Synthesis, Characterization, Thermal and Flame-Retardant Properties of Silicon-Based Epoxy Resins

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Received 4 May 1998; accepted 5 October 1998

ABSTRACT: A new silicon-containing oxirane triglycidyl phenyl silane oxide (TGPSO) and its corresponding silicon-containing epoxy resins are synthesized and characterized. The activation energies of TGPSO curing reaction with various curing agents, including 4,4-diaminodiphenylmethane, 4,4-diaminodiphenylsulfone, and dicyanodiaminde, are found to be 180, 196.5, and 154 kJ/mol. The curing reaction of TGPSO with diamines is determined to be a first-order reaction through means of Arrhenius plots. The introduction of the silicon-containing group results in higher curing reactivity. This silicon-containing resin possesses higher char yield as well as higher limiting oxygen index (LOI = 35) than the commercial epoxy resins, confirming the usefulness of these silicon-containing epoxy resins as flame retardants. Char yields and LOI measurements demonstrate that incorporating silicon into epoxy resins is able to improve their flame retardancy. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1231–1238, 1999

Keywords: silicon; epoxy; char yield; limiting oxygen index

INTRODUCTION

Epoxy resins are widely used in casting, coating, adhesion, and composite applications. In some applications, epoxy resins require versatile and special functions, such as high adhesion to the substrates, low shrinkage, and low thermal stress after cure, good toughness, low flammability, and good chemical resistance. To meet some application requirement, several approaches have been utilized to enhance the thermal properties of epoxy.[1,2] Apart from that, the flammability of epoxy resins is a major disadvantage in their application. Recently, some organosilicon compounds have been found highly effective as epoxy flame retardant. Organofunctional alkoxysilanes or polysiloxane are frequently used as epoxy modifiers,[3–5] polymer composites,[6] and in polymeric organic–inorganic hybrids.[7] Organosilicon compounds exhibit higher flame retardancy, without generating toxic gas and smoke, than the halogen-containing compounds. Silicon-containing compounds have been known to possess many excellent properties, such as high resistance to thermal oxidation, imparting nonflammability, low glass transition temperature, and low surface energy to the resin.[8] The conventional practice of introducing siloxane compounds into polymers has been achieved by blending those polymers with polydimethylsiloxanes.[9] Most epoxy resins, such as the diglycidyl ether of bisphenol A (DGEBA), are carbon based, whereas the silicon-containing epoxies are inorganic based; therefore they are usually immiscible and phase separation limits incorporation of a large amount of silicon compound. Such limitation leads to a more serious problem of bleeding of silicon components. Therefore, in order to reduce the above limitation,

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Journal of Applied Polymer Science, Vol. 73, 1231–1238 (1999)
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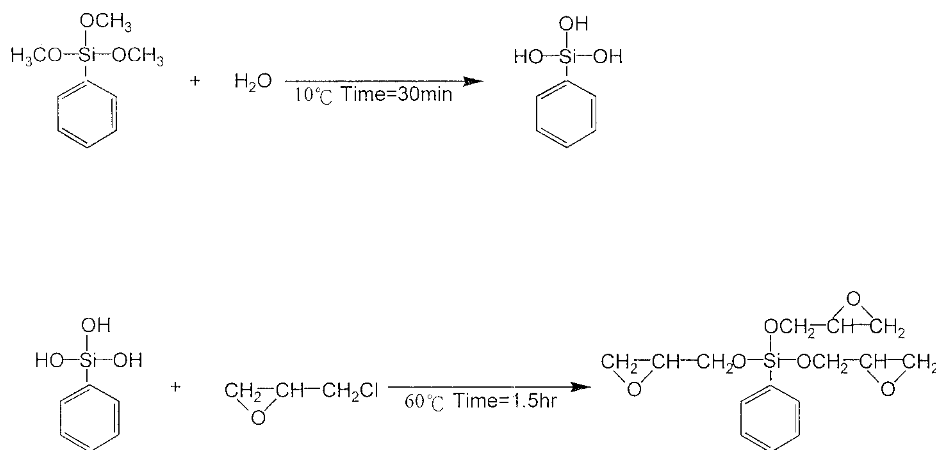

Figure 1 Synthesis scheme of phosphorus-containing compounds: TGPSO.

silicones with reactive groups are utilized to prepare polymers that possess siloxane bond in the backbones or on side chains. Several approaches for reaching the above goal have been reported.[10–14] Making these compounds for flame-retardant epoxy resin involves complicated schemes in organic synthesis, and they have lower curing reactivity with commercial curing agents and are immiscible with the organic system. These characteristics limit the application of these compounds as flame retardants.

In this study, phenyltrimethoxyl silane was used to react with epichlorohydrin in order to prepare the trifunctional epoxy monomer containing silane linkages. Therefore, these silicon-containing oxiranes, made by simple synthesis processes with high silicon contents, are of great interest as flame retardants for epoxy resins. A new silicon-containing oxirane, phenyltri(3-glycidyloxy) silane oxide (TGPSO, Fig.1), was previously synthesized and characterized. The curing reactivity and kinetics of this silicon-containing monomer are investigated. This silicon containing oxirane with high silicon content of 9% by weight exhibits high efficiency in enhancing the flame retardance of the epoxy resin.

EXPERIMENTAL

Reagents

Phenyltrimethoxyl silane and *p*-toluene sulfonic acid monohydrate were purchased from Tokyo Chemical Industry Co. Epichlorohydrin, sodium hydroxide, and toulene were from Merck and used as received. The 4,4-diaminodiphenylmethane (DDM), 4,4-diaminodiphenylsulfone (DDS), and dicyanodiaminde (DICY) were acquired from Aldrich and used as received. The DER 331, a low molecular weight liquid diglycidyl ether of DGEBA with an epoxide equivalent weight of 186–192, Eponex 1015, and DER 732, were purchased from Dow Chemical Co.

Synthesis of TGPSO

Twenty grams (0.1 mol) phenyltrimethoxyl silane with 5.4 g (0.3 mol) water, and 0.1 g *p*-toluene sulfonic acid monohydrate were added to a 1000 mL three-necked flask equipped with a stirrer, thermometer, condenser, and dropping funnel. The reaction time was 30 min and the temperature was controlled at 20°C; epichlorohydrin and 0.1 g benzyl trimethylammonium chloride were subsequently added. The mixture was heated to 60°C with stirring. The amount of 0.3 mole NaOH was added and the system was maintained at 60°C for 1.5 h. After completion of the reaction, the excess of epichlorohydrin was distilled off at 60°C under vacuum. The residue was cooled to room temperature and then dissolved in 100 mL dichloromethane. The undissolved salt was removed by vacuum filtration. After distilling off the dichloromethane, a viscous liquid silicon-containing epoxy resin TGPSO was obtained.

Preparation of Polymers

Silicon-containing epoxy resins were obtained via thermal curing of the TGPSO with various curing agents. The reactant compositions were mixed homogeneously with stoichiometric equivalents of the epoxy and curing agents, such as the di-

Table I The Curing Cycle of Epoxy Resin

Epoxy Resin Compositions	Curing Temp. (°C)	Curing Time (min)	Postcure Temp. (°C)	Postcure Time (min)
Epon 828/DDM	115	90	170	180
TGPSO/DDM	80	90	140	120

amines, DDS, DICY, and DDM. The curing cycles are listed in Table I.

Kinetic Studies

The kinetic studies of the TGPSO curing reaction were performed by a differential scanning calorimetry (DSC) technique with two analytical methods presented as Dynamic Method I and Dynamic Method II.

Dynamic Method I[15,16]

In this method only one reaction curve is analyzed. As the temperature of the system is increased continuously, a series of rate constants at different temperatures can be obtained by

$$k = (dH/dT)/\Delta H \quad (1)$$

where $\Delta H = \Delta H_o - \Delta H_T$. ΔH_T is the enthalpy at temperature T and ΔH_o is the total reaction enthalpy of cure reaction. The activation energy can be determined from these rate constants at various temperatures. This formula is based on the assumption that the curing reaction is first order.

Dynamic Method II

A simple but accurate relationship among activation energy (E_a), heating rate (ϕ), and temperature of exothermic peak (T_p) as

$$E_a \approx \frac{-R}{1.052} \frac{\Delta \ln \phi}{\Delta(1/T_p)} \quad (2)$$

This method provides an easy calculation for the activation energy.

Characterizations

IR spectra were obtained by using a Bio-Red FTS-155 infrared spectrophotometer. ^{1}H-NMR spectra were recorded with a Bruker MSL-300 (300Mhz) NMR spectrometer using $CDCl_3$ as a solvent. Differential scanning calorimeter (DSC) thermograms were recorded by using a Seiko SSC-5200 DSC at a heating rate of 10°C/min under nitrogen atmosphere. In the epoxy curing kinetic analysis, experiments were carried out at heating rates of 5, 10, and 20°C/min, respectively. Thermogravimetric analysis (TGA) was performed by a Seiko TG/DT 6200 Thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen or air atmosphere. Limiting oxygen index (LOI) values were measured on a Stanton Redcroft flame meter by a modified method as reported in the literature.[19]

RESULTS AND DISCUSSION

Synthesis of TGPSO

The synthesis scheme of the silicon-containing epoxy (TGPSO) was obtained by reacting phenyltrihydroxyl silanol with epichlorohydrin (Fig. 1). The product was purified by column chromatography with a yield of 40 and then was characterized by Fourier transform IR and ^{1}H-NMR. The IR spectrum of TGPSO is shown in Figure 2. The peak at 922 cm^{-1} indicates the formation of epoxide ring. The peak at 1085 cm^{-1} is from the SiO stretching vibration, 2950 cm^{-1} arises from the

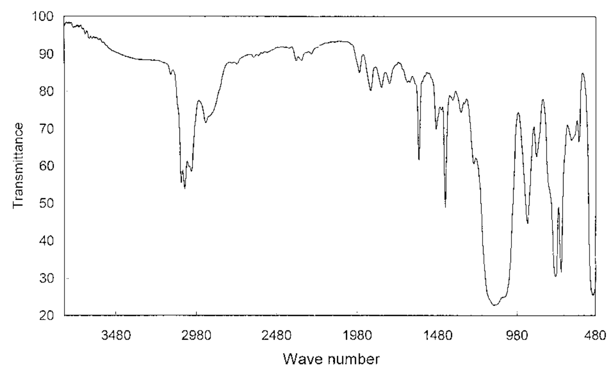

Figure 2 IR spectrum of TGPSO.

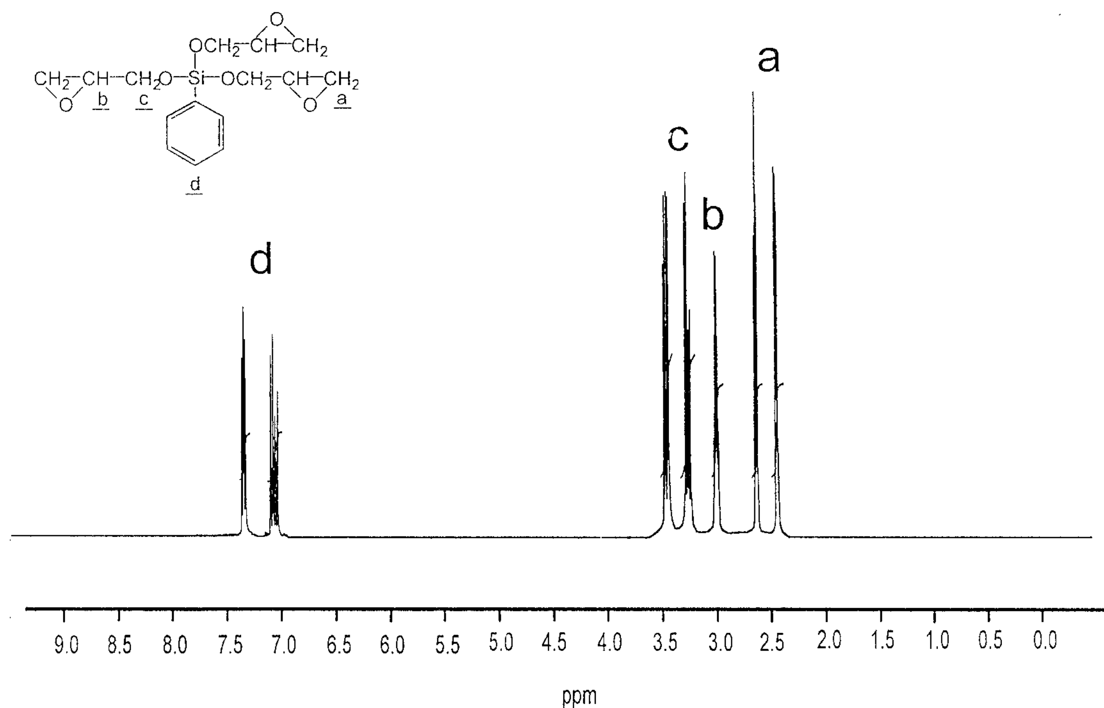

Figure 3 ^{1}H-NMR spectrum of TGPSO.

CH stretching vibration of SiCH, and 1594 cm^{-1} is associated with the vibration of the phenyl group. These characteristic absorption peaks are consistent with the proposed TGPSO chemical structure. Further characterization of TGPSO was performed by NMR analysis (Fig. 3). Assignments of the chemical shifts from ^{1}H-NMR analysis are as follows: δ = 2.60–3.21 ppm (oxirane ring protons), δ = 3.28–3.92 ppm (Si—O—$C\underline{H}_2$), and δ = 7.07–7.48 ppm (aromatic protons). The epoxy equivalent weight of TGPSO was determined to be 108 by titration.

Curing Reactivity and Kinetics

The curing reactions of TGPSO with various curing agents were studied by DSC (Fig. 4). Dynamic DSC studies provided information for choosing cure cycles (Table I) to be used in making cured castings. Figure 5 shows typical DSC thermograms of TGPSO and other commercial epoxies cured with DDM. The reactivities of the epoxies were directly read from the starting temperatures of the exothermic peaks.[21] Therefore, as shown in the DSC thermograms, TGPSO is more reactive with amine curing agents than the other epoxies. The observed higher reactivity of TGPSO is probably due to the electronic effect. The silane, serving as an electron-withdrawing group in the epoxy, reduces the electron density of the oxirane rings. This effect makes TGPSO more electrophilic in the reaction between oxirane ring and amine, i.e., more reactive toward amine curing agents.

In addition to the reactivity of TGPSO, the kinetics of TGPSO curing reactions were further

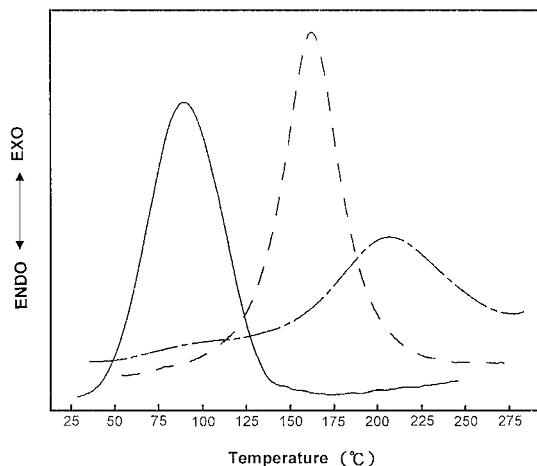

Figure 4 DSC thermograms of curing reaction of TGPSO/DDM (—), Epon828/DDM (———), and DER 732/DDM (– · –).

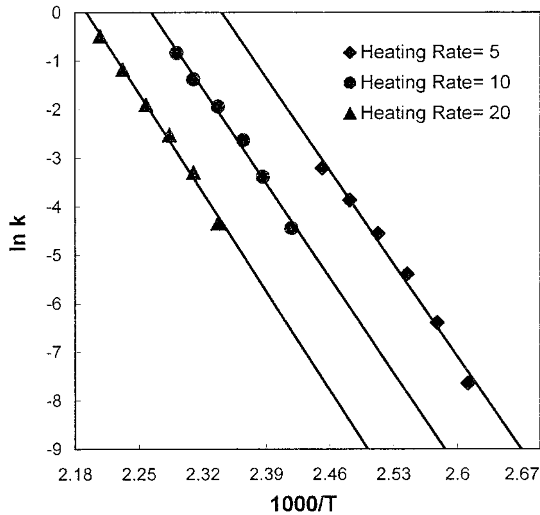

Figure 5 Arrhenius plot from dynamic method I of TGPSO/DICY curing reaction.

studied. The enthalpy of complete curing reaction was first obtained from the DSC dynamic scan. Values of the enthalpies were obtained at several heating rates. Variation in heating rate did not have a significant effect on the value of the complete curing enthalpy (Table II). The reaction enthalpies were found to be 180, 196.5, and 154 J/g for TGPSO/DDM, TGPSO/DICY, and TGPSO/DDS, respectively.

To calculate the activation energy by eq. (1), the reaction is assumed to be a first-order reaction in the first place. The dH/dT and ΔH were obtained at various temperatures from the DSC thermograms. Table III summarizes the values of rate constant k of the curing reactions of TGPSO with DDM at various heating rates. The maximum value of dH/dT increased with increasing heating rates. On the other hand, the value of rate constant k at a constant temperature decreased with increasing heating rates. The beginning temperature of the curing reaction reveals that DDM is the most reactive toward TGPSO among the curing agents employed. This is also confirmed by the rate constants obtained for these curing reactions at a certain temperature.

The activation energy was obtained from the Arrhenius plots (Figs. 6 and 7). It is important to notice that the Arrhenius plots for all curing reactions are linear. This verifies that the assumption of first-order reaction is correct. The observed activation energy varies with heating rates, However, the variation is not very significant (Table

Table II Enthalpies of the Curing Reaction of TGPSO with Various Curing Agents

Curing Agent	Heating Rate (°C/min)	Enthalpy (J/g)
DDS	5	154
DDS	10	141
DDS	20	133
DDM	5	180
DDM	10	161.64
DDM	20	140.72
DICY	5	196.5
DICY	10	136.88
DICY	20	102.45

Table III Rate Constant of TGPSO Curing Reaction from Dynamic Method I at 10°C/min

Curing Agent	Temperature (°C)	Rate Constant $k \times 10^3$ (s^{-1})
DDS	100	0.36
DDS	105	0.805
DDS	110	1.66
DDS	115	3.17
DDM	40	1.62
DDM	45	2.61
DDM	50	3.89
DDM	55	5.92
DICY	120	4.57
DICY	125	10.51
DICY	130	20.94
DICY	135	40.58

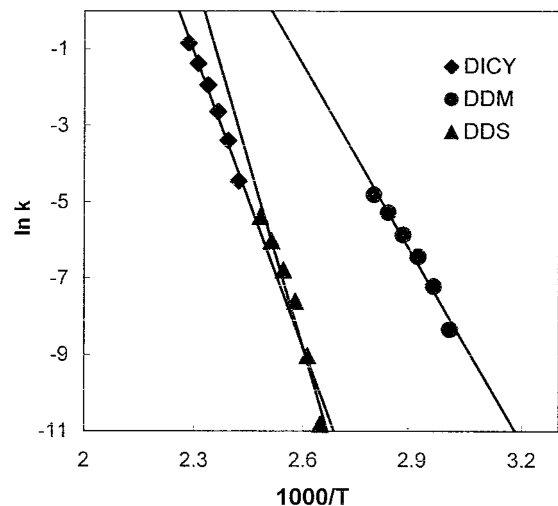

Figure 6 Arrhenius plot from dynamic method I at 10°C/min.

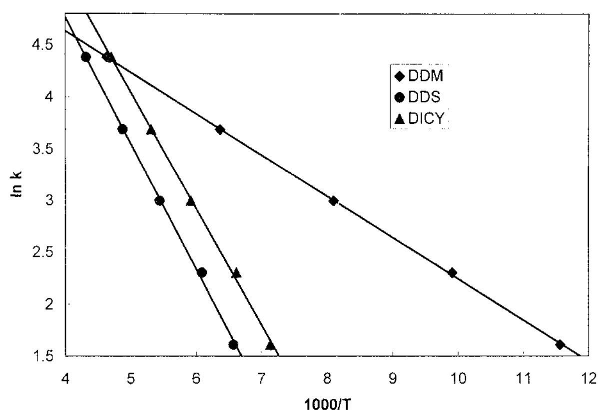

Figure 7 Determination of the activation energy by dynamic method II.

V). For examples, the values of 128.5–134.24 kJ/mol and 204.8–212.5 kJ/mol for TGPSO/DDM and TGPSO/DICY, were obtained. More values of activation energy are summarized in Table IV.

Dynamic method II provides another convenient way to obtain the activation energy of a curing reaction without resorting to the evaluation of the reaction order and reaction rate constant. The plot based on eq. (2) for determining the activation energy is shown in Figure 8. The activation energies determined by this method are also listed in Table IV. The activation energies of the curing reactions for TGPSO with various curing agents were found to be in the order of DDM < DDS < DICY. However, the values obtained from this method were smaller than those from the Dynamic Method I. This difference has been described in literature. Activation energy based on the variation of peak position with different heating rates (Dynamic Method II) generally gives smaller values than the dynamic method I.

Thermal and Flame-Retardant Properties

The glass transition temperatures (T_gs) of the cured epoxy resins are listed in Table V. TGPSO-based epoxy resins show lower T_gs than the commercial system of Epon 828/DDM. This can be understood from the TGPSO structures that contain no aromatic moiety in the backbones. A conventional additive-type flame retardant usually behaves as a plasticizer in the epoxy resin systems to reduce the resins' T_gs as well as to affect their mechanical properties.[23,24] The reactive-type flame retardants presented here show advantages of better physical properties than the additive type.[1]

Table IV Activation Energies (kJ/mol) of TGPSO Curing Reaction with Various Curing Agents

Curing Agent	Dynamic Method I	Dynamic Method II
DDS	242.05	83.2
DICY	212.47	80.9
DDM	134.24	52.3

Figure 9 shows the TGA thermograms of the cured Epon 828/DDM and TGPSO/DDM resins in nitrogen. The corresponding weight loss data based on TGA analysis are listed in Table V. Epon 828/DDM resin (Fig. 9b) exhibited 5% weight loss at around 360°C and then a rapid weight loss at 390°C. This dramatic weight loss was due to the decomposition of the resin matrix, which resulted in a constant char weight at temperatures higher than 550°C. Therefore, the Epon 828/DDM resin gives a one-stage weight loss behavior. However, the weight loss behavior of the silicon-containing resins is somewhat different. TGPSO/DDM resin (Fig.9a) shows 5% weight loss at about 215°C and additional weight loss at 260°C. Unlike the silicon-free Epon 828/DDM resin, which showed a one-stage weight loss behavior, a second stage of weight loss was found at 450°C for this silicon-containing TGPSO/DDM resin. It is noteworthy that the percentage of the first weight loss of the silicon-containing TGPSO/DDM resin is less than 10%. This small percentage of weight loss probably comes from the decomposition of the silane

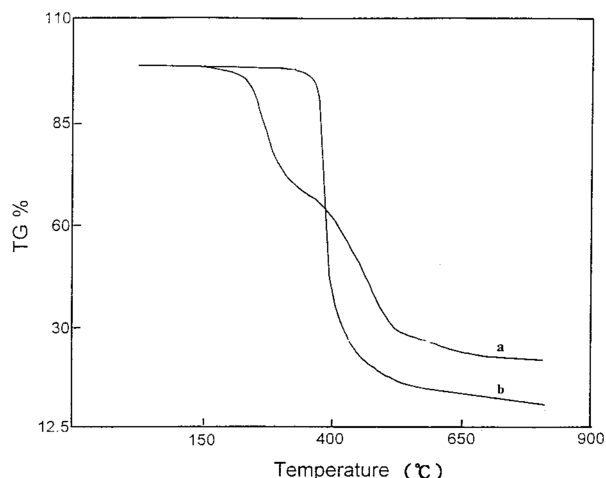

Figure 8 TGA thermograms of TGPSO/DDM (a) and Epon 828/DDM (b) in nitrogen.

Table V Thermogravimetric Data and Limiting Oxygen Index of the Silicon-Containing Epoxy

Epoxy Resin Composition	T_g (°C)	Temperatures of 1% Weight Loss (°C)		Char Yields at 850°C (%)		LOI
		N_2	Air	N_2	Air	
Epon 828/DDM	140	360	345	18	0	24
TGPSO/DDM	120	215	205	40	31	35

groups, since this stage of weight loss was not observed for the silicon-free Epon 828/DDM resin.

The two-stage weight loss results from the complicated decomposition of silane groups in TGPSO and the resin matrix. The decomposition of silane groups is able to form a silicon-rich residue after the initial stage of weight loss to slow down further decomposition of the resins. This phenomenon plays an important role in improving the flame-retardant properties of the resins and will be discussed later. Thus, the thermal stability at high temperatures of the resins is improved as the silicon is covalently incorporated in the resin. While in fire, the silane groups first decompose and then SiO_2 is formed.[24] This silicon-rich residue is able to prevent further decomposition of the polymer, raise the decomposition temperature of the polymer, and result in a high char yield. This speculation is confirmed by the char yield study. At 700°C, Epon 828/DDM resin exhibited a char yield of 18, whereas TGPSO/DDM gave 40%.

The thermogravimetric analyses of the epoxy resins were also carried out in air (Fig. 10). The weight loss behavior of these epoxy resins in air was found to be similar to that in nitrogen at temperatures less than 400°C. The weight loss from the decompositions of silane groups was also found to occur independently at around 205°C for TGPSO-based epoxy resins. While in air, Epon 828/DDM also showed a two-stage weight loss. Other weight losses at higher temperature were observed for Epon 828/DDM and TGPSO/DDM, respectively. These weight losses were brought about by the oxidation of the polymers at high temperatures. As a result of this oxidation process, the char yield is decreased. Char yields of Epon 828/DDM and TGPSO/DDM in air were found to be 0 and 31.1%, respectively. Furthermore, the silicon-free resin, Epon 828/DDM, was less thermally stable in air than in nitrogen. The temperature of the first rapid weight loss decreases from 390°C in nitrogen to 296°C in air. On the other hand, the thermal stability of the silicon containing epoxy resin TGPSO/DDM show little difference between nitrogen and air as shown in Figures 9 and 10.

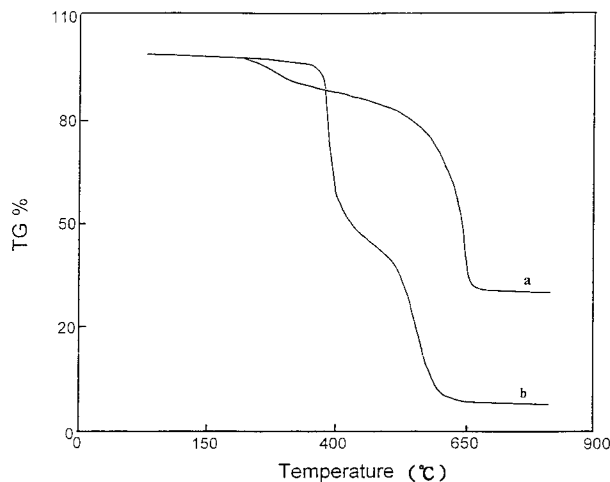

Figure 9 TGA thermograms of TGPSO/DDM (a) and Epon 828/DDM (b) in nitrogen.

The TGA thermograms of TGPSO based resins cured by diamine curing agents are shown in Figure 8. Polymers of TGPSO, reacted with diamine curing agents, showed similar weight loss behavior (Table V). The pyrolysis temperatures of the resins were raised when the silicon-containing TGPSO epoxy was incorporated. The rapid weight loss temperature of TGPSO-based resin, as mentioned, is about 130°C higher than that of Epon 828-based resin. The temperature of oxidation pyrolysis of TGPSO-based resin in air is at about 645°C. On the other hand, the silicon-free Epon 828-based resins showed their oxidation pyrolysis temperature at 540°C. Moreover, the TGPSO based resin does not show the notable reduction in thermal stability in air.

The flame-retardant properties of these epoxy resins were further examined by measuring their LOI. TGPSO-based resins exhibit LOI values of about 35 while the silicon-free Epon 828/DDM epoxy resin exhibit an LOI value of 24, as shown in Table V. The LOI values of these cured epoxy

resins are high enough to be considered flame-retardant systems.

Conclusions

A new silicon-containing oxirane compound was synthesized and used in preparing silicon-containing epoxy resins. The resulting epoxy resins showed high char yields and high LOI values. Furthermore, combination of the silicon-containing epoxy and diamine curing agent provided epoxy resin systems with a silicon content higher than 9%. This high silicon content thus led to epoxy resin with excellent flame-retardant properties with high char yield of 42% and high LOI value of 39. These silicon-containing compounds have been shown to be effective flame-retarding epoxy resins.

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