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Silicon-containing flame retardant epoxy resins: Synthesis, characterization and properties

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Abstract

Epoxy resins with different silicon contents were prepared from silicon-containing epoxides or silicon-containing prepolymers by curing with 4,4′-diaminodiphenylmethane. The reactivity of the silicon-based compounds toward amine curing agents was higher than that of the conventional epoxy resins. The T_g of the resulting thermosets was moderate and decreased when the silicon content increased. The onset decomposition temperatures decreased and the char yields increased when the silicon content increased. Epoxy resins had a high LOI value, according to the efficiency of silicon in improving flame retardance.

Keywords: Flame retardant polymers; Epoxy resins; Thermogravimetrical analysis; Limiting oxygen index

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1. Introduction

A number of future industrial and commercial applications will require polymers with improved fire retardancy. Demands for flame retardant epoxy resins are extremely strong because they are widely used in adhesives, coatings and advanced composites in the aerospace and electronic industries. Traditionally, flame retardant polymers can be prepared by blending polymers with flame retardant additives, such as halogenated compounds [1]. This is the most economical way of promoting flame retardancy, but problems such as poor compatibility, leaching and reduced mechanical properties limit their application. The most effective way of improving flame retardancy in epoxy resins is the reactive approach: that is to say, the flame retardant compound is incorporated into the polymer backbone through the epoxide or the curing agent. Moreover, the use of halogenated compounds as flame retardants has clear disadvantages such as the toxicity and environmental impact of the decomposition products evolved during combustion. It is essential that flame retardant systems meet the requirements of new regulations and the development of new halogen-free epoxy resins is attracting considerable interest [2].

Research has shown that the addition of relatively small amounts of silicon compounds to various polymeric materials has a flame retardant effect. This is partly because these compounds dilute the more combustible organic components and partly because the silicaceous residues can form a barrier to an advancing flame [3]. Silicon, like phosphorus and nitrogen, is regarded as an environmentally friendly flame retardant because it can reduce the harmful impact on the environment more than the existing materials. Some approaches that prepare epoxy resins with silicon covalently bonded to the epoxy network have been reported. Hydroxyl-terminated siloxanes have been used directly in the epoxy resin formulation and diamino-terminated siloxanes can also be used as curing agents to effectively introduce silicon into an epoxy resin [4]. A more complicated approach is to synthesize silicon-containing epoxides, which can be cured on their own or blended with other epoxy comonomers. In this way, the synthesis of triglycidyloxyphenyl silane (TGPS), a silicon-based epoxy monomer has been described [5,6]. The monomer obtained was blended in various proportions with DGEBA and cured with

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diaminodiphenylmethane as hardening agent. Phase separation was not observed during the curing process and the materials obtained showed good thermal and flame retardant properties.

Epoxy-containing silsesquioxanes have also been used to prepare nano-reinforced epoxy networks [7,8]. In this approach, the most important concept is that a phase separation process may take place when a POSS-bearing organic group is used that is not compatible with the epoxy network. The results suggest that it should be possible to develop a formulation in which the phase separation process takes place in the course of the polymerization, leading to a dispersion of micro-particles in the thermosetting polymer and the *in situ* generation of a reinforced polymer.

The present study uses two different approaches to prepare silicon-containing epoxy resins. Silicon-containing glycidyl monomers (DGDPS, BGDMSB and TGPS, Scheme 1) were obtained and cured by 4,4′-diaminodiphenylmethane as hardening agent. We also examined the incorporation of silicon into the epoxy resin by reacting silanols and DGEBA to obtain prepolymers (EpSi 2-1 and EpSi 3-2, Scheme 2) that have been cured with DDM. The thermal stability of the final polymers was assessed by TGA and the flame retardant properties were evaluated by the limiting oxygen index.

2. Experimental part

2.1. Materials

Phenyltrimethoxy silane, dimethoxydiphenyl silane, allyl alcohol, titanium tetraisopropoxide and *m*-chloroperbenzoic acid (MCPBA) were supplied by Fluka. 4,4′-Diaminodiphenylmethane (DDM), glycidol, diphenylsilanediol, 1,4-bis(hydroxydimethyl silyl) benzene and tin (II) chloride were supplied by Aldrich. Diglycidylether of bisphenol A (Epikote 828; EEW = 192 g/equiv) was obtained from Shell Chemical Co. All solvents were purified by standard procedures.

2.2. Synthesis of diglycidyloxydiphenyl silane (DGDPS)

Dimethoxydiphenyl silane (10.0 g; 0.041 mol), allyl alcohol (40.0 g; 0.688 mol) and titanium tetraisopropoxide (0.3 g; 0.001 mol) were added to a 250-ml two-necked flask equipped with magnetic stirrer and condenser. The reaction was carried out in toluene at reflux temperature for 24 h. The progress of the reaction was monitored by thin-layer chromatography (5:3 hexane/ethyl acetate). The reaction mixture was washed twice with 5 wt% tartaric acid, three times with 5 wt% $NaHCO_3$, and with water and brine. The organic layer was dried over $MgSO_4$, filtered and then the solvent was evaporated at reduced pressure. The product obtained was used in the next step without purification.

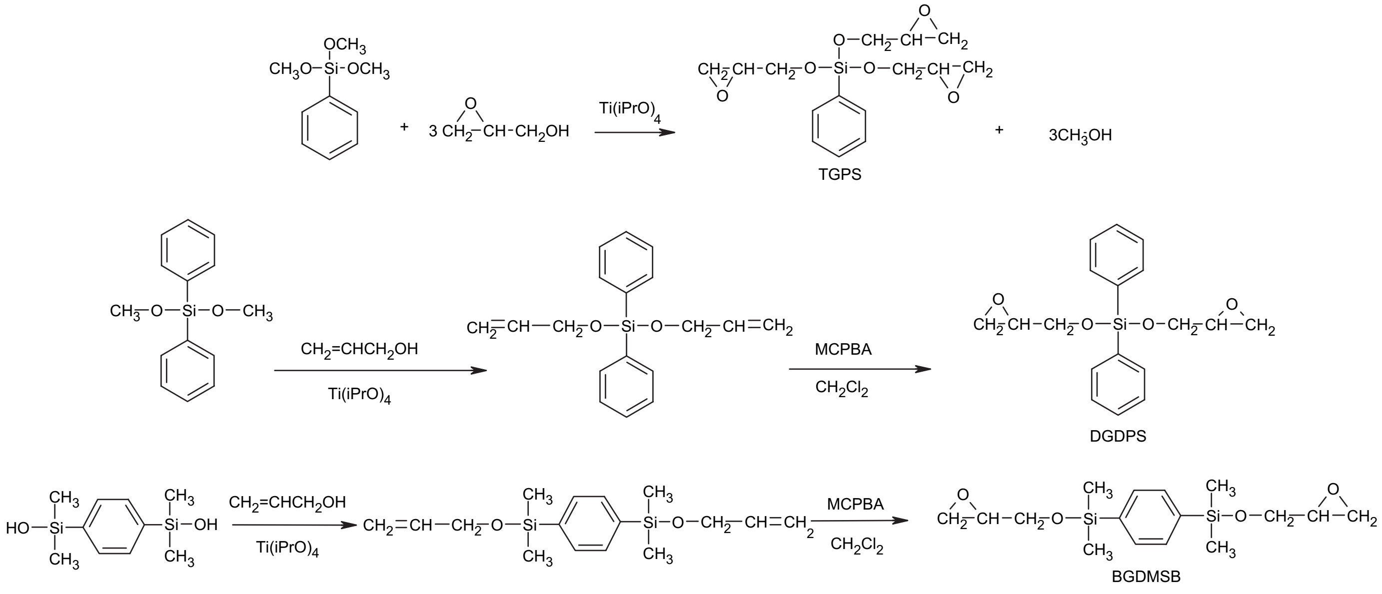
The allyloxy derivative (10 g; 0.034 mol) and MCPBA (30 g; 0.174 mol) were stirred with 250 ml of dichloromethane in a 500-ml two-necked flask at 50 °C for 48 h. The progress of the reaction was monitored by thin-layer chromatography (7:3 hexane/ethyl acetate). The reaction mixture was washed with 5 wt% Na_2SO_3, three times with 5 wt% $NaHCO_3$, and with water and brine. The organic layer was dried over $MgSO_4$, filtered and then the solvent was evaporated at reduced pressure. The product obtained was purified by flash chromatography (7:2 hexane/ethyl acetate). The final product was obtained in a 65% yield.

^{1}H NMR ($CDCl_3$/TMS, δ (ppm)): 7.65 (4H, m); 7.42 (6H, m); 4.03 (2H, dd, 12.0, 3.2 Hz); 3.75 (2H, dd, 12.0, 5.2 Hz); 3.15 (2H, m); 2.78 (2H, dd, 4.4, 2.8 Hz); 2.65 (2H, dd, 4.4, 2.8 Hz).

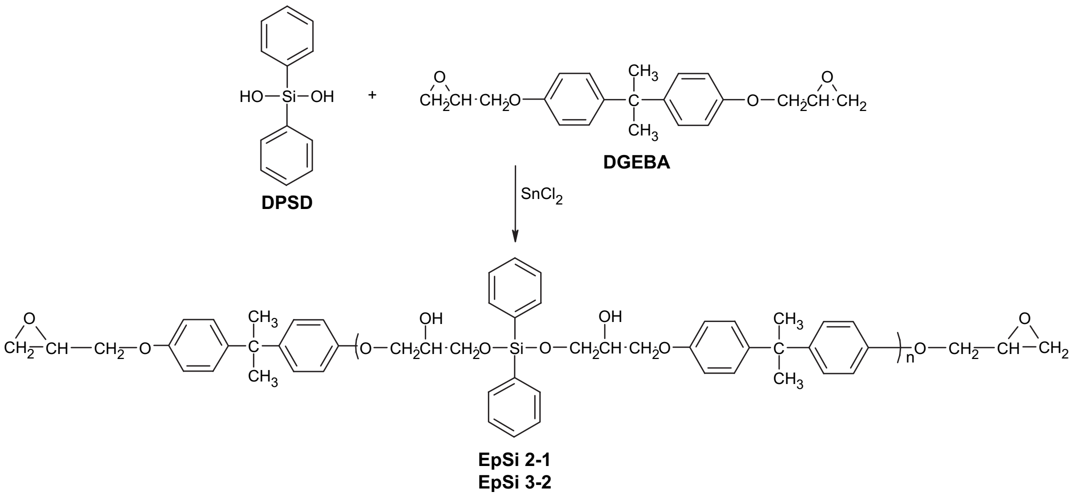
^{13}C NMR ($CDCl_3$/TMS, δ (ppm)): 134.9 (d); 132.2 (s); 130.6 (d); 127.9 (d) 63.8 (t); 52.0 (d); 44.5 (t).

2.3. Synthesis of 1,4-bis(glycidyloxydimethyl silyl)-benzene (BGDMSB)

1,4-Bis(hydroxydimethyl silyl) benzene (0.5 g; 0.002 mol), allyl alcohol (10.0 g; 0.170 mol) and titanium tetraisopropoxide



Scheme 1.



Scheme 2.

(0.019 g; 6.6×10^{-5} mol) were added to a 250-ml two-necked flask equipped with magnetic stirrer and condenser. The reaction was carried out in toluene at reflux temperature for 48 h. The progress of the reaction was monitored by thin-layer chromatography (5:3 hexane/ethyl acetate). The reaction mixture was washed twice with 5 wt% tartaric acid, three times with 5 wt% $NaHCO_3$, and with water and brine. The organic layer was dried over $MgSO_4$, filtered and then the solvent was evaporated at reduced pressure. The product obtained was used in the next step without purification.

The allyl derivative (0.6 g; 0.002 mol) and MCPBA (2.4 g; 0.010 mol) were stirred with 50 ml of dichloromethane in a 100-ml two-necked flask at 50 °C for 48 h. The progress of the reaction was monitored by thin-layer chromatography (5:3 hexane/ethyl acetate). The reaction mixture was washed with 5 wt% Na_2SO_3, three times with 5 wt% $NaHCO_3$, and with water and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. The product obtained was purified by flash chromatography (7:2 hexane/ethyl acetate). The product was obtained in a 58% yield.

^{1}H NMR ($CDCl_3$/TMS, δ (ppm)): 7.58 (4H, s); 3.82 (2H, dd, 12.0, 3.3 Hz); 3.60 (2H, dd, 12.0, 5.4 Hz); 3.09 (2H, m); 2.76 (2H, dd, 5.2, 4.1 Hz); 2.59 (2H, dd, 5.2, 2.9 Hz); 0.42 (12H, s).

^{13}C NMR ($CDCl_3$/TMS, δ (ppm)): 139.7 (s); 132.8 (d); 63.8 (t); 52.1 (d); 44.6 (t); −1.9 (q).

2.4. Synthesis of triglycidyloxyphenyl silane (TGPS)[6]

Phenyltrimethoxy silane (10.0 g; 0.052 mol), glycidol (23.1 g; 0.312 mol) and titanium tetraisopropoxide (0.3 g; 0.001 mol) were added to a 250-ml round-bottomed flask. The progress of the reaction was monitored by thin-layer chromatography (8:2 hexane/ethyl acetate). After 10 h of stirring at room temperature, the reaction was complete. The excess of glycidol was distilled off at 40 °C under vacuum and the residue was dissolved in 150 ml of toluene and washed twice with 5 wt% tartaric acid, three times with 5 wt% $NaHCO_3$, and with water and brine. The organic layer was dried over $MgSO_4$, filtered and then the solvent was evaporated at reduced pressure. The product obtained was purified by flash chromatography (8:2 hexane/ethyl acetate). The final product was obtained in a 75% yield.

^{1}H NMR ($CDCl_3$/TMS, δ (ppm)): 7.65 (2H, m); 7.42 (3H, m); 4.03 (3H, dd, 12.0, 3.2 Hz); 3.75 (3H, dd, 12.0, 5.2 Hz); 3.15 (3H, m); 2.78 (3H, dd, 4.4, 2.8 Hz); 2.65 (3H, dd, 4.4, 2.8 Hz).

^{13}C NMR ($CDCl_3$/TMS, δ (ppm)): 134.9 (d); 132.2 (s); 130.6 (d); 127.9 (d) 63.8 (t); 52.0 (d); 44.5 (t).

2.5. Preparation of DGEBA–DPSD epoxy prepolymers

DGEBA–DPSD epoxy prepolymers (EpSi) were prepared by reacting DGEBA (Epikote 828) with DPSD and using 500 ppm tin (II) chloride as a catalyst. Two compositions of reactants were used to result in epoxy compounds with different silicon contents (see Table 1). The EpSi 2-1 was obtained by means of a bulk reaction of 12.0 g of DGEBA, 3.4 g of DPSD and 0.008 g of $SnCl_2$. The reaction mixture was stirred at 180 °C for 30 min. The EpSi 3-2 was obtained by the same procedure using 9.0 g of DGEBA, 3.4 g of DPSD and 0.006 g of $SnCl_2$ at 165 °C for 25 min. EpSi 2-1: EEW = 510 (calculated: 488); EpSi 3-2: EEW = 713 (calculated: 730).

2.6. Curing reactions

The curing conditions for monomers and prepolymers were established by Differential Scanning Calorimetry. Samples

Table 1
Prepolymers from DGEBA/DPSD

Prepolymer	% Si[a] (wt.)	Molar ratio		Reaction conditions		EEW (g/mol)	
		DGEBA	DPSD	T (°C)	t (min)	Calculated	Experimental
EpSi 2-1	2.9	2	1	180	30	488	510
EpSi 3-2	3.6	3	2	165	25	730	713

[a] Theoretical value.

were prepared by dissolving epoxy monomer and DDM in CH_2Cl_2. This solution was then evaporated at room temperature *in vacuo*. For epoxy prepolymers, mixtures were obtained by mechanical mixing with the stoichiometric amount of hardener. About 5 mg of a known weight of the mixture was put into an aluminum pan, and the polymerization was monitored in a dynamic DSC experiment using a heating rate of 10 °C/min. The curing conditions are shown in Table 2.

Molded epoxy resins for DMTA and LOI measurements were obtained by molding about 1.5 g of a known weight of the mixture obtained as described above. The prepolymers were compression molded with a manual 15-ton hydraulic press (SPECAC) equipped with water-cooled heated plates.

2.7. Instrumentation

^1H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were obtained with a Varian Gemini 300 spectrometer with Fourier Transform, $CDCl_3$ as a solvent, and TMS as an internal standard. The IR spectra were obtained with an ATR-FTIR JASCO 680.

Calorimetric studies were carried out on a Mettler DSC821e thermal analyser using N_2 as a purge gas (20 ml/min). Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 and air as a purge gas at scan rates of 10 °C/min. Mechanical properties were measured using a dynamic mechanical thermal analysis (DMTA) apparatus (TA DMA 2928). Specimens ($3 \times 6 \times 10$ mm^3) were tested in a three point bending configuration. The thermal transitions were studied in the −100 to 250 °C range at a heating rate of 5 °C/min and at a fixed frequency of 1 Hz. LOI values were measured on a Stanton Redcroft, provided with an oxygen analyser, on bars of the polymers $100 \times 6 \times 4$ mm^3.

3. Results and discussion

In this study, two different approaches were used to introduce silicon into the epoxy resins: using new reactive silicon-containing monomers and reacting a silanol with DGEBA in a chain extension process (Schemes 1 and 2). Three silicon-containing epoxy monomers were obtained. When cured with DDM, triglycidyloxyphenyl silane (TGPS) and diglycidyloxydiphenyl silane (DGDPS), lead to a crosslinked epoxy resin with ca. 6.5% of silicon, but with different crosslinking densities because of the tri- and bifunctional natures of the monomers. 1,4-Bis(glycidyloxydimethyl silyl) benzene (BGDMSB), which has a higher silicon content provides final resins with 12.8% of silicon.

TGPS can be synthesized by two methods: [5,6] (1) condensation of trihydroxyphenyl silane with epichlorohydrin and (2) catalysed transetherification of the trimethoxyphenyl silane with glycidol. As a first approach, we synthesized TGPS by hydrolyzing starting trimethoxyphenyl silane with the stoichiometric amount of water and using *p*-toluene sulfonic acid as a catalyst. The trihydroxyphenyl silane obtained was condensed with an excess of epichlorohydrin and the siloxane derivative was obtained as the main product because the hydrolyzed silane self-condensed.

The transetherification of trimethoxyphenyl silane has been shown to lead to higher yields. The reaction is carried out at room temperature using titanium tetraisopropoxide as a catalyst and stoichiometric amounts of the reactants. In our case it was necessary to add a 100% excess of glycidol to obtain the expected product in a 70% yield after 10 h of reaction. TGPS was characterized by ^1H and ^{13}C NMR spectroscopies.

DGDPS was synthesized by the transetherification method. The reaction rate was lower and after 24 h a mixture of mono- and diglycidyl compounds was obtained. Increasing the reaction temperature to 60 °C led to a shorter reaction time and a higher yield, but the main reaction was the polymerization of the glycidol.

To overcome these problems, the silicon-containing epoxy monomer was synthesized in two steps: Lewis acid catalysed transetherification of dimethoxydiphenyl silane with allyl alcohol and further epoxidation with MCPBA (Scheme 1). In this way, DGDPS was obtained in good yield and characterized by ^1H and ^{13}C NMR spectroscopies.

BGDMSB was obtained in a similar way, but using silanol as starting material. The first step was condensation with allylic alcohol followed by the epoxidation of the intermediate compound. Fig. 1 shows the ^1H and ^{13}C NMR spectra with their signal assignments, which confirm the expected structure.

Silicon-containing advanced epoxy resins were obtained by reacting diphenylsilanediol (DPSD) and DGEBA using $SnCl_2$ as a catalyst (Scheme 2). Various DPSD/DGEBA ratios were used to obtain different silicon contents in the prepolymer. The reaction was monitored by DSC and showed an exotherm centered at 198 °C. From this result, the reaction conditions

Table 2
Curing conditions of monomers and prepolymers

Sample	% Si (w/w)	T_{onset} (°C)	T_{max} (°C)	Curing		Postcuring		T_g (°C)	
				T (°C)	t (min)	T (°C)	t (min)	$1/2\Delta C_p$	Tan δ
DGEBA/DDM	–	135	168	120	120	180	120	155	158
EpSi 2-1/DDM[a]	2.4	96	136	140	60	160	60	124	131
EpSi 3-2/DDM[a]	3.3	106	135	130	60	160	60	110	112
DGDPS/DDM	6.5	128	167	120	150	170	120	94	103
TGPS/DDM	6.6	93	135	120	150	170	120	100	106
BGDMSB/DDM	12.8	106	160	120	180	170	120	60	64

[a] Compression molded at 0.4 MPa.

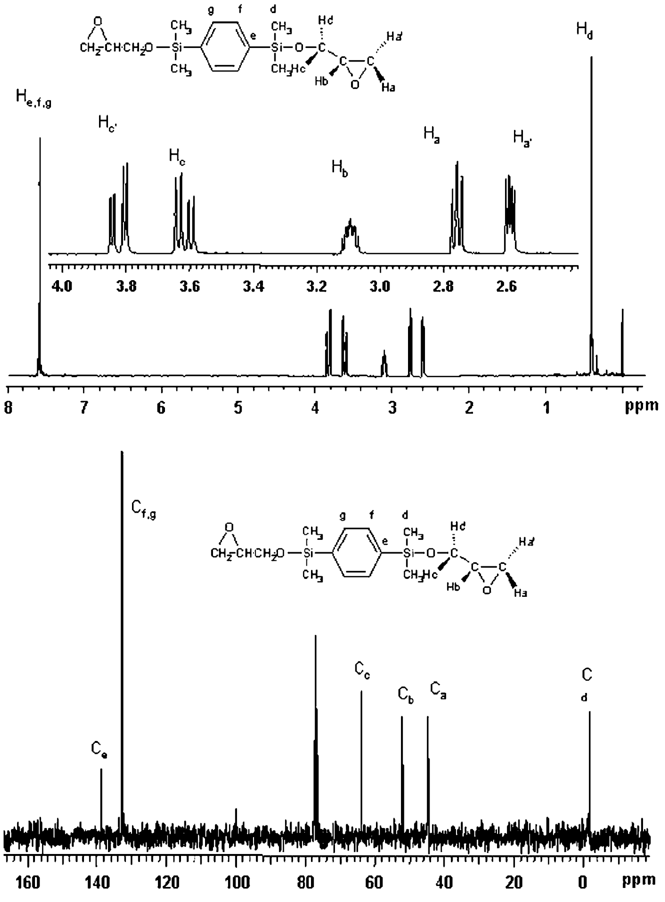


Fig. 1. ^{1}H and ^{13}C NMR spectra of 1,4-bis(glycidyloxydimethyl silyl) benzene (BGDMSB).

were established (Table 1) and prepolymers with different silicon contents were prepared with 2:1 and 3:2 DGEBA/DPSD molar ratios. The EEW values of the epoxy prepolymers obtained by titration were similar to those calculated from the feeding composition. IR and ^{13}C NMR spectroscopies were used to confirm the opening of the oxirane ring by the hydroxyl oxygen and the existence of Si—O—C bonds.

To obtain silicon-containing epoxy networks, the monomers and prepolymers were crosslinked using primary diamines as curing agents. Fig. 2 shows the crosslinking exotherms of EpSi 3-2, TGPS, BGDMSB and DGDPS cured by stoichiometric amounts of diaminodiphenylmethane. The crosslinking exotherm of the DGEBA/DDM system has been included for the purpose of comparison.

The epoxy resin with the lowest peak exothermic temperature under the same curing conditions was more reactive toward the curing agent. The EpSi prepolymer showed the highest reactivity. This can be explained by the presence of hydroxyl groups formed during the ring opening reaction in the chain extension process, which catalyses the epoxy-amine reaction. The higher reactivity of the oxirane group in silicon-containing epoxides is probably due to electronic effects. The silicon atom acts as a π acceptor, withdrawing the electron density of the oxygen atom. Therefore, its electron density is low, and its electron-withdrawing character increases, which in turn increases the electrophilic character of the oxirane carbons [9]. Table 2 summarizes the crosslinking data, the curing conditions and the T_gs of the final materials. As can be seen, the T_g of the materials from the prepolymers is higher than from the monomers. This difference must be attributed to the chemical structure of DGEBA which contains aromatic moieties that restrict the segmental mobility. The T_gs of epoxy resins from TGPS are higher than epoxy resins from DGDPS. Since their chemical structure is similar, the difference can be attributed to the higher crosslinking density of the resin from the trifunctional monomer. Thermosets from BGDMSB have a low T_g value that must be related to the higher proportion of the larger volume fraction of Si—O and Si—C units in the backbone [10].

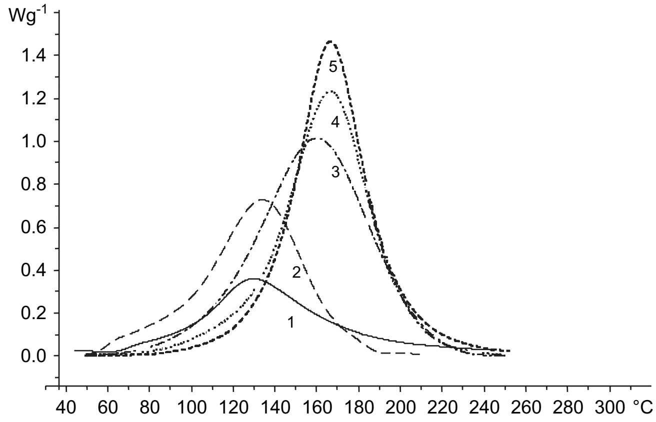


Fig. 2. Crosslinking exotherms of EpSi 3-2 (1), TGPS (2), BGDMSB (3), DGDPS (4), and DGEBA (5) cured by stoichiometric amounts of diaminodiphenylmethane (10 °C/min).

The dynamic mechanical behavior of the silicon-containing epoxy resins was obtained as a function of the temperature beginning in the glassy state of each composition to the rubbery plateau of each material (Fig. 3). The crosslinking density was estimated from the plateau of the elastic modulus in the rubbery state. However, this theory is valid only for lightly crosslinked materials and was therefore used to make qualitative comparisons of the crosslinking density among the various polymers [11]. As can be seen, resins from EpSi 3-2, EpSi 2-1 and TGPS have higher crosslinking densities than the ones from silicon-containing monomers DGDPS and BGDMSB.

Fig. 3 shows the plots of loss factor versus temperature. As can be seen, β relaxations occur around −60 °C, which may be due to the motion of [$-CH_2-CH(OH)-CH_2-O-$] aliphatic segments from the epoxide ring opening [12]. The T_gs of the crosslinked materials can be detected as the α relaxation peak of the loss factor (Table 2). As can be seen, the T_g values from DMTA follow the trend mentioned above. Because the height of the tan δ peak is the ratio of viscous components to elastic components, it can be assumed that the decreasing height is associated with lower segmental mobility and fewer relaxing species and therefore indicates that the networks for the DGEBA-containing samples and for the TGPS-containing samples are tighter.

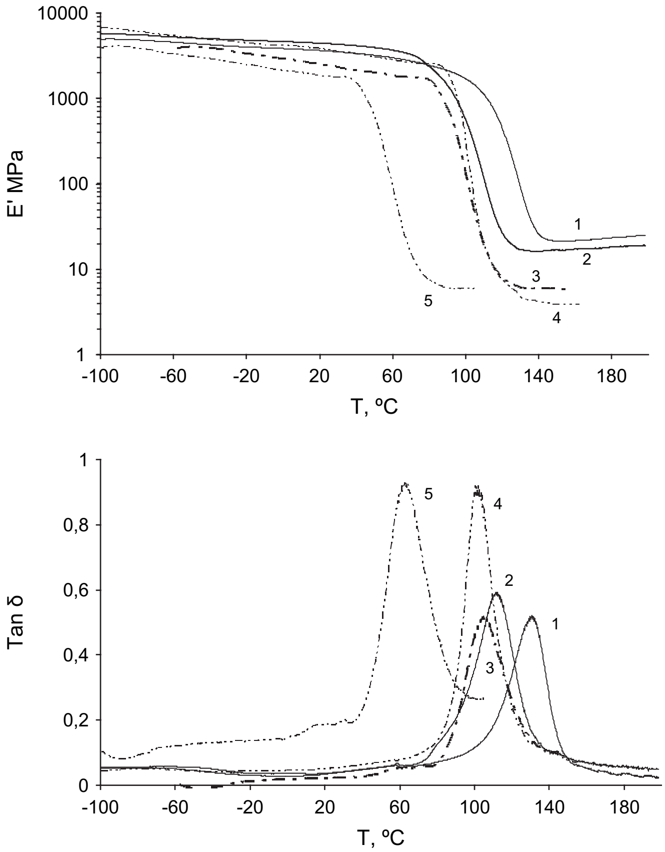


Fig. 3. Storage modulus and loss factor of crosslinked polymers EpSi 2-1 (1), EpSi 3-2 (2), TGPS (3), DGDPS (4), and BGDMSB (5).

The peak width at half height broadens as the number of branching modes increases, which produces a wider distribution of structures. The range of temperatures at which the different network segments gain mobility therefore increases. There were no significant differences among the samples, so the branching distribution for all resins was similar.

The thermal properties of the cured epoxy resins were evaluated by TGA under nitrogen and air. Fig. 4 shows the weight loss with the temperature under nitrogen for the epoxy compositions and also the derivative curves. Table 3 summarizes the temperature of the 5% weight loss (onset decomposition temperature), the temperature of the maximum rate of weight loss and the char yield at 700 °C.

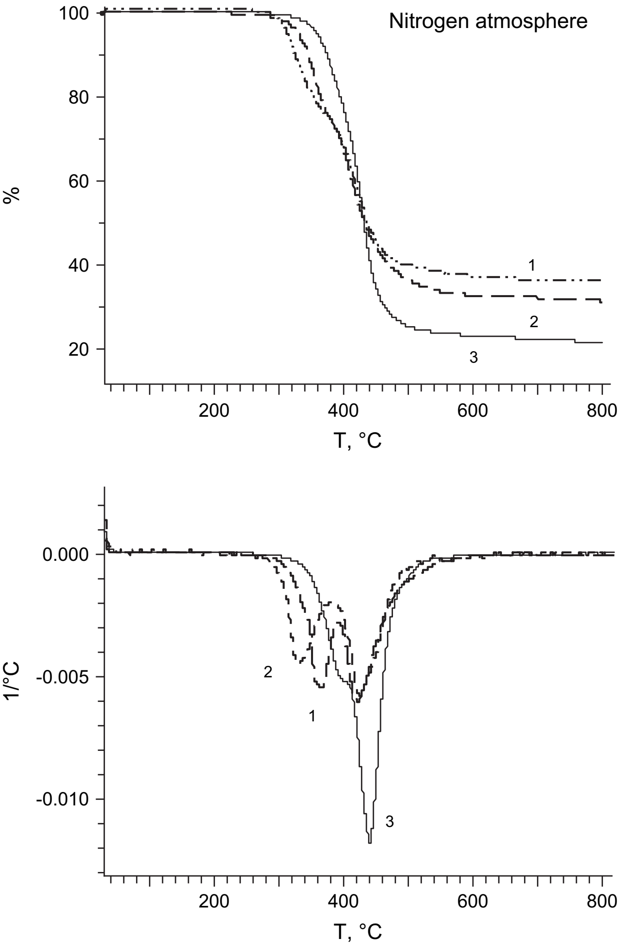


Fig. 4. TGA plots (10 °C/min) and derivative curves of crosslinked polymers TGPS/DDM (1), DGDPS/DDM (2), and BGDMSB/DDM (3).

The onset decomposition temperatures in nitrogen and air of the EpSi 2-1/DDM and EpSi 3-2/DDM resins are very close to those of the DGEBA/DDM system, to suggest that incorporating silyl groups into the epoxy compound did not apparently alter the thermal stability of the epoxy resin. This can be explained by the high thermal stability of the oxydiphenylsilane group (O—SiPh$_2$—) [13]. On the other hand, the thermal stability of the resins obtained from the silicon-containing monomers DGDPS and TGPS is significantly lower, even though the DGDPS contains the oxydiphenylsilane moiety. The resins from BGDMSB show a higher $T_{5\%}$, which may be due to the presence of a rigid silphenylene moiety [14] in the backbone.

Table 3
TGA data and LOI values of the polymers

Sample	% Si (w/w)	Nitrogen				Air					LOI %O$_2$
		$T_{5\%}$ (°C)	T_{m1}[a] (°C)	T_{m2}[a] (°C)	Char (%)	$T_{5\%}$ (°C)	T_{m1}[a] (°C)	T_{m2}[a] (°C)	T_{m3}[a] (°C)	Char (%)	
DGEBA	0.0	351	383	–	17	330	381	559	–	0	26.1
EpSi 2-1	2.4	364	416	–	33	342	417	655	–	5	–
EpSi 3-2	3.3	350	415	–	33	329	419	641	–	3	–
DGDPS	6.5	317	325	418	36	301	321	400	650	13	27.2
TGPS	6.6	282	330	430	40	263	320	425	622	12	30.0
BGDMSB	12.8	370	388	439	21	355	427	486	687	12	33.5

[a] Temperature of the maximum weight loss.

In nitrogen, the resins from the prepolymers have a single major break in their decomposition curves. The temperature of the maximum weight loss rate for these resins is higher than that of the DGEBA resin. The weight loss behavior in nitrogen of the epoxy resins from silicon-containing monomers shows that more than one process occurs during thermal degradation. When the amount of silicon increases, a first degradation step appears at low temperatures, which shifts to higher temperatures at higher silicon contents. This behavior is in accordance with the mechanism of improved fire performance via silicon modification. It has been indicated that the decomposition of silane groups forms a silicon-rich residue after the initial weight loss, which acts as a thermal insulator and prevents gas evolution, and thus slows down further decomposition and retards flame formation [6]. The higher char yield at 700 °C for the silicon-containing resins indicates that the formation of a silicon-rich protective layer plays an important role in flame retardation.

The decomposition in air starts at lower temperatures than in nitrogen for all the resins. The shape of the derivative curves of the thermograms in air indicates that there is a second step for EpSi 2-1 and EpSi 3-2, and a third step for DGDPS, TGPS and BGDMSB at temperatures higher than 600 °C. These steps are attributable to the thermooxidative degradation. As can be seen, the introduction of silicon into the epoxy is able to cause carbonization of the structure and leads to higher oxidation temperatures, lower maximum weight loss oxidation rates and enhanced char formation at high temperatures. We investigated the flame retardant properties of the materials by measuring the LOI values. As can be seen, the presence of silicon increases the LOI values and significant differences can be observed with the silicon content.

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