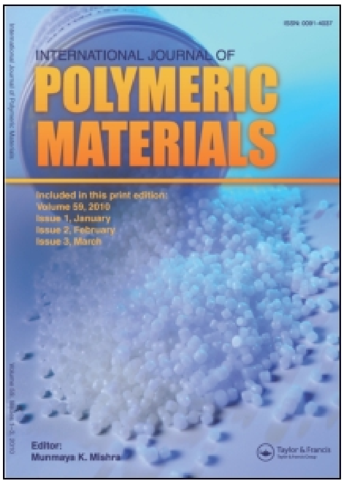

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Kinetics of Curing and Thermal Degradation of POSS Epoxy Resin/DDS System

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Polyhedral oligomeric silsesquioxanes epoxy resin (POSSER) was prepared from 3-glycidypropyl-trimethoxysilane (GTMS) and tetramethylammonium hydroxide (TMAH) by hydrolytic condensation. POSSER was characterized using Fourier-transformed infrared spectroscopy (FTIR), ^{1}H-NMR, and liquid chromagraphy/mass spectrometry (LC/MS). The epoxy value of POSSER is 0.50 mol/100 g. The LC/MS analysis indicated that T_{10} is the majority and contain some amount of T_8, besides, a trace T_9 also exists. The curing kinetics of POSSER with 4,4′-diaminodipheny sulfone (DDS) as a curing agent was investigated by means of differential scanning calorimetry (DSC). The curing reaction order n is 0.8841 and the activation energy Ea is 61.06 kJ/mol from dynamic DSC analysis. Thermal stability and kinetics of thermal degradation were also studied by thermal gravimetric analysis (TGA). TGA results indicated that the temperature of POSSE/DDS system 5% weight loss is approximately 377.0°C, which is higher by 12.6°C than that of pure POSSER, and the primary degradation reaction (300–465°C) followed first order kinetics; the activation energy of degradation reaction is 75.81 kJ/mol.

Keywords: cure kinetics, epoxy resin, silsesquioxanes, thermal degradation

INTRODUCTION

Organic–inorganic hybrid nanocomposite materials have attracted a great deal of attention because of their potential applications in optics, electronics, engineering, and bioscience. Organic–inorganic hybrid polymers with an in situ created inorganic phase are typical examples

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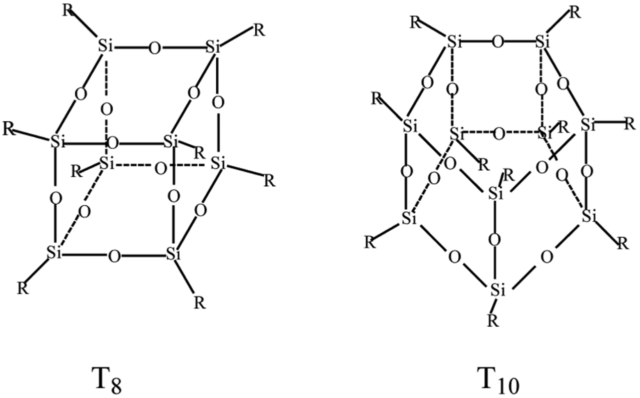


SCHEME 1 Cage structures of T_8 and T_{10}.

of nanocomposite materials, which have received significant interest in the past few years. The hydrolytic condensation of organotrialkoxysilanes, $RSi(OR')_3$, performed in the presence of water and an acid or base as catalysts, leads to products that are generically called polyhedral oligomeric silsesquioxanes (POSS). These compounds have acquired increasing importance for the synthesis of functionalized organic–inorganic hybrid materials. Species present in a POSS may vary form perfect polyhedra of formula $(RSiO_{1.5})_n$ ($n \geq 6$), denoted as T_n or as polyhedral oligomeric silsesquioxanes (POSS), to partially condensed (but completely hydrolyzed) products of generic formula $T_n(OH)_m$, where $T = RSiO_{1.5\text{-}m/2n}$ [1–7]. Scheme 1 shows the cage structure of T_8 and T_{10}. Silsesquioxane nanocomposites combine the excellent properties of organic polymer materials with inorganic materials.

Epoxy resin, which is thermosetting resin, is being used extensively at present, and the dopes prepared from epoxy resin as matrix are provided with excellent adhesive strength, rigidity, and chemical alkalinity-resistance, and so on. But heat-resistance and toughness of cured products need to be improved, which restrict the use of epoxy resin in some high-tech fields, such as aviation.

By now, the POSS epoxy resin (POSSER) of substituent on silicon atom of the polyhedral oligomeric silsesquioxanes by an epoxy group have been synthesized [1,7–10], and the curing kinetics of POSSER/BPAER (bisphenol-A epoxy resin) with 4,4′-diaminodiphenylmethane (DDM) also have been studied [9]. However, the studies on kinetics of curing and thermal degradation of POSSER with 4,4′-diaminodipheny sulfone (DDS) as a curing agent have been lacking until now. In this work, the POSSER was synthesized from 3-glycidyloxypropyltrimethoxysilane by hydrolytic condensation catalyzed by tetramethylammonium hydroxide, and the product was characterized by liquid chromatography/mass spectrometry (LC/MS). The kinetics of curing and thermal degradation of POSSER/DDS system was investigated with DSC and TGA.

EXPERIMENTAL

Materials

3-glycidyloxypropyl-trimethoxysilane (GTMS), isopropyl alcohol (IPA), toluene, tetramethylammonium hydroxide (TMAH), and acetone were all analytically pure grade and were supplied by Beijing Reagent Co. of China. HPLC grade methanol was obtained from Tedia Co. of USA.

Synthesis of POSSER

The POSSER was synthesized by hydrolytic reaction of GTMS catalyzed with TMAH. 60.38 g GTMS, 15.6 g 5 % TMAH aqueous solution and 200 mL IPA were put into a four-necked flask, equipped with a stirrer, a thermometer, and condenser. After the reaction mixture was stirred for 6 h at 25°C, the water and IPA were removed in vacuum. Then the hydrolytic product was dissolved by adding 200 mL toluene and heated to 90°C, and maintained at this temperature for 4 h, during which the Si−O−Si bonds were formed through the reaction of intramolecular cyclizations of Si−OH groups. After that, the toluene was removed in vacuum and the POSSER of pellucid and viscous liquid was obtained.

The yield of this reaction was above 90 %, and the epoxy value was determined according to Jay [11] to be 0.50 mol/100 g.

Characterization

A FTIR spectrometer (FTS-40, Bro-Rad Co., USA) was used to determine the structure of POSSER. The POSSER was dissolved in acetone and then coated as a thin film on a potassium bromide plate. When the solvent in the film was completely evaporated in vacuum, the plate was scanned by the FTIR instrument.

^{1}H-NMR spectra were recorded with a NMR spectrometer (bruker 400 K, Switzerland), using $CDCl_3$ as the solvent and TMS as a reference.

The LC/MS analysis was performed using an Agilent 1100 (Agilent Co. USA). The mobile phase was 90 % methanol containing 0.5 % formic acid and water containing 10 % formic acid. The flow rate was 0.15 mL/min and the injection volume was 1 μL. The column temperature was kept at 30°C.

The mass spectrum was recorded with an ion trap mass spectrometer LCQ-DecaXP (Thermo Quest Co. USA) equipped with a UV spectrophotometer. The range of wavelength detected was from 198 nm to 800 nm. The spectra were collected in the positive ion mode (MS^+), and a mass range of 395.00–2000.00 u(m/z) scanned with a 0.20–0.50 u(m/z) step-size and a dwell time of 2.0 ms. The mass spectrometer parameters were optimized using "Xcalibur" in the Analyst 1.2 Software.

Curing studies were carried out with differential scanning calorimeter (DSC) (Diamond, Perkin-Elmer Co. USA). It was calibrated with high-purity indium and operated under a 20 mL/min nitrogen flow. The sample (about 10 mg) was placed in a sealed aluminum sample pan. Dynamic scans were conducted from 50°C to 300°C at a heating rate of 5, 10, 15 and 20°C/min, respectively.

The thermal stability and degradation kinetics of POSSE/DDS system were determined by using a thermogravimetric analyzer (TGA) (Pyris-6, Perkin-Elmer Co., USA) operating under a 20 mL/min nitrogen flow. About 10 mg of completely cured sample were put into a ceramic cell and placed on detector places, and then heated to 900°C at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

FTIR Spectra of the POSSER

Figure 1 shows the FTIR spectra of the POSSER. As seen in Figure 1, the strong absorption band at 1103 cm^{-1} is Si–O–Si linkage. The absorption bands at 2870 and 2933 cm^{-1} result from the stretching vibration of CH_2 groups. The Si–CH_2 absorption band is at 1255 cm^{-1}, and the characteristic absorption peaks of epoxy group are at 907 cm^{-1} and 851 cm^{-1}, respectively. FTIR results are in agreement with the assignments of literature [2,9]. In addition, it can be seen that the IR spectrum of –OH has a broad and weak absorption peak at 3498 cm^{-1}, suggesting that a trace amount of silanol groups also exists, which is probably due to incomplete dehydration in POSSER (due to incomplete condensation of silanol groups).

^{1}H-NMR Spectra

^{1}H-NMR analyses provide useful information for the characterization of POSSER, in particular the structure of alkyl group attached to silicon atoms. Figure 2 shows the ^{1}H-NMR spectrum of POSSER in $CDCl_3$.

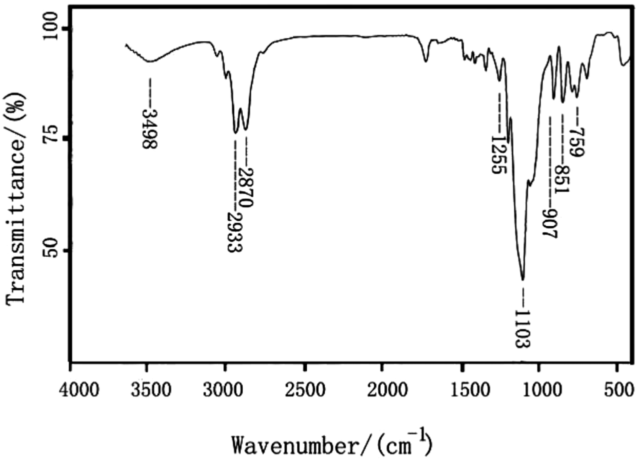


FIGURE 1 The FTIR spectra of POSSER.

According to Figure 2, one can find two narrow and strong peaks at δ (ppm) 0.018 and 7.286, which are attributed to the TMS and $CDCl_3$, respectively. There are 8 peaks between δ (ppm) 0.018 and 7.286, and the integral areas of peaks are 0.925, 1.982, 1.000, 0.989, 0.998, 0.901, 1.947, and 1.927, respectively. According to them, the ratio of different integral areas is 1:2:1:1:1:1:2:2. The peaks corresponding to alkyl chains are present at δ (ppm) 0.644 (2H, 1-H), 1.680 (2H, 2-H), 3.753

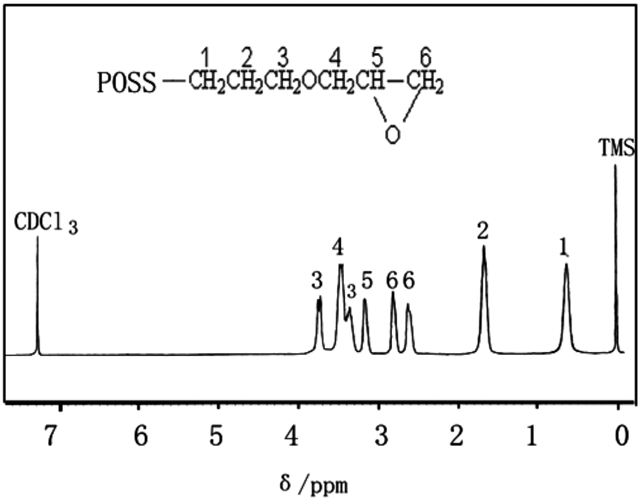


FIGURE 2 ^{1}H-NMR spectrum of POSSER.

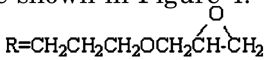
and 3.460 (2H, 3-H), 3.483 (2H, 4-H), 3.172 (H, 5-H of epoxy), 2.629 and 2.813 (2H, 6-H of epoxy). The ^{1}H-NMR spectrum of POSSER exhibits no peak at over 5.00 ppm, independent of the nature of the solvent. Furthermore, no extra protons are detected other than the expected quantities, suggesting that significant amounts of Si–OH groups are not present in the products or only a trace amount of silanol groups exist.

LC/MS Analysis

Recently, LC/MS analysis has become a very powerful tool for the investigation of siloxanes [12] and silsesquioxane [13–14]. In this study, LC/MS was used for the determination of the components of POSSER and the detailed structure.

After drying in vacuum for 4 h, the POSSER was dissolved in methanol and then diluted to 0.10 mg/mL. Figure 3 shows the liquid chromatography (LC) spectrum of POSSER.

As indicated in Figure 3, several species were separated due to different molecular weights, and UV detector cannot determine these species at the wavelength of 198 nm. But these species can be recorded clearly by mass spectrum. The mass spectra are shown in Figure 4.

According to the formula $(RSiO_{1.5})_n$, where  $R{=}CH_2CH_2CH_2OCH_2\overset{O}{CH\text{-}CH_2}$, the theoretic molecular weight can be calculated: T_8 is 1337.8 g/mol, T_9 is 1505.1 g/mol, and T_{10} is 1672.7 g/mol. Table 1 shows the mass data of POSSER determined in the experiment of LC/MS analysis.

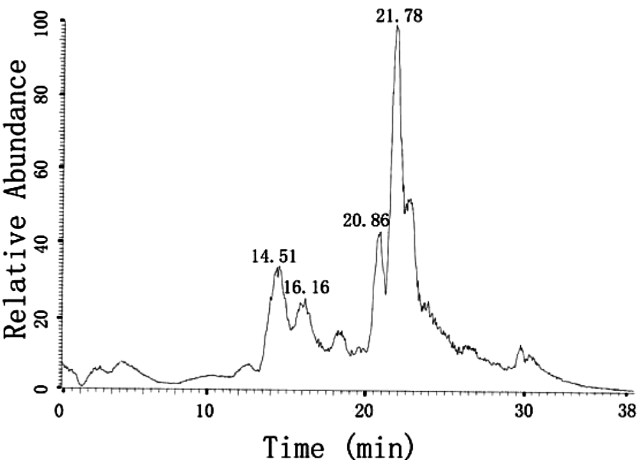


FIGURE 3 Liquid chromatography (LC) spectrum of POSSER.

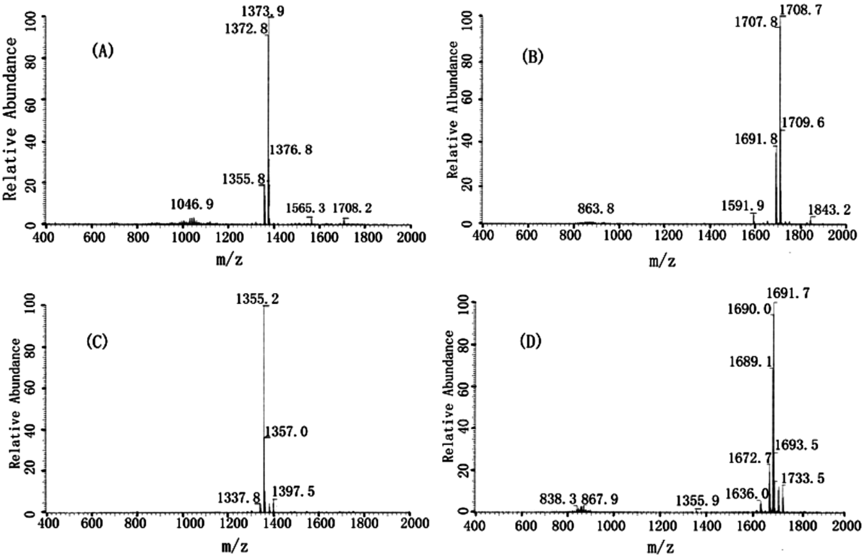


FIGURE 4 MS of the liquid chromatography at different times.

As indicated in Figures 3 and 4 and Table 1, the POSSER is a mixture of T_{10}, T_8, and T_9. The T_{10} is the main products of the POSSER synthesized from GTMS by this method, and contain some amount of T_8. The T_9 exists in a trace amount. It is coincident with literature [15], but it does not affect the reaction with DDS.

Curing Kinetics of POSSER/DDS

According to the epoxy value of POSSER, the POSSER and DDS were mixed homogeneously in stoichiometric amount. The dynamic DSC

TABLE 1 The Mass Data of POSSER

m/z(exp.)	Species
1337.8	T_8
1355.2	$T_8 + 1H_2O$
1373.9	$T_8 + 2H_2O$
1505.1	T_9
1523.4	$T_9 + 1H_2O$
1544.5	$T_9 + 2H_2O$
1672.7	T_{10}
1691.7	$T_{10} + 1H_2O$
1709.6	$T_{10} + 2H_2O$

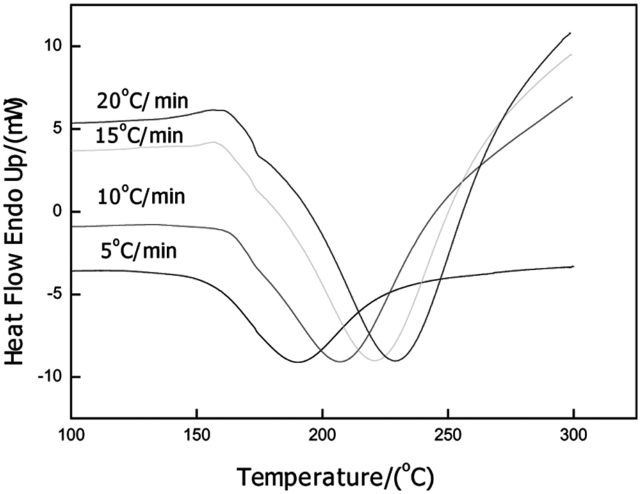


FIGURE 5 DSC curves of POSSER/DDS curing at different heating rates.

curves of curing reaction and conversion of POSSER/DDS at different heating rates are shown in Figures 5 and 6, respectively. As seen from Figure 5, it is found that the initial curing reaction temperature of POSSER/DDS system is approximately 160°C, which is higher than

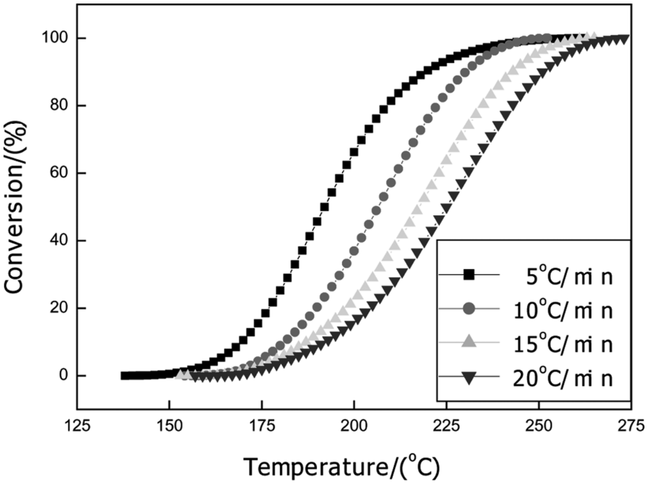


FIGURE 6 Conversions curves of POSSER/DDS at different heating rates.

TABLE 2 Thermal Data of Cured-System at Different Heating Rates

Heating rate β/°C·min^{-1}	T_i/°C	T_p/°C	T_f/°C	t/min	$-\Delta H$/J·g^{-1}
5	162.4	190.3	250.4	17.60	235.28
10	163.2	207.8	256.4	9.32	226.06
15	165.1	220.7	265.2	6.67	219.84
20	167.8	228.7	273.5	5.28	205.47

that of common epoxy resin. Table 2 shows the thermal data of cured product at different heating rates.

As shown in Table 2, the initial temperature T_i, peak temperature T_p and end temperature T_f for this exothermic curing reaction increase and the reaction heat ΔH decreases with increasing heating rates, respectively. This is due to the reaction time decrease with increasing heating rates. According to Table 2, the values of ΔH at 5°C/min and 20°C/min are 235.28 J/g and 205.47 J/g, respectively.

Based on the fact that the exothermic peak temperature varies with the heating rates, the apparent activation energy E_a of curing reaction can be obtained by the Kissinger method [16]. Kissinger's technique assumes that the maximum reaction rate occurs at peak temperatures.

$$\frac{d[\ln(\beta/T_p^2)]}{d(\ln 1/T_p)} = -\frac{E_a}{R} \tag{1}$$

where T_p is the peak temperature, β is the linear heating rate, R is the universal gas constant.

According to Eq. 1, a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$, the apparent activation energy E_a can be obtained from the slope of the line, and it is 61.06 kJ/mol. The correlation coefficient and standard deviation for E_a is 0.9992 and 0.0263, respectively.

The reaction order of this curing process can be calculated from Eq. 2 according to the Crane method [17].

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\left(\frac{E_a}{nR} + 2T_p\right) \tag{2}$$

where n is the order of curing reaction. When the $E_a/nR \gg 2T_p$, $2T_p$ can be ignored. According to Eq. 2, the reaction order n can be obtained at different heating rates from fitting the ln β versus $1/T_p$ plot. It is 0.8841. The correlation coefficient and standard deviation for n is 0.9994 and 0.0257, respectively.

Thermal Stability and Degradation Kinetics

Figure 7 is the TG curves of POSSER and POSSER/DDS. As seen from Figure 7, the thermal weight loss for POSSER was 5% at 364.3°C and the maximum degradation rate is at 444.7°C. The thermal stability of POSSER is excellent because of the existence of Si−O−Si bonds. According to Figure 7, the thermal weight loss for POSSER is 60% at 800°C, and the residual weight no longer changes until 900°C, which is in agreement with the literature [2].

According to the epoxy value determined, Stoichiometric amount of POSSER and DDS were dissolved in acetone and mixed adequately. After being dried in vacuum at the temperature of 60°C for 2 h, the mixture was cured for 2 h at 165°C.

According to Figure 7, the weight loss for the cured system is 5% at 377.0°C, which is higher than that of POSSER by 12.6°C, suggesting that the heat resistance of the cured system is better than that of pure POSSER. The temperature of maximum degradation rate for the cured system is about 435.0°C, which is lower than that of pure POSSER by 9.7°C, and the degradation continued until 900°C. The reason is probably due to the existence of residual and not completely reacted DDS monomers because of steric hinderance. According to the TG curves of POSSER/DDS, the degradation can be divided into two

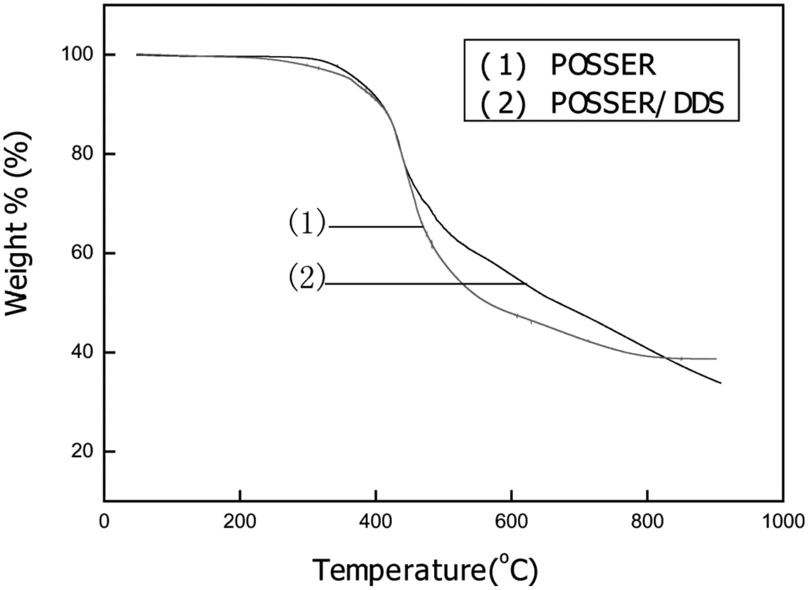
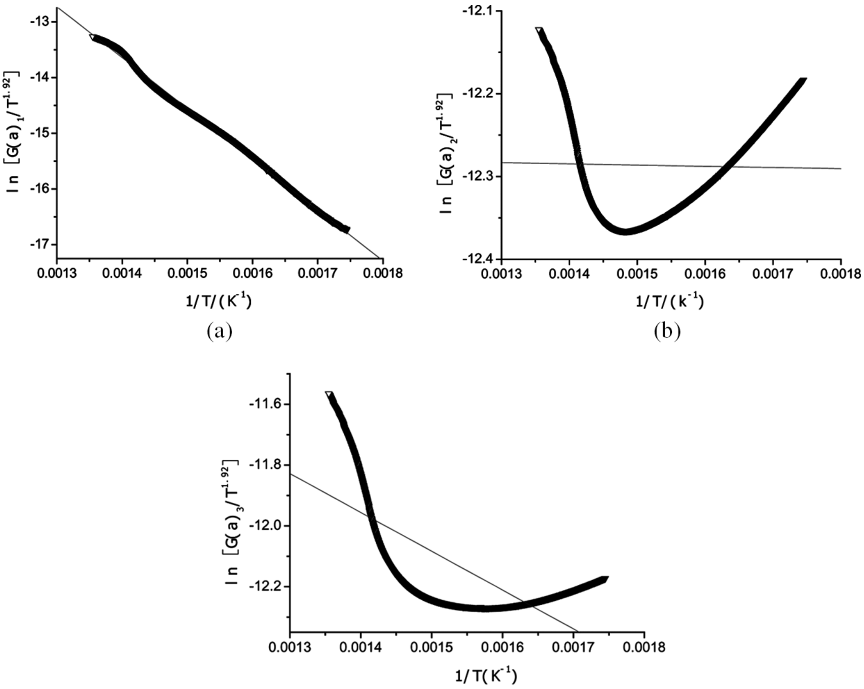


FIGURE 7 TG curves of POSSE and POSSER/DDS.

stages. In the first stage (about 300–465°C), which is the main stage, the total weight loss at the heating rates of 20°C/min is about 27.83%. In the second stage (about 465–900°C), the total weight loss is 39.59%. In the present study, the TGA data were analyzed on the basis of the Madusdanan-Krishnan-Ninan method [18–19] to the main stage, which can be expressed by Eq. 3:

$$\ln\frac{G(a)}{T^{1.92}} = \ln\frac{AE}{\Phi R} + 3.77 - 1.92\ln E - \frac{E}{RT} \tag{3}$$

where A is the pre-exponential factor in the Arrhenius equation, E is the apparent activation energy, R is the universal gas constant, Φ is the heating rate, T is absolute temperature, and $G(a)$ is the integrals form of the conversion dependence function. The correct form of $G(a)$ depends on the proper mechanism of degradation reaction [18]. Different expression of $G(a)$ for some solid-state reaction mechanism can be described as following: in first order ($n = 1$), $G(a)$ is $-\ln(1-a)$; in



(a) (b)

(c)

FIGURE 8 Plots of $\ln[G(a)/T^{1.92}]$ vs. $1/T$ for different mechanisms. (a) $n = 1$; (b) $n = 2$; (c) $n = 3$.

second order ($n = 2$), $G(a)$ is $1/(1 - a)$; in third order ($n = 3$), $G(a)$ is $1/(1 - a)^2$.

In dynamic TGA experiments, the weight change of the sample is regarded as a function of temperature and the conversion α can be expressed as:

$$\alpha = \frac{W_0 - W_T}{W_0 - W_\propto} \tag{4}$$

where W_0 is the initial weight, W_T is the residual weight at temperature T, and $W_\propto$ is the final weight. Therefore, with the TGA curves and using Eq. 4, the conversions are calculated for the main degradation stage. Figure 8 shows the plots of $\ln(G(\alpha)/T^{1.92})$ versus $(1/T)$ with different mechanism functions.

As can be seen in Figure 8(a), (b), (c), the linear correlation coefficient obtained by using first order mechanism is 0.9988, and the standard deviation is 0.0499, which were much bigger and smaller than that of using second and third mechanism, respectively. In conclusion, the main thermal degradation reaction of POSSER/DDS system follows a first order kinetics. According to the values of the line slope and intercept, the apparent activation energy E and pre-exponential factor ln A can be calculated as 75.81 kJ/mol and 12.56, respectively.

CONCLUSIONS

POSSER can be synthesized by a hydrolytic condensation from 3-glycidypropyl-trimethoxysilane as catalyzed by TMAH, and T_{10} is the majority of the POSSER with some amount of T_8. Besides, a trace T_9 also exists when POSSER is prepared by this method. The epoxy value of POSSER is 0.50 mol/100 g.

The curing reaction order of POSSER/DDS is 0.8841, and the apparent activation energy is 61.06 kJ/mol.

The thermal weight loss for POSSER/DDS is 5% at 377.0°C, which was higher than that of pure POSSER by 12.6°C, and the maximum degradation rate is at 435.0°C. The stage from 300°C to 465°C is the main degradation, and the thermal degradation of this stage follows a first order kinetics with an apparent activation energy of 75.81 kJ/mol.

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