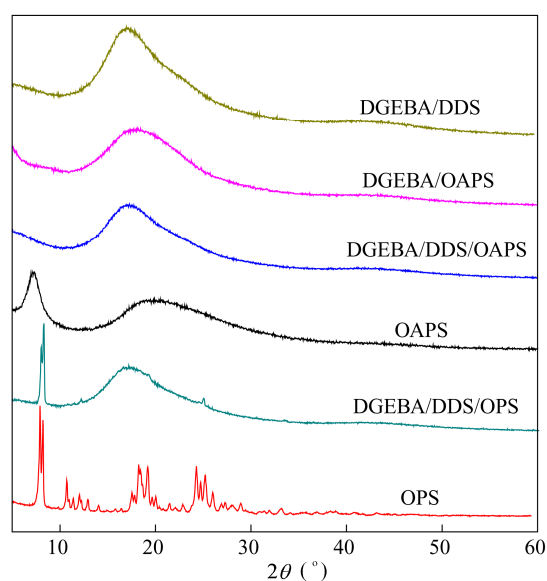


Fig. 7 X-ray diffraction patterns of OPS, OAPS and epoxy resins

X-ray Diffraction Analysis

Figure 7 displays the X-ray diffraction patterns for the pure OPS, OAPS and epoxy resins. The diffraction peaks of OPS and OAPS are at $2\theta = 7.92^\circ$ and $2\theta = 7.75^\circ$, respectively, corresponding to the local order of the POSS molecule structures. In the X-ray pattern of DGEBA/DDS/OPS, the sharp peak at 7.92° of OPS can be observed clearly with only 3% OPS loading, which illustrates that there is no covalent bond exists between the epoxy resin matrix and OPS^[39]. However, in the case of DGEBA/DDS/OAPS or DGEBA/OAPS, the sharp peak at 7.75° of OAPS disappears totally. This result indicates that the amino groups in OAPS have reacted with DGEBA. It can be speculated that the reaction between OAPS and DGEBA is helpful to the homogeneous distribution of OAPS in the epoxy resin matrix.

Glass Transition Behavior

DSC measurements are performed for both DGEBA/DDS and DGEBA/OAPS systems and the curves are presented in Fig. 8. DGEBA/DDS resin shows a glass transition at 186°C , but DGEBA/OAPS resin doesn't show evident glass transition. Glass transition temperature (T_g) can provide a direct insight into the mobility of polymer chains. These results indicated that the large Si—O cage of OAPS limits the mobility of the epoxy chains in the cross-linking network.

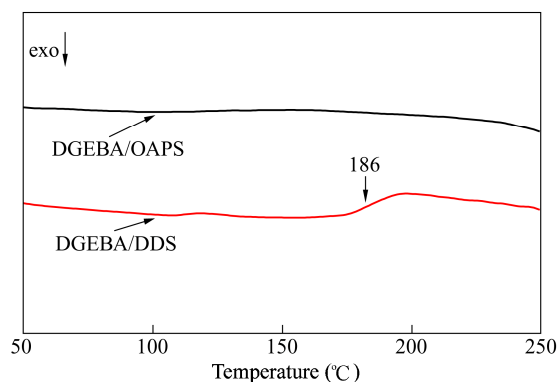


Fig. 8 DSC curves of DGEBA/DDS and DGEBA/OAPS

Thermal Stability

The TGA and DTG curves of DGEBA/DDS, DGEBA/OAPS and OAPS in nitrogen and air atmospheres are presented in Figs. 9 and 10. Table 3 and Table 4 list the TGA results, including T_{d5} , defined as the temperature at 5% weight loss, the T_{max} defined as the temperature at maximum weight loss rate, and the char residues at 800°C .

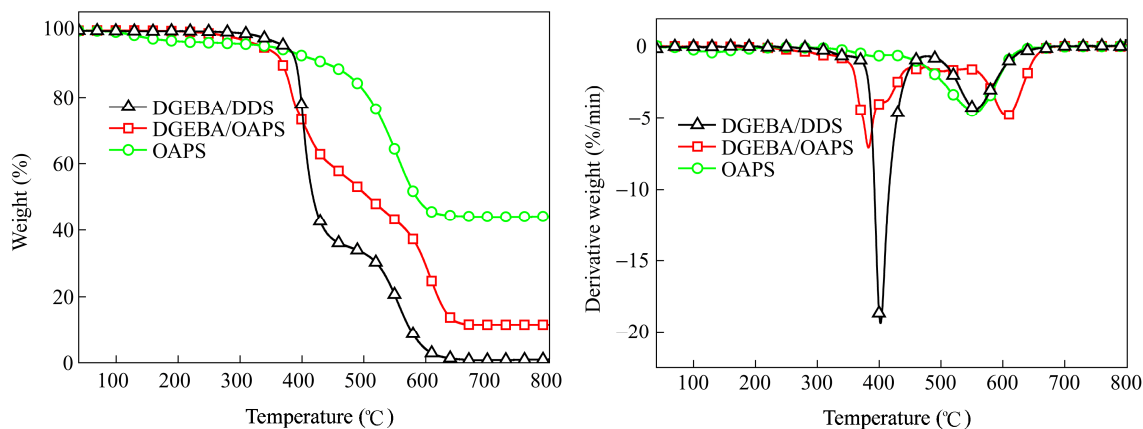


Fig. 9 TGA and DTG curves of DGEBA/DDS, DGEBA/OAPS and OAPS in air

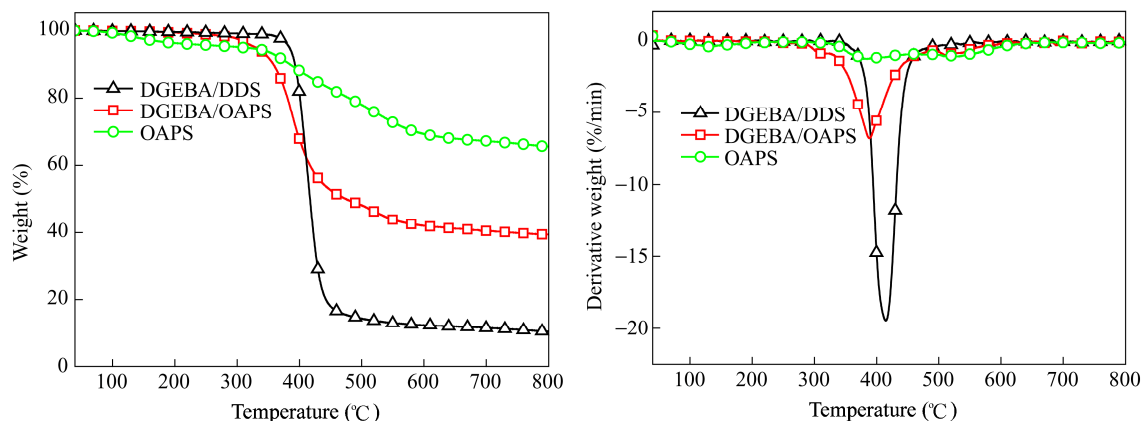


Fig. 10 TGA and DTG curves of DGEBA/DDS, DGEBA/OAPS and OAPS in N_2

Table 3. TGA data of DGEBA/DDS, DGEBA/OAPS and OAPS in air

Samples	T_{d5} (°C)	$T_{max\ 1}$ (°C)	$T_{max\ 2}$ (°C)	$T_{max\ 3}$ (°C)	Residues (%)
DGEBA/DDS	376.1	402.3	555.6	—	0.99
DGEBA/OAPS	340.0	382.8	489.0	606.5	11.63
OAPS	356.5	553.8	—	—	44.22

Table 4. TGA data of DGEBA/DDS, DGEBA/OAPS and OAPS in N_2

Samples	T_{d5} (°C)	T_{max} (°C)	Residues (%)
DGEBA/DDS	384.3	415.0	10.37
DGEBA/OAPS	329.6	402.3	39.35
OAPS	310.3	465.0	65.55

The incorporation of OAPS into epoxy system increases thermal stability of the resins under high temperatures and results in an enhanced char yield with change of decomposition process. But the initial decomposition of DGEBA/OAPS seems to be earlier than that of DGEBA/DDS, which may be attributed to the weak bonds caused by the imperfect curing. In the air, thermal oxidation of the epoxy resins reduces yield of the char at high temperatures.

Micrographs of Scanning Electron Microscopy

Morphologies of the DGEBA/DDS and DGEBA/OAPS are observed by SEM. In Fig. 11, it is seen that the curing epoxy resins show homogenous and smooth morphologies. No phase separation appears for DGEBA/OAPS.

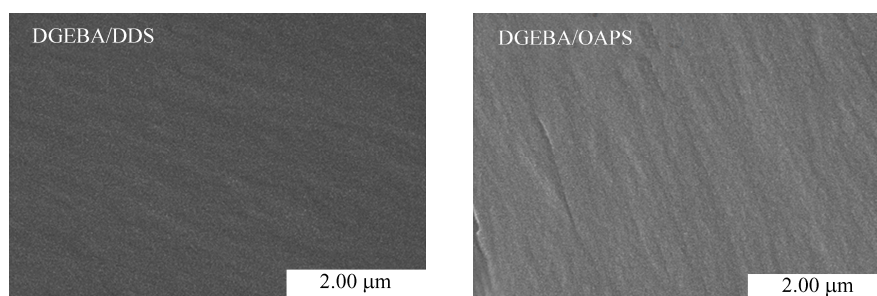


Fig. 11 SEM micrographs of DGEBA/DDS and DGEBA/OAPS

CONCLUSIONS

The study on comparison of DGEBA/OAPS with DGEBA/DDS epoxy resins indicated that OAPS had very good compatibility with DGEBA in molecular level, and could form a transparent DGEBA/OAPS resin. The DGEBA/OAPS resin showed a larger contact angle with water than the DGEBA/DDS resin. DSC measurements showed that the curing reaction heat of DGEBA/DDS was 1.5 times as that of DGEBA/OAPS, and the curing reaction of DGEBA/OAPS could occur under low temperatures compared with DGEBA/DDS. The calculated rate constant k of the DGEBA/OAPS prepolymer was higher than that of the DGEBA/DDS prepolymer at the same reaction temperature. In addition, the DGEBA/OAPS resin exhibited no glass transition, but the DGEBA/DDS did, which implied that the large OAPS cage limited the segmental motion between the cross-linking points. TGA results indicated that DGEBA/OAPS showed low mass loss rate and high char yield, but the initial decomposition temperature seemed to be lowered due to the imperfect curing. In air the thermal oxidation of the epoxy resins reduced the char yield at high temperatures.

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