

Synthesis of Polysiloxane-Type Multifunctional Flame Retardant and Its Application in Epoxy Systems

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ABSTRACT: Polymethyl(3-glycidyloxypropyl)siloxane (PMGS) was synthesized as a flame-retardant additive, which were cured with diglycidyl ether of bisphenol-A (DGEBA) using 4,4'-diaminodiphenylsulfone as a curing agent. The structure of PMGS was confirmed through Fourier transform infrared and $^1\text{H-NMR}$ spectra. The cured products were characterized with dynamic mechanical thermal analysis, thermogravimetric analysis, and oxygen index analyzer. With

PMGS incorporated, the cured epoxy resin showed better thermal stability, higher limited oxygen index, and higher char yield. At moderate loading of PMGS, the storage modulus and glass transition temperature of the cured epoxy resin based on neat DGEBA were obviously improved. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4915–4919, 2012

Key words: flame retardant; epoxy resins; polysiloxane

INTRODUCTION

Epoxy resin, especially diglycidyl ether of bisphenol A (DGEBA), is a widely used thermosetting resin due to its outstanding properties, including excellent chemical and corrosion resistance, superior mechanical/electrical properties, and good thermal and dimensional stability.^{1–5} However, epoxy resin product is easy to combust when it is ignited, which limited its applications in some fields that require flame-retardant performance.^{6–9}

The flame retardancy could be improved by incorporating epoxy monomer and/or curing agent containing phosphorus, silicon, boron, and nitrogen as reactive flame retardants.^{10–15} Among those, the silicon-based ones were attractive because it could improve not only flame retardancy but also electrical properties, thermal stability, and flexural and impact properties of the epoxy resin.^{16–18} Besides, they were considered to be environment-friendly additives for their less harmful impact on environment compared with other ones.^{18–21} Nevertheless, some drawbacks, such as low efficiency in flame retardation, high cost, and complicated synthesis procedures. Nevertheless, some drawbacks, such as low efficiency in flame retardation, high cost, and complicated synthesis procedures limited its application.

In this work, polymethylhydrosiloxane (PMHS) was chosen as a starting material to prepare a silicon-based flame retardant. Through addition of allyl

groups of allyl glycidyl ether (AGE) to Si—H groups in PMHS up to 30 AGE groups could be incorporated onto the backbone of polysiloxane. About 30 allyl glycidyl ether groups could be incorporated onto the backbone of polysiloxane through addition reaction of allyl groups of allyl glycidyl ether (AGE) with Si-H groups in polymethylhydrosiloxane (PMHS). When cured with DGEBA, these epoxy groups may greatly enhance the density of crosslinking, thus increased the glass transition temperature and modulus of the cured system. Particularly, when burned, the silicon atoms on the backbone formed silica on the surface of the burning polymer, which acted as a heat shield to retard further decomposition of the cured products, thus increased the flame retardancy of epoxy resins.

EXPERIMENTAL SECTION

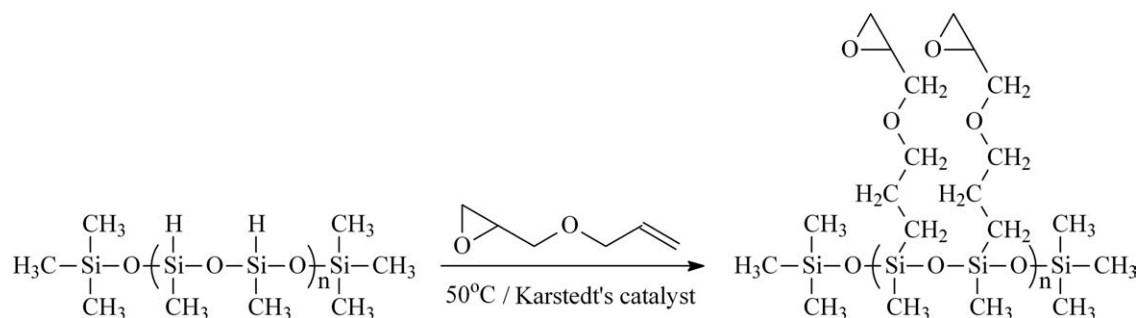
Materials

PMHS (viscosity 25–35cST) was supplied by Jilin Huafeng Organosilicon, China. AGE and 4,4'-diaminodiphenyl sulfone (DDS) were obtained from Aladdin reagent Shanghai. Karstedt's catalyst (complex of platinum with divinyltetramethyldisiloxane in toluene, 3000 ppm) was supplied by Dalian Toyonger Chemical, China, and was used as the catalyst of hydrosilation. DGEBA (epoxy equivalent weight EEW 196) was obtained from Wuxi Resin Factory, China.

Synthesis of the polymethyl(3-glycidyloxypropyl)siloxane

A 100-mL flask equipped with a magnetic stirrer, thermometer, reflux condenser, and a pressure-

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Scheme 1 Synthesis scheme of PMGS.

equalizing dropping funnel was charged with 13.70 g (0.12 mol) of AGE and five drops (about 100 μL) of Karstedt's catalyst. After the mixture was heated to 50°C with stirring, a solution of 5.0 g PMHS in 20 mL of THF was introduced dropwise. The addition lasted for about 1h, after which time the mixture was further stirred at 50°C for additional 6 h for the reaction between Si-H and C=C double bond to occur. After completion of the reaction, the flask was connected to a vacuum system to remove THF and the excess AGE leaving a colorless, transparent liquid product, which would be denoted as polymethyl(3-glycidyloxypropyl)siloxane (PMGS) later. The reaction was shown in Scheme 1.

Preparation of cured epoxy resins samples

DGEBA was mixed with PMGS at various weight ratios at 120°C followed by removal of air bubbles and moisture under vacuum. DDS was added as a curing agent with a stoichiometric amount. The mixture was cured at 130°C for 2 h, 180°C for 2h, and finally postcured at 200°C for 1h.

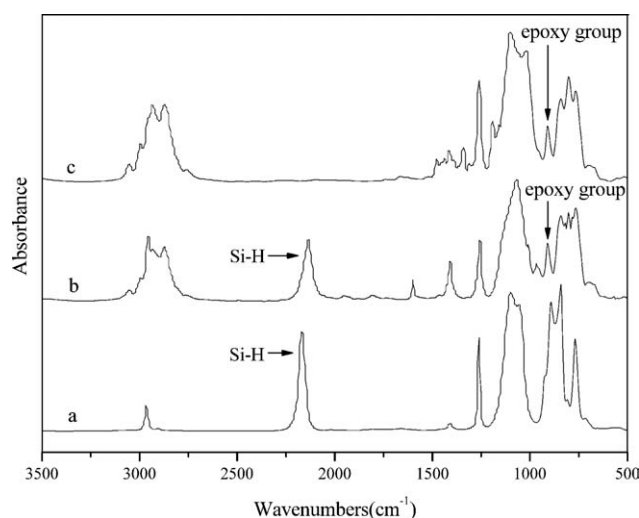


Figure 1 FTIR spectra of PMHS (a), intermediate product at the reaction time of 3h (b), and PMGS (c).

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Nexus 670 infrared spectrometer. ^1H nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were obtained by a Bruker AV600 NMR spectrometer at 300 MHz using CDCl_3 as solvent with tetramethylsilane as internal standard. Thermogravimetric analysis (TGA) was carried out on NETZSCH STA 449C TG-DSC simultaneous analyzer at a heating rate of 10°C/min under argon and air atmosphere.

Limiting oxygen index (LOI) was determined using a HD-2 oxygen index apparatus with a magnetodynamic oxygen analyzer according to ASTM D-2863. The sample ($65 \times 3.0 \times 0.5 \text{ mm}^3$) was clamped vertically in the center of the combustion column and was ignited by a butane burner with a mixture of oxygen and nitrogen continuously going through a flow rate of 10 L/min. The flammability was determined by the minimum concentration of oxygen for supporting the combustion.

Dynamic viscoelastic properties were measured using a Rheometric Scientific DMTA-V Analyser using $2 \text{ mm} \times 5 \text{ mm} \times 30 \text{ mm}$ rectangular samples

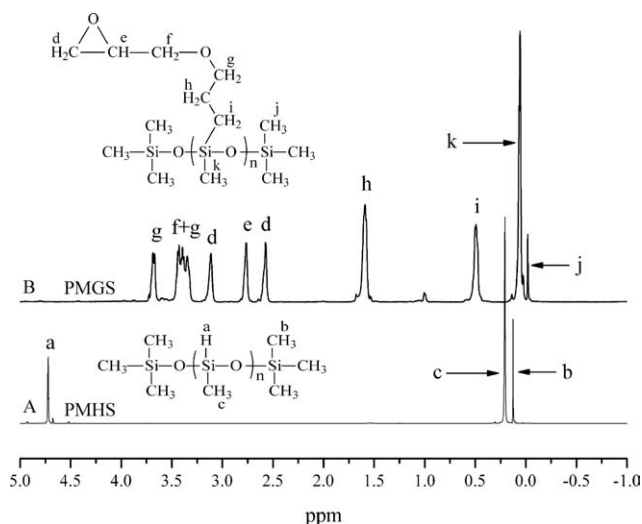


Figure 2 $^1\text{H-NMR}$ spectrum of PMHS (a) and PMGS (b).

TABLE I
Area Integration Ratios of the H-Band in the NMR Spectra of PMHS and PMGS

Assignment	C_a	C_d	C_e	$C_f + C_g$	$C_h + C_i$	$C_b + C_c$	$C_j + C_k$
PMHS	1.00	—	—	—	—	3.85	—
PMGS	0	1.92	1.00	3.99	4.04	—	3.91

at a programmed heating rate of 5°C /min at a frequency of 1 Hz under nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis and characterization

FTIR spectra of PMHS and PMGS were shown in Figure 1. PMGS was obtained through hydrosilylation between PMHS and AGE. On the spectrum of PMHS (trace a), absorption peaks for Si—H (2134 cm^{-1}) was clearly observed, which became smaller with increasing reaction time (trace b) and disappeared when PMGS (trace c) was formed. This indicated that the hydrosilylation was almost complete. In the trace of b, the appearance of peak at 2134 cm^{-1} (Si—H) and 911 cm^{-1} suggested partial substitution of Si—H in PMHS. In the trace c, the appearance of epoxy feature at 911 cm^{-1} suggested the introduction of epoxy groups onto PMHS. All the spectra in Figure 1 demonstrated qualitatively the successive preparation of PMGS.

Figure 2 showed the $^1\text{H-NMR}$ spectra of PMHS (A) and PMGS (B). For PMHS, characteristic shifts at 4.72, 0.21, and 0.13 ppm can be attributed to Si—H, Si— CH_3 , and Si—(CH_3) $_3$, respectively. Taking the peak integral of Si—H as 1.00, the peak integrals of Si— CH_3 and Si—(CH_3) $_3$ were 3.24 and 0.61, respectively. That suggests that the n in Scheme 1 is about 15. For PMGS, the chemical shifts are assigned as follows: 3.11, 2.58, and 2.76 ppm (epoxy group), 3.35–3.44 ppm, 3.69 ppm (— CH_2 —O— CH_2 —), 1.59 ppm (Si—C— CH_2), 0.50 ppm (Si— CH_2 —C), 0.07 ppm (Si— CH_3), and 0.02 ppm (Si—(CH_3) $_3$). The chemical shift signal of Si—H at 4.72 ppm disappeared, which confirmed that the hydrosilylation between PMHS and AGE was almost complete. All these characteristic NMR bands indeed match the expected PMGS structures. The integrated value of these peaks also matches well to the number of hydrogen atoms in the PMGS structure as list in Table I.

Mechanical and thermal properties

The dynamic mechanical thermal analysis (DMTA) curves in Figure 3(b) showed the effect of PMGS content on the storage modulus (E') and tangent loss angle ($\tan \delta$) of the modifier epoxy resin measured via DMTA. It could be noticed that when the contents of PMGS were lower than 15 wt %, the storage moduli of the samples were higher than that of the

neat DGEBA/DDS system; when the PMGS content was 20 wt %, E' decreased to below the value of the neat system. The reason could be explained as a competitive process. The modifier PMGS played a twofold role: (i) it possessed a functionality of 30, when incorporating the curing reaction, the cross-linking density of the resulted network would be increased and thus stiffening the product; (ii) it contained —Si—O— bonds, which may promote the movement of the segments, resulting in softening of the material. On moderate loading of PMGS, most epoxy groups on PMGS would participate the curing reaction, the effect of enhancing crosslinking density was more important and the material was stiffened. If the PMGS loading increased to a critical value (say, 15 wt %), the epoxy groups in the system

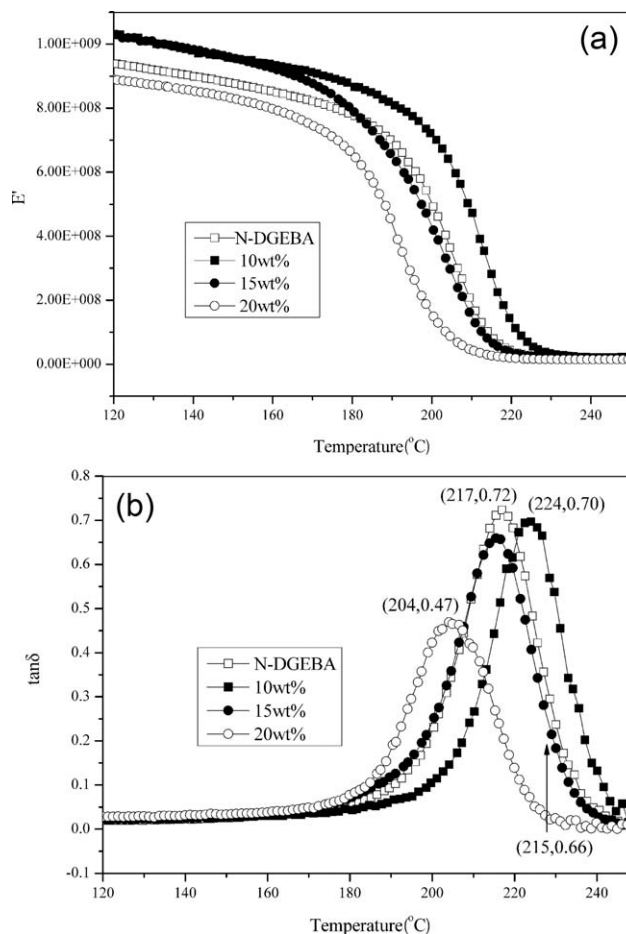


Figure 3 Temperature dependences of storage modulus E' and $\tan \delta$ for cured epoxies with various contents of PMGS.

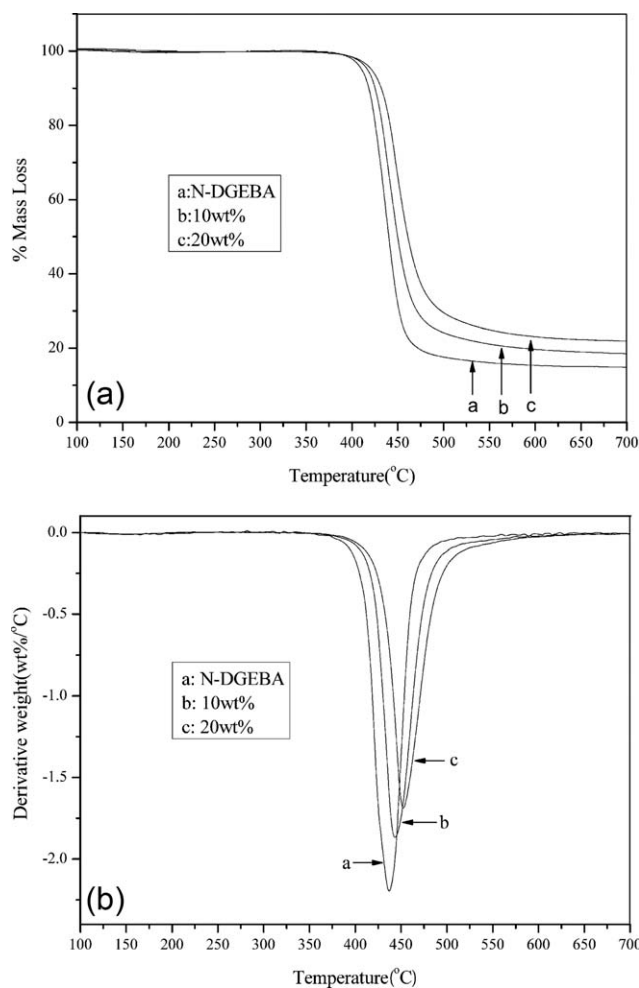


Figure 4 TGA weight loss curves of the cured PMGS/DGEBA in argon at a rate of 10°C/min to 700°C.

became too crowded and a considerable fraction of them were remaining unreacted, as a result, the softening effect of the $-\text{Si}-\text{O}-$ bonds became overwhelming and the E' was lowered.

Similar competitive effects were also reflected in the change of glass transition temperature. When the content of PMGS was moderate, the glass transition temperature was higher than that of the neat DGEBA/DDS system, which was attributed to the

TABLE II
Thermal Properties of Cured PMGS/DGEBA Products Under Argon Atmosphere

PMGS content (wt%)	T_5^a (°C)	T_{max}^b (°C)	Char yield at 700°C (%)
0	410.5	437.4	14.8
10	417.0	443.5	18.6
20	421.4	452.6	22.0

^a T_5 represents the onset decomposition temperature of 5% weight loss.

^b T_{max} represents the temperature of maximum rate of weight loss.

enhanced crosslinking density. When the content of PMGS was high (15~20 wt%), the glass transition temperature of the system became lower than that of the neat system, which was obviously resulted from the softening effect of the $-\text{Si}-\text{O}-$ bonds.

The thermogravimetric curves up to 700°C of the cured PMGS/DGEBA products under argon atmosphere are shown in Figure 4. The measured data were also summarized in Table II. It was seen that the higher the content of PMGS, the higher the temperatures for 5 wt % weight loss (T_5) and for maxima weight loss rates. This indicated that the thermal stability of the samples was improved after incorporation of PMGS into epoxy resin network. The $-\text{O}-\text{Si}-\text{O}-$ backbone of PMGS is able to absorb more thermal energy and its vibration can dissipate the thermal decomposition energy. The decomposition leads to the formation of a glassy char, which will participate in the crosslinked carbonization, and effectively retard the flame formation at higher temperature. In the case of thermal stability, the effects of crosslinking density were no

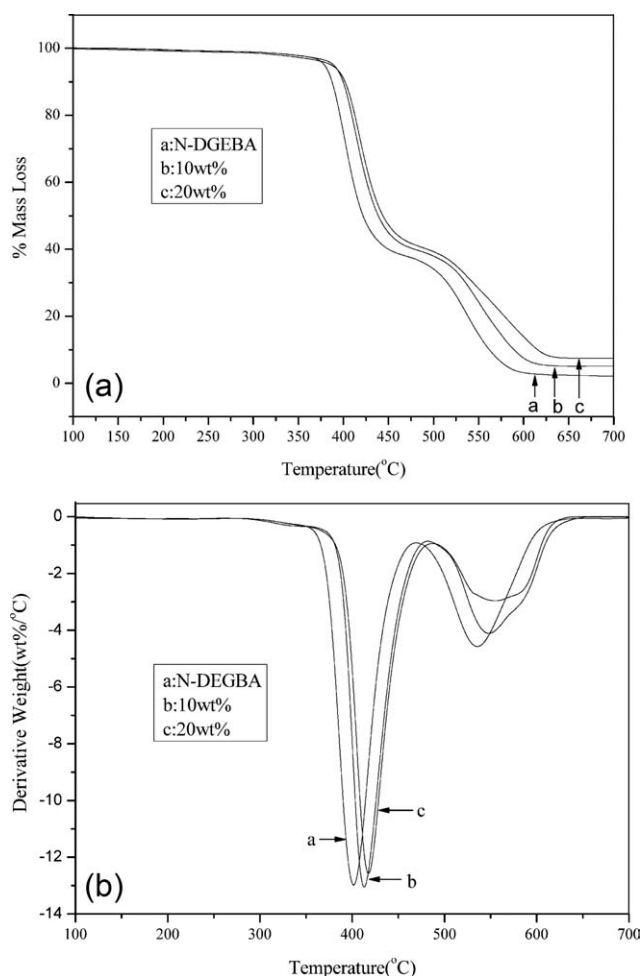


Figure 5 TGA weight loss curves of the cured PMGS/DGEBA in air at a rate of 10°C/min to 700°C.

TABLE III
Thermal Properties and Limiting Oxygen Indices of Cured PMGS/DGEBA Products Under Air Atmosphere

PMGS content (wt %)	T_5 (°C)	T_{max1} (°C)	T_{max2} (°C)	Char yield at 700°C (%)	LOI
0	379.0	404.2	544.4	2.1	23.2
10	389.2	418.9	563.7	5.1	26.4
20	386.6	422.8	586.5	7.4	29.5

longer competitive but cooperative; both made the material more thermal stable.

The thermogravimetric curves up to 700°C of the cured PMGS/DGEBA products under air atmosphere are shown in Figure 5. The measured data were also summarized in Table III. The carbonization mechanism dominates the first stage process. During combustion, silica layer forms on the surface of a burning cured product and may not only serve as a heat shield to retard further decomposition of the sample but also participate in the crosslinked carbonization. For decomposition at even higher temperature corresponding to the second stage, the surface layer of protective char reacts with oxygen in air and results in loss of weight. The introduction of PMGS into the epoxy structure is able to cause the crosslinked carbonization and results in higher oxidation temperature and, thus, raises flame retardation significantly.

Flame-retardant properties

Flame-retardant properties of the cured samples with varying contents of PMGS were evaluated by LOI measurement, and the data were presented in Table III. When the PMGS content was 20 wt %, the LOI value reached 29.5, which contrasted to 23.2 of the neat system. Such an improvement in flame retardancy was believed to arise from the silicon moieties. During combustion, silicon formed silica on the surface of a burning epoxy resin. The formation of silica layer serves as a heat shield to retard further decomposition of char at high temperature. As a result, as shown in Table III, the char yield of the samples containing 10 and 20 wt % of PMGS (5.1 and 7.4 wt %, respectively) were much higher than that of the neat DGEBA (2.1 wt %), the higher the content of PMGS, the higher the char yields.

CONCLUSIONS

A silicon containing polymer, PMGS was synthesized as a flame retardant additive, which was

cocured with DGEBA using DDS as a curing agent. The structure of PMGS was confirmed through FTIR and $^1\text{H-NMR}$ spectra. The cured products were characterized with DMTA, TGA, and oxygen index analyzer. With PMGS incorporated, the cured epoxy resin showed better thermal stability, higher LOI, and higher char yield.

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