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Characterization and properties of new silicone-containing epoxy resin

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Abstract

A new epoxy monomer, triglycidyloxy phenyl silane (TGPS) has been synthesized. By curing of TGPS, Epon 828 and DER 732, with 4,4-diaminodiphenyl methane (DDM), the curing rate and conversion efficiency of these epoxy resins are in the order of TGPS > Epon 828 > DER 732. In the mixed epoxy system of TGPS/Epon 828/DDM, homogenous products are obtained from all proportions. In addition, the glass transition temperature of the blend decreases with increasing amount of TGPS from 140 to 100°C. By using TGA in a N_2 environment, the onset decomposition temperature of silicone-containing epoxy resin system of TGPS is 80°C lower than that of Epon 828, and the decomposition of TGPS is a two-stage process with maxima weight loss rates at 330 and 430°C, respectively. The first stage involves the breaking of the silicone-containing group in TGPS and the second-stage is carbonization. In the second stage of carbonization, the temperature for maximum weight loss rate is 15°C higher than that of the Epon 828 in the first stage. This result indicates that the silicone-containing group is in favor of the carbonization mechanism and the solid char yield at 800°C for TGPS is 40 wt%. Based on EDX analysis on the surface elements, the presence of Si and C is indicative of the above observation. In addition, the result by using TGA in an air environment shows that the silicon-containing carbon residue is superior in preventing oxidative burning. The high limiting oxygen index (LOI) of TGPS at 35 is considered as an excellent flame retardant in the epoxy system. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Triglycidyloxy phenyl silane; Silicone-containing epoxy; Flame retardant

1. Introduction

As one of the most widely used industrial thermo-curing resins, silicone-containing epoxy resin processes thermal resistance, dimensional stability and physical strength to meet the requirements of electronic and information sectors, PCB, aerospace components, and composites [1,2].

Products from the polysiloxane modified epoxy resins give more flexibility, low thermal expansion, and thermal stability [3–13]. However, very few reports have addressed the improvement of flame resistant properties. One approach to achieve flame retardation is to prepare the epoxy resin monomer with flame resistance followed by curing. Another approach is to introduce the flame-resistant functional group to the hardening agent in the epoxy formulation followed by curing. At present, brominated epoxy systems [14–15] and phosphorous-containing epoxides [16–20] are available as flame retardants. Due to environmental problems, the use of non-halogenated flame retardants shall become mainstream in the future. Among them, the silicone-containing epoxy flame retardants shall be one of the choices.

Traditionally, polysiloxane modified epoxy resins possess thermal stability and flame resistance that have been used in polymer modification [21]. For these polysiloxane modified epoxies [22], the conversion to the stable silicon dioxide in air can form a glassy layer on polymer surfaces to cut off the heat and oxygen transfer and thus improve the flame retardation of the polymers. The absence of toxic gases from the silicone-containing flame retardant is advantageous over these halogen-containing compounds. However, this system contains large amounts of oxygen, leading to phase separation and substantial lower glass transition temperatures [13]. The variation of substituted siloxane groups affects compatibility and glass transition temperatures of the system [23–25]. If the substitution group is a phenyl group, both glass transition temperature and compatibility are better than that of an alkyl group. In this study, phenyltrimethoxy silane has been selected as the raw material for synthesizing the corresponding epoxy monomer to form the triglycidyloxy

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Table 1
Reaction conditions of curing epoxy resins

Epoxy resin	Precure process temperature (°C)	Curing time (min)	Postcure process temperature (°C)	Curing time (min)
Epon 828/DDM	115	90	170	180
TGPS/DDM	80	90	140	120

phenyl silane (TGPS) monomer [26], which is subsequently used as a flame retardant in the bisphenol A type epoxy resin (DGEBA) in evaluating the flame retardant performance.

This new reactive monomer, TGPS has been characterized by ^{1}H NMR, ^{29}Si NMR and FTIR for structure identification. It was also blended in various portions with DGEBA resin (Epon828) and cured by diamine type 4,4-diaminodiphenylmethane (DDM) hardening agent. The thermal stability was assessed by TGA and finally with the limiting oxygen index (LOI) in evaluating its flame retardant properties of the system.

2. Experimental

2.1. Materials

Phenyltrimethoxyl silane (PTMOS), and *p*-toluene sulfonic acid were obtained from Tokyo Chemical Industry Co. of Japan. Chloropropylene oxide, sodium hydroxide, toluene, tetrabutyl titanium, and 4,4diaminodiphenylmethane were supplied by Aldrich Co. of USA. Epon 828 was obtained from Shell Chemical Co. USA. Der 732 was supplied by the Dow Chemical Co. of USA.

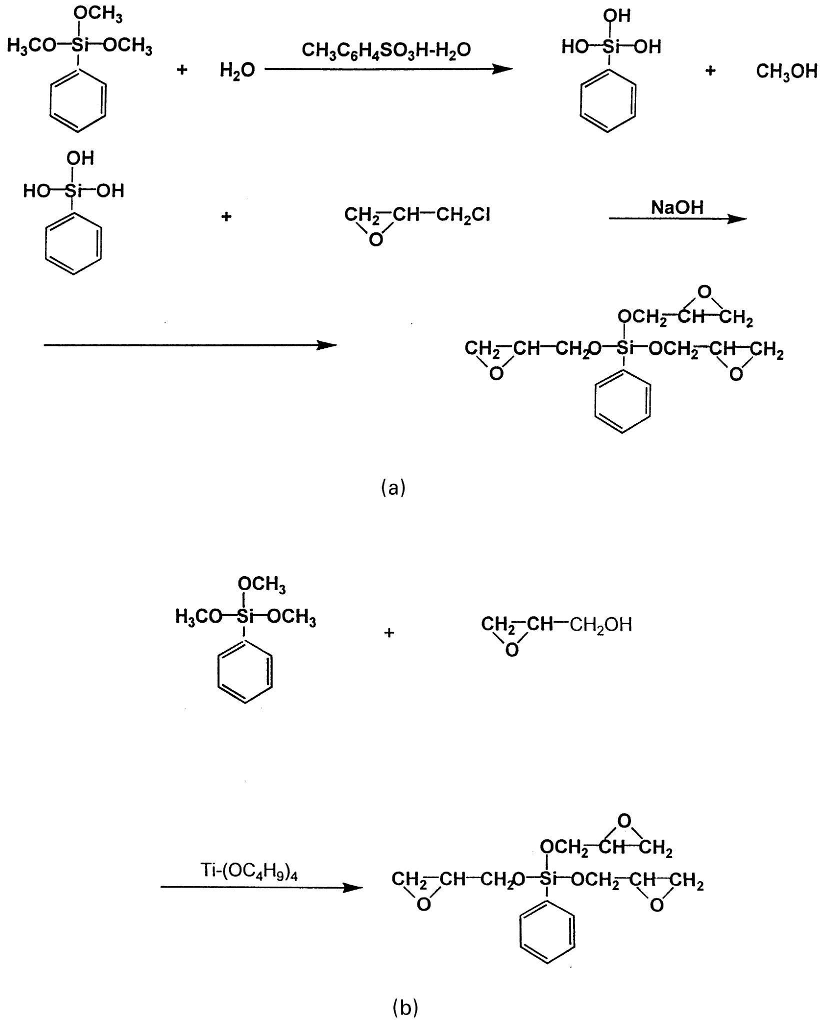


Fig. 1. Synthesis scheme of TGPS: (a) method A; (b) method B.

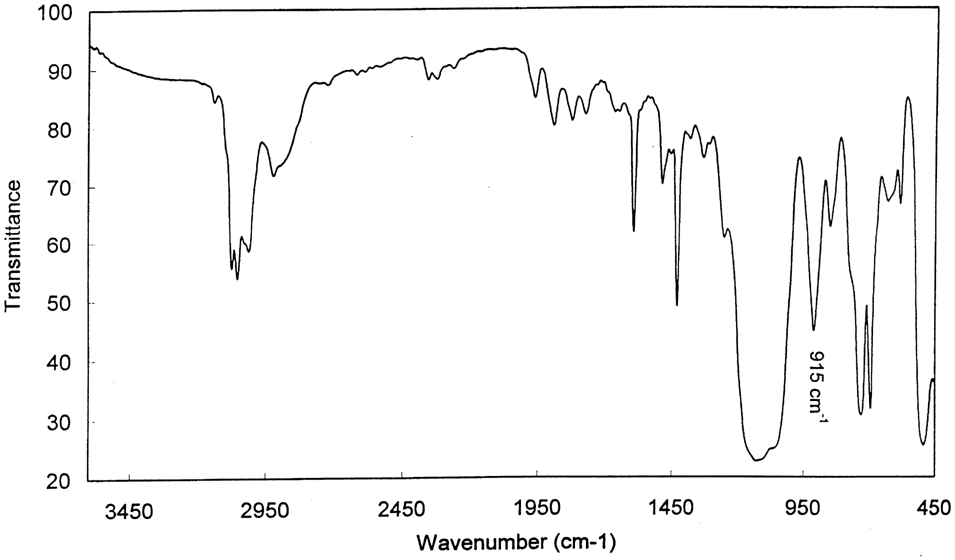


Fig. 2. IR spectrum of TGPS by method A.

2.2. Synthesis of TGPS monomer

2.2.1. Method A

Hydrolysis of the PTMOS was carried out by placing 0.1 mol PTMOS and 0.3 mol water in a reactor, followed by adding 0.5 g *p*-toluene sulfonic acid with proper stirring under room temperature for 30 min. Phenyltrihydroxyl silanol was obtained by removal of the methanol by distillation under reduced pressure. 0.15 mol of 40% $NaOH_{(aq)}$ was added dropwisely into a mixture of 0.1 mol of phenyltrihydroxyl silanol and 0.15 mol of epichlorohydrin at 60°C within 3 h. Finally, the TGPS product was separated by alternative extractions by water and toluene.

2.2.2. Method B: transetherification

Transetherification was carried out by adding 0.5 g of tetraisopropyl titanium catalyst into a mixture of 0.3 mol glycidol and 0.1 mol PTMOS with proper agitation. The progress of the transetherification monitored the Si–O–Me content by FTIR until complete disappearance of the Si–O–Me group.

2.3. Blending of epoxy resin

Various composition mixtures of TGPS/Epon 828 were cured by stoichiometric DDM and the curing conditions were monitored by dynamic DSC using a heating rate of 10°C/min. The initial exothermic temperature plus 20°C was taken as the precure temperature of the blend mixture and the exothermic peak temperature plus 10°C was taken as the postcure temperature for the isothermal curing. The cured conditions for base resins are shown in Table 1.

2.4. Instrumental analyses

1. *FTIR:* The Bio-Red 155 IR spectrophotometer was employed to obtain the FTIR spectrum.
2. *NMR:* The Bruker MSL-400 NMR spectrometer was used in both ^1H NMR and ^{29}Si NMR. Unless otherwise specified, the solvent was $CDCl_3$ and the internal standard for ^1H NMR was tetramethylsilane (TMS) in obtaining the spectra with chemical shift in ppm.
3. *DSC:* The Seiko SSC-5200 was used for DSC analyses under nitrogen atmosphere using a scanning rate of 10°C/min.
4. *TGA:* Seiko 6000 type TGA was used to obtain weight loss data at a scanning rate of 10°C/min under nitrogen and air, respectively.
5. *SEM/EDX:* A Hitachi S-2300 type SEM-EDX was used to examine the cured epoxy film, to observe the surface morphology and elemental distribution.
6. *Oxygen index analyzer:* A Stanton Redcraft Rombustion Analyzer was used with a mixture of oxygen and nitrogen for a flow rate of 17 l/min to obtain the percentage concentration of oxygen in supporting combustion of the sample as the LOI. This procedure is modified from the method reported in Ref. [17].

3. Results and discussion

3.1. Synthesis of TGPS monomer

This silicone-containing epoxy monomer TGPS was prepared by condensation (method A) and catalyzed by transetherification (method B) as shown in Fig. 1. The product TGPS from the condensation of PTMOS and epichlorohydrin (Method A, Fig. 1) was monitored and

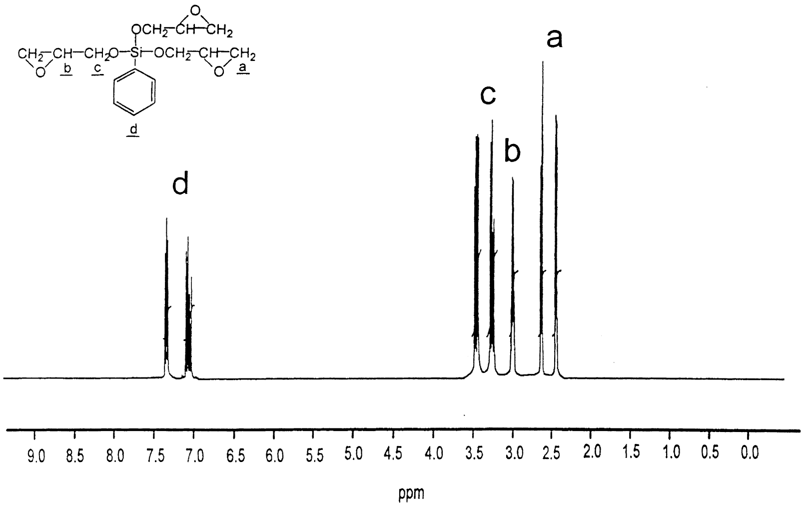


Fig. 3. ^{1}H NMR spectrum of TGPS prepared by method A.

identified by FTIR and NMR, respectively. The IR spectrum in Fig. 2 shows the disappearance of the Si–O–Me peak at 2834 cm^{-1}, an indication of complete hydrolysis of the Si–O–Me group of the PTMOS, and the appearance of the Si–O–CH$_2$ peak at 1085 cm^{-1}. The other absorption peak at 910 cm^{-1}, corresponds to the epoxy ring that confirms the expected structure of TGPS as shown in Fig. 1.

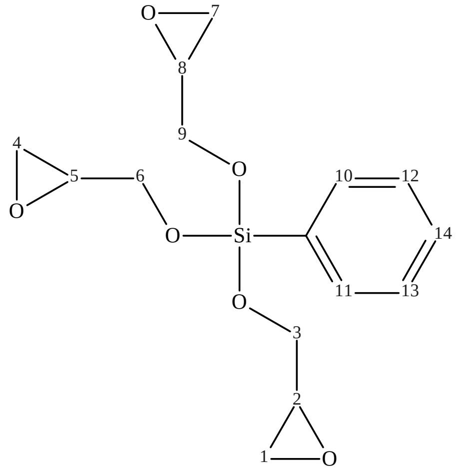
Fig. 3 gives the NMR spectrum of the prepared TGPS with characteristic shifts of hydrogen at $\delta = 2.32$–3.08 ppm (three H on the epoxy ring), $\delta = 3.32$–3.61 ppm (–Si–O–CH$_2$), and $\delta = 7.02$–7.41 ppm (H on benzene ring). All these characteristic NMR bands indeed match the expected TGPS structure. The integrated value of these peaks also matches well to the number of hydrogen atoms in the TGPS structure as listed in Table 2. Further structural confirmation was made by means of the ^{29}Si NMR spectrum. Fig. 4 gives only the single absorption band with the chemical shift for silane structure, indicating the correctness of the TGPS structure and high purity.

Method A two-step synthesis of the TGPS as shown is Fig. 1(a) is relatively simple but the yield is only about 50% due to self-condensation of the hydrolyzed silane.

Method B catalyzed by transetherification as shown in Fig. 1(b) used tetrabutyl titanium as the catalyst. The IR

Table 2

Area integration ratios (calculated values as the area of (C_{12}, C_{13}, C_{14}) is 3) of the H-band in the NMR spectra of TGPS



Assignment[a]	C_1, C_4, C_7	C_2, C_5, C_8	C_3, C_6, C_9	C_{10}, C_{11}	C_{12}, C_{13}, C_{14}
Method A	6.10	3.05	5.99	2.04	3
Method B	5.98	3.07	6.01	2.01	3

[a] The positions of carbon in the table are shown in the chemical formula.

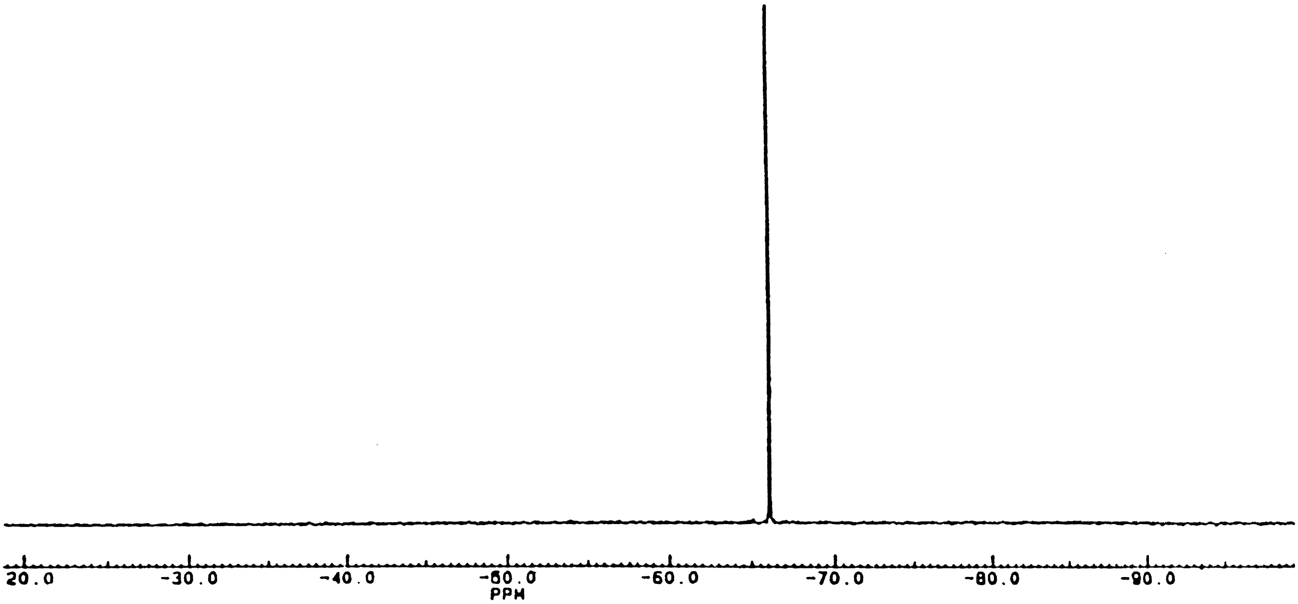


Fig. 4. ^{29}Si NMR spectrum of TGPS.

spectrum and ^{1}H NMR of the TGPS product obtained from method B are similar to that prepared from method A (Figs. 2 and 3) but the yield by method B is higher at 85%.

3.2. Curing with diamine

Fig. 5 shows DSC exotherms of TGPS, Epon 828 and DER 736 cured by stoichiometric DDM under nitrogen atmosphere. TGPS system has the lowest onset (55°C) and peak maximum (120°C) temperatures but has the high exothermic heat ($\Delta H = 166$ kcal/mol). The mechanism of curing epoxy with diamine involves the electrophilic attack on the epoxy group for the ring opened by nucleophilic S_N reaction [27]

The Si–O bond in TGPS is partially ionic with the double bond nature of the pπ–dπ interaction [28] which shows a strong electron pulling effect to decrease the electron density of the epoxy group and increase the reactivity for the epoxy ring opened. By introducing the Si–O group, the epoxy group in TGPS has the lower electron density and

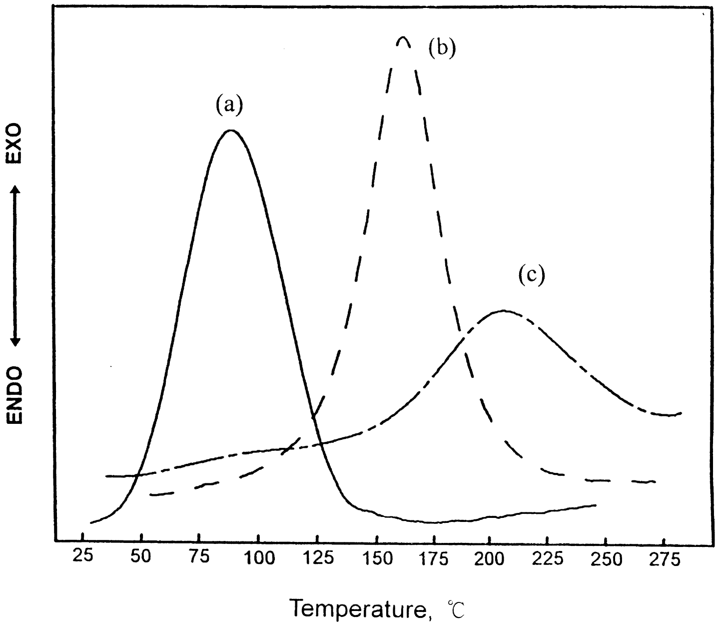


Fig. 5. Curing exotherms of various epoxy resins: (a) TGPS/DDM; (b) Epon 828/DDM; (c) DER 732/DDM.

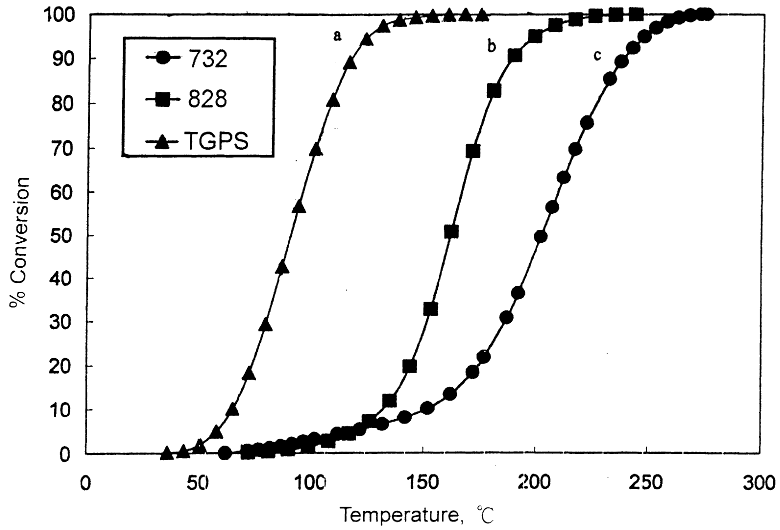


Fig. 6. Plot of conversion versus temperature by DDM curing of epoxy resins: (a) TGPS; (b) Epon 828; (c) DER 732.

higher reactivity. Fig. 6 shows the plot of the epoxy conversion versus temperature which again clearly shows the highest conversion rate of TGPS relative to Epon 828 and DER 736.

3.3. Compatibility of TGPS with commercial epoxy resins

Fig. 7 gives DSC curves of various cured TGPS/Epon 828/DDM mixtures. The TGPS/DDM gives the lowest T_g due to the large free volume caused by Si–C_6H_5 and Si–O groups in TGPS. The T_g of Epon 828/DDM is 140°C. The rest of the mixed epoxy systems all exhibit single T_g between T_gs of TGPS and Epon 828. This single T_g phenomenon indicates a homogeneous morphology of these mixed epoxy systems. Fig. 8 shows the SEM micrographs of these blends after curing. The result shows that no phase separation can be detected. Fig. 9 shows the corresponding Si-mapping micrographs by SEM-EDX analyses. The silicon element (small white spots) is evenly distributed and its density increases with the increase of the TGPS content in the mixed epoxy blends. This result again suggests that these TGPS/Epon828/DDM mixtures are totally miscible without phase separation.

3.4. Thermal and flame retardation properties

The thermogravimetric curves up to 800°C of the cured TGPS, TGPS/Epon 828, and Epon 828 products under nitrogen atmosphere are shown in Fig. 10. The onset decomposition temperature, $T_{5\%}$, of the TGPS/DDM occurs around 282°C. Two maxima weight loss rates occur at 330 and 430°C, an indication of a two-stage decomposition of the TGPS/DDM. The Epon 828/DDM is an one-stage

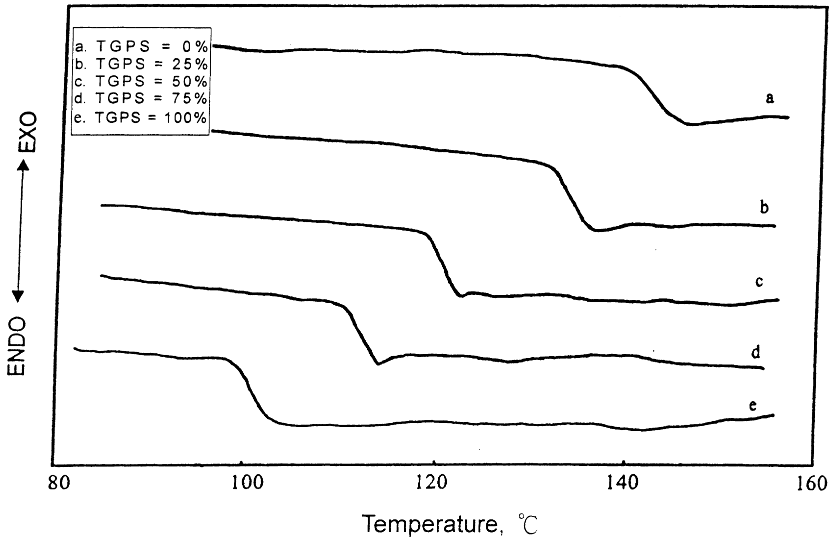


Fig. 7. DSC curves of the cured TGPS/Epon 828/DDM mixtures in N_2 at a heating rate of 10°C/min.

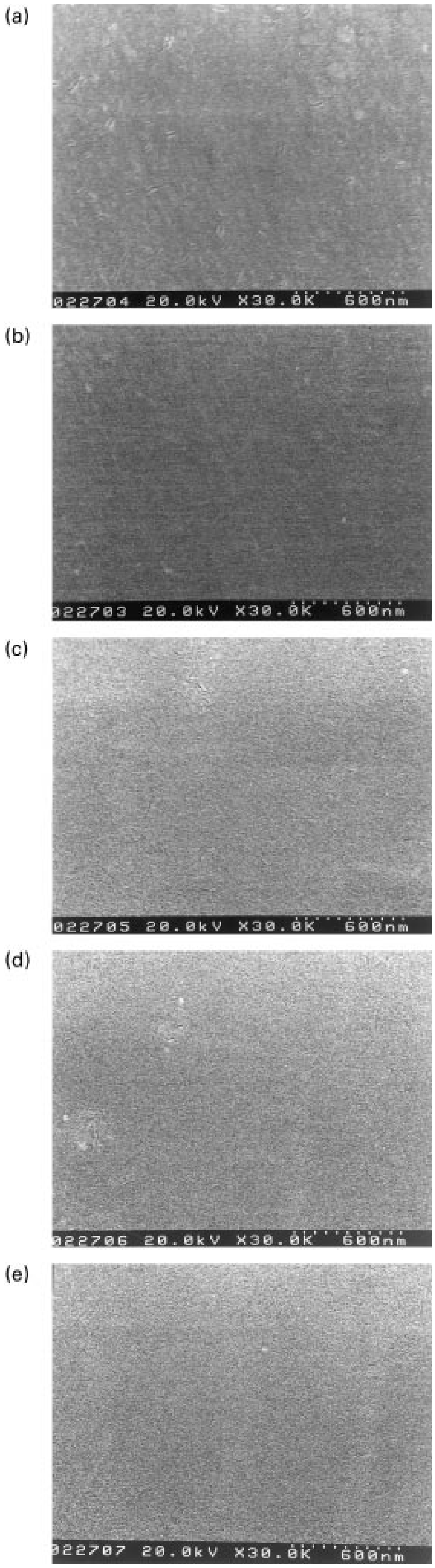


Fig. 8. The SEM micrographs of the product prepared by reaction of TGPS/Epon828 cured by DDM after curing in N_2: (a) TGPS/Epon828 = 0/100; (b) TGPS/Epon828 = 25/75; (c) TGPS/Epon828 = 50/50; (d) TGPS/Epon828 = 75/25; (e) TGPS/Epon828 = 100/0.

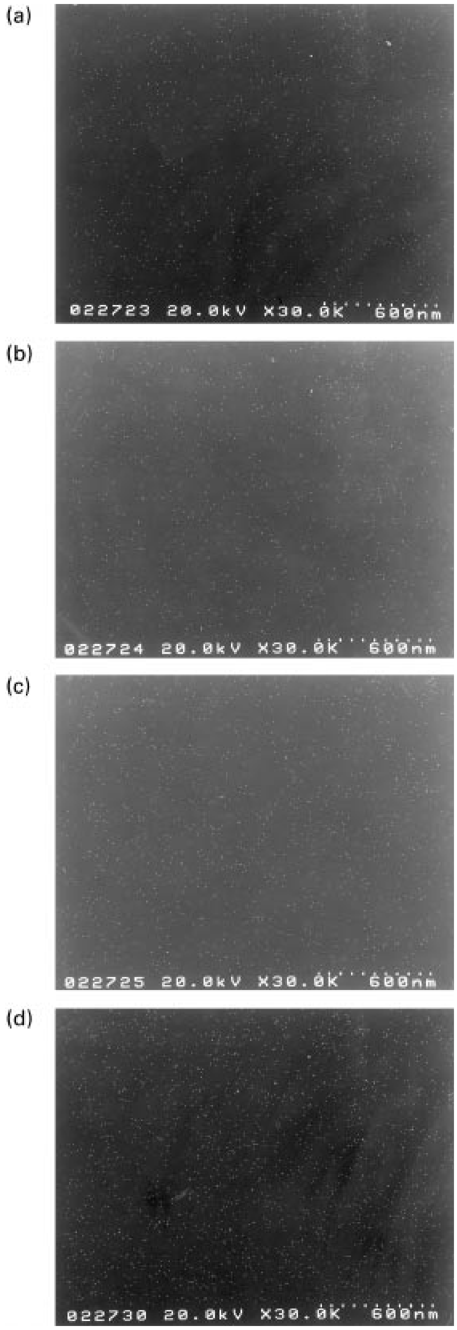


Fig. 9. The Si-Mapping micrographs of the product prepared by the reaction of TGPS/Epon828 cured by DDM after curing in N_2: (a) TGPS/Epon828 = 25/75; (b) TGPS/Epon828 = 50/50; (c) TGPS/Epon828 = 75/25; (d) TGPS/Epon828 = 100/0.

decomposition process with the $T_{5\%}$ about 80°C higher than that of the TGPS/DDM. The thermal stability of the TGPS appears to be lower than that of Epon 828 because the first stage decomposition of the TGPS occurs at a much lower temperature. The Si–O group of the TGPS is able to absorb more thermal energy and its vibration can dissipate the thermal decomposition energy [29]. The decomposition leads to the formation of the silicone-containing group which will participate in the crosslinked carbonization in

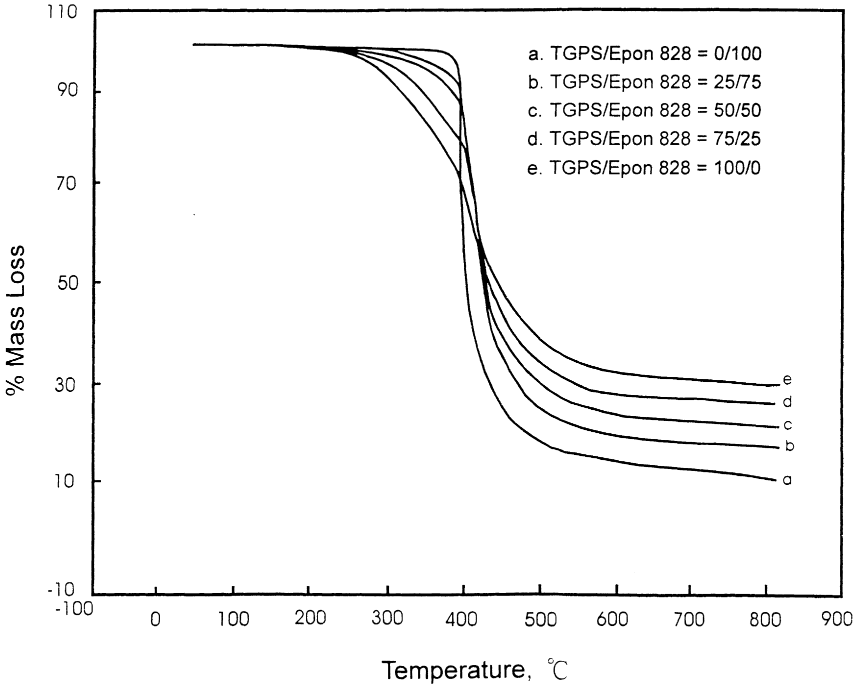


Fig. 10. TG weight loss curves of the cured TGPS/Epon 828/DDM mixtures in N_2 at a heating rate of 10°C/min to 800°C.

the second stage decompsition, and effectively retard the flame formation at higher temperature. The temperature of the maximum weight loss rate of TGPS is about 15°C higher than that of Epon 828. With the presence of the silicone-containing TGPS, it can convert the usual organic decomposition to partially inorganic decomposition by forming the carbon–silicon residue to act as thermal insulation [30–32] and to prevent gas evolution, and achieve ultimate improvement on flame retardation of this silicone-containing epoxy system.

The thermogravimetric curves in air atmosphere to 800°C of these cured TGPS/Epon 828/DDM mixtures are shown in

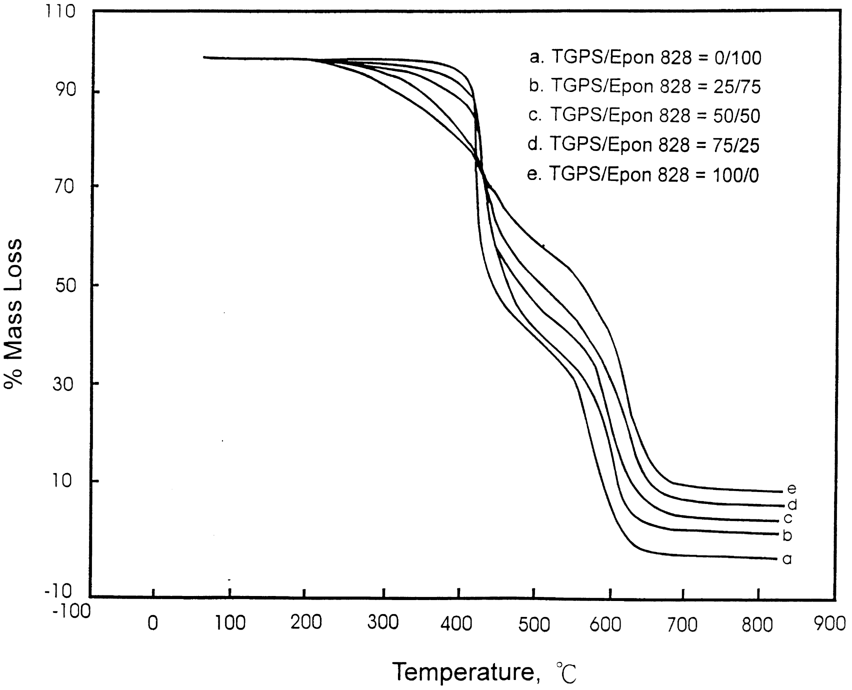


Fig. 11. TG weight loss curves of the cured TGPS/Epon 828/DDM mixtures in air at a heating rate of 10°C/min to 800°C.

Table 3
Thermal properties and limiting oxygen indices of finally cured products

TGPS/ Epon828	T_g (°C)	$T_{5\%}$ (°C)[a]		T_{max1} (°C)[b]		T_{max2} (°C)[b]		T_{max3}(°C)[b]		Char (wt%)		LOI
		Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2	
100/0	100	263	282	320	330	425	430	622	–	12	40	35
75/25	110	285	286	340	345	426	430	611	–	9	35	32
50/50	120	328	330	370	378	426	430	596	–	5	27	29
25/75	135	343	348	380	386	420	425	590	–	3	23	26
0/100	140	362	362	410	415	567	–	–	–	0	14	22

[a] $T_{5\%}$ represents the onset decomposition temperature of 5% weight loss for the cured TGPS/Epon828 system.

[b] T_{maxn} represents the temperature of maximum weight loss rate in the n-stage decomposition for the cured TGPS/Epon828 system.

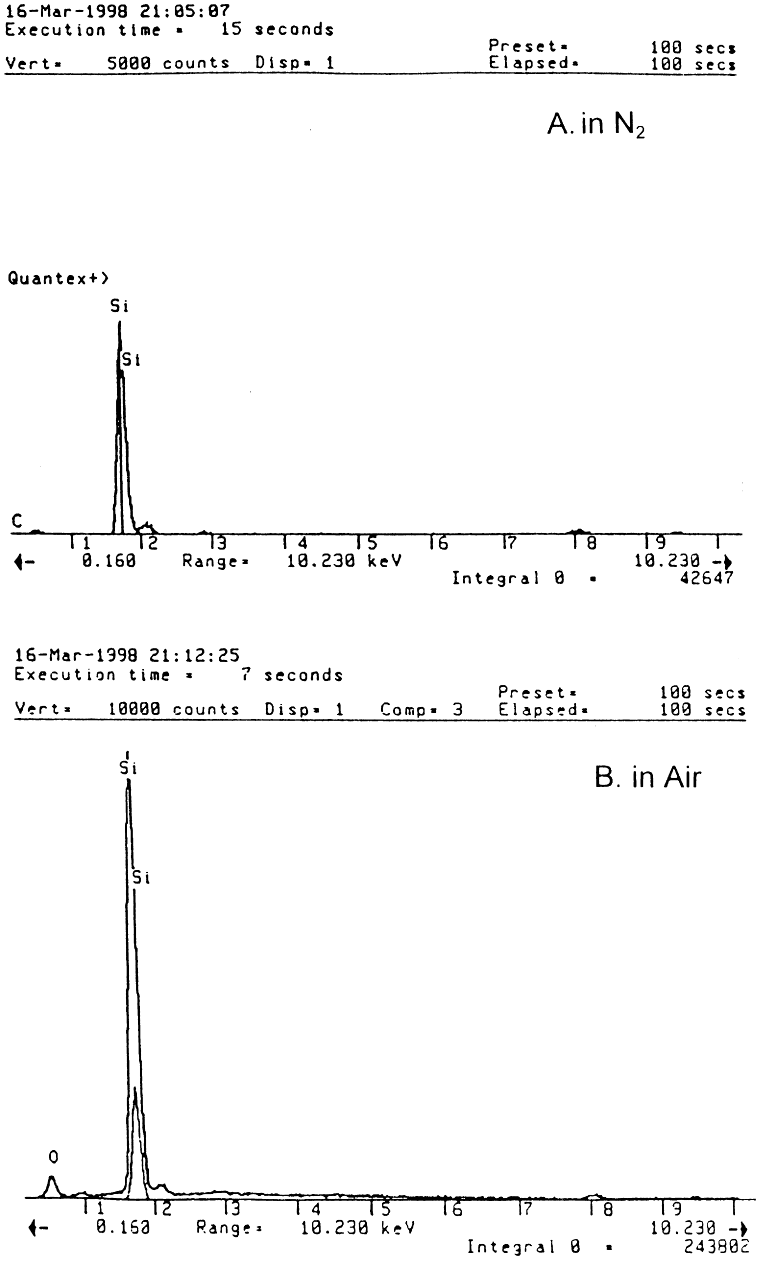


Fig. 12. EDX elemental distribution analysis on solid residue surface of the cured TGPS/Epon 828/DDM mixtures after curing in: (A) N_2; and (B) air at a heating rate of 10°C/min to 800°C.

Fig. 11. Decomposition of the TGPS/DDM in air atmosphere involves a three-stage process, while that of the Epon 828/DDM is a two-stage process. The $T_{5\%}$ of TGPS/DDM is 99°C lower than that of Epon 828/DDM. This result indicates that the Si–O group of TGPS can be oxidized more easily at a lower temperature relative to that of Epon 828. For the first stage decomposition of the TGPS in air atmosphere, the maximum weight loss rate occurs at a temperature of about 10°C lower than that in nitrogen atmosphere. Therefore, the decomposition of TGPS starts at a lower temperature as the result of oxidation in breaking off the silicone-containing group. The carbonization mechanism dominates the second stage of TGPS and the first stage of Epon 828, the former being about 15°C higher than the latter. For decomposition at even higher temperatures corresponding to the third stage for TGPS and the second stage for Epon 828, the temperature of maximum weight loss rate for TGPS is about 55°C higher than that for Epon 828. The introduction of this silicone-containing group into the epoxy structure is able to cause the crosslinked carbonization and results in higher oxidation temperature, and thus raises flame retardation significantly.

Thermodynamic data of decomposition of various TGPS/Epon 828/DDM mixtures in nitrogen and in air, and the corresponding LOI data are listed in Table 3. For decomposition either in air or nitrogen atmosphere the onset decomposition temperature and the temperature of maximum weight loss rate in the first stage, increases with decreasing amount of TGPS. In the second stage decomposition, the temperature of maximum weight loss rate increases with increasing amount of TGPS due to the solid carbonization mechanism of the system. The solid char yield in nitrogen at 800°C is 40%, which is significantly higher than that of Epon 828 at 13%. The solid char yield in air at 800°C for TGPS is 12% which is also higher than that of Epon 828 at 0%. The observed higher char yield from the TGPS indicates that the carbonization mechanism indeed plays an important role in flame retardation. Element analysis on surfaces of the solid residue from the decomposition of cured TGPS/Epon 828/DDM mixtures in nitrogen by EDX mainly shows the silicon with minor carbon content as shown in Fig. 12A. While in air, silicon is again the major content with minor oxygen content as shown in Fig. 12B. The LOI value of the TGPS is 35, which is substantially higher than that of the Epon 828 at 22. The LOI of TGPS/Epon 828 mixtures increases with increasing amount of TGPS as shown in Table 3.

4. Conclusions

A new silicone-containing trifunctional epoxy monomer, TGPS, has been synthesized by two different routes, condensation and transetherification. Unlike most silicone-containing compounds, this TGPS is compatible with the conventional epoxy monomer (DGEBA) in all proportions. The results from the glass transition temperature and elemental analyses show homogeneous distribution in the TGPS/Epon828/DDM blending process to increase the flame retardation effect. The solid char yield in nitrogen at 800°C for TGPS is 40% that is significantly higher than that of the conventional epoxy (Epon 828) at 12%. The solid char yield in air at 800°C for TGPS is also substantially higher than that of the conventional epoxy. The LOI value of 35 for TGPS can be advantageous in its use as a reactive flame retardant.

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