

Syntheses of Epoxy-Bridged Polyorganosiloxanes and the Effects of Terminated Alkoxysilanes on Cured Thermal Properties

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ABSTRACT: A series of epoxy-bridged polyorganosiloxanes have been synthesized by reacting multifunctional aminoalkoxysilanes with diglycidyl ether of bisphenol A (DGEBA) epoxy resin. The reactions of trifunctional 3-aminopropyltriethoxysilane (APTES), difunctional 3-aminopropylmethyldiethoxysilane (APMDS), and monofunctional 3-aminopropyltrimethylethoxysilane (APDES) with DGEBA epoxy have been monitored and characterized by FTIR, ^1H NMR, and ^{29}Si NMR spectra in this study. The synthesized epoxy-bridged polyorganosiloxanes precursors, with different terminated alkoxysilane groups, are thermally cured with or without the addition of curing catalysts. Organometallic dibutyltindilaurate, and alkaline tetrabutylammonium hydroxide have been used as curing catalysts to investigate the thermal curing behaviors and cured properties of epoxy-bridged polyorganosiloxanes precursors. The maximum exothermal curing temperatures of epoxy-bridged polyorganosiloxanes precursors are found to appear around the same region of 120°C in DSC analysis. The addition of catalysts to the epoxy/APTES precursor shows significant influence on the cured structure; however, the catalysts exhibit less influence on the cured structure of epoxy-APMDS

precursor and epoxy/APDES precursor. Curing catalysts also show significant enhancement in increasing the thermal decomposition temperature ($T_{d50\%}$) of cured network of trifunctional epoxy-bridged polyorganosiloxane (epoxy/APTES). High $T_{d50\%}$ of 518.8 and 613.6 in the cured hybrids of epoxy/APTES and epoxy/APMDS precursors are also observed, respectively. When trialkoxysilane-terminated epoxy-bridged polyorganosiloxanes precursor are cured, with or without the addition of catalyst, no obvious T_g transition can be found in the TMA analysis of cured network. The cured network of trialkoxysilane-terminated epoxy-bridged polyorganosiloxanes also exhibits the lowest coefficient of thermal expansion (CTE) among the three kinds of alkoxysilane-terminated epoxy-bridged polyorganosiloxanes investigated. The organic-inorganic hybrid, from epoxy-bridged polyorganosiloxanes after the thermal curing process, shows better thermal stability than the cured resin network of pure epoxy-diaminopropane. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3491–3499, 2006

Key words: epoxy resin; aminoalkoxysilane; polyorganosiloxanes; thermal curing

INTRODUCTION

Epoxy resin has been utilized in many applications such as composite materials, electronic materials, and insulation materials because of its excellent adhesion, mechanical, and insulation properties. However, such properties are challenged in recent years by newly emerging requirements from the fast development of computer systems and electronic optical devices.¹ The development of organic-inorganic epoxy hybrid composites provide potential to meet the requirement of future application. There has been much research^{2–8} in studying the effect of polyorganosiloxane on the enhancement of thermal, optical, and mechanical properties of epoxy resin. Various kinds of organic-

inorganic polyorganosiloxane-epoxy hybrid systems have been developed in the past few years.^{9–11} The most popular synthetic route, to prepare an epoxy-polyorganosiloxane hybrid system, is to form polyhedral oligomeric polysilsesquioxanes (POSS) from the sol-gel process of TEOS, followed by the incorporation of epoxide group on the polyhedral terminal site. Such epoxy-terminated polyhedral oligomeric polysilsesquioxanes can be crosslinked with various kinds of curing agent to form an organic-inorganic epoxy-polyorganosiloxane hybrid networks.¹² Hybrid structure from this synthetic method is able to form nano size pore structure via the control of the forming of POSS structure. Utilizing the sol-gel process to obtain POSS structure is very sensitive to the conditions and catalyst used during synthesis process. The yield and purity of POSS precursor becomes a barrier for the preparation of epoxy-polyorganosiloxane hybrid system.

To overcome such disadvantages in preparing epoxy-polyorganosiloxane hybrid system from sol-gel

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process of TEOS, the use of organoalkoxysilanes has been considered as an effective starting compound to synthesize organic–inorganic hybrid. The reaction and kinetics of aminosilane with epoxy was first reported by Serier.^{13,14} The prepolymer from aminotrialkoxysilane with epoxy was synthesized and their final structures were discussed after the sol–gel process. Although the reaction of epoxide with aminosilane was reported by Serier,^{13,14} there is no discussion and comparison of the structural effects of terminated alkoxysilanes on the properties of final epoxy–polyorganosiloxane hybrid. The sol–gel process was used to obtain the epoxy polyorganosiloxane hybrid from the synthesized prepolymer. To develop a convenient process for the establishment of organic–inorganic hybrid network, from the epoxy–polyorganosiloxane precursors, a series of new epoxy-bridged polyorganosiloxanes have been prepared in this study to investigate the structural effects of terminated alkoxysilanes on the cured hybrid structures from direct thermal curing. Various kinds of epoxy-bridged polyorganosiloxanes precursors were prepared by reacting multi- or mono-functional aminoalkoxysilanes with difunctional epoxy resins in this study. Instead of a sol–gel process, the synthesized epoxy-bridged polyorganosiloxanes precursors were cured by the same traditional thermal curing condition to avoid the sensitive sol–gel process of alkoxysilanes. Good film strength and transparency of the organic–inorganic hybrid were obtained from the thermal curing process of epoxy-bridged polyorganosiloxanes precursors. Different kinds of catalysts have also been added to the precursor systems to study the effect of catalyst on the curing behavior and cured thermal properties of cured epoxy-bridged polyorganosiloxanes. Thermal curing behaviors and cured properties of the epoxy-bridged polyorganosiloxanes precursors corresponding to the structural of terminated alkoxyalkoxysilanes are also discussed and compared in this study.

EXPERIMENTAL

Materials

The diglycidyl ether of bisphenol A (DGEBA) epoxy used in this study was supplied by Nan Ya Plastic Co. Ltd. Taiwan, with epoxide equivalent weight of 190 g/eq. 3-Aminopropyltriethoxysilane (APTES, Z-6011) was purchased from Dow Corning, Co. (Midland, MI) with MW of 221.37, and 3-Aminopropylmethyldiethoxysilane (APMDS, M.W.: 191.34) was obtained from TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan. 3-Aminopropyltrimethylethoxysilane (APDES, M.W.: 161.32) was provided by GELEST Inc. (Morrisville, PA). Diaminopropane (DAP) was supplied from TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan. Both dibutyltindilaurate and tetrabutylammonium hydroxide were

obtained by TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan, which were used as curing catalysts for epoxy-bridged polyorganosiloxanes precursors.

Synthesis

Preparation of epoxy-bridged polyorganosiloxanes precursors

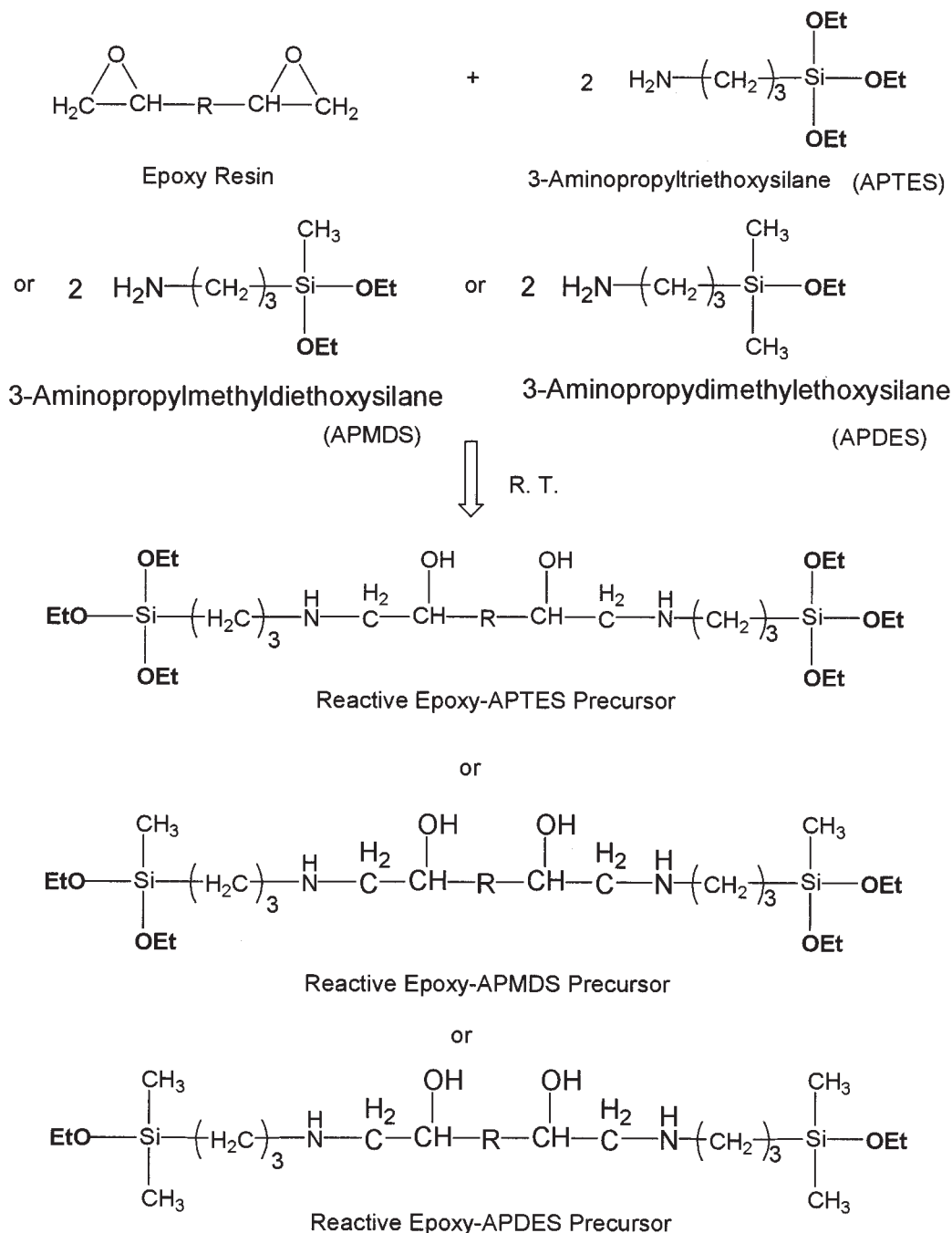
Stoichiometric amounts of APTES, APMDS, or APDES were added, respectively, to a 100-mL single-necked flask equipped with DGEBA epoxy in molar ratio of 1:2($n_{\text{epoxy}}:n_{\text{aminosilane}}$). The reaction mixture was then mixed with a magnetic stirrer at room temperature. FTIR was used to detect the changes of reactive group at various reaction times during synthetic process. After 4–5 h of reaction time, clear and low viscosity APTES, APMDS, or APDES-terminated epoxy-bridged polyorganosiloxanes precursors were obtained and characterized by FTIR and NMR. The reaction schemes of these three types of precursors are shown in Scheme 1.

Curing of epoxy-bridged polyorganosiloxanes precursors

The obtained reactive epoxy-bridged polyorganosiloxanes precursors were mixed without or with 1phr catalyst such as dibutyltindilaurate (DBTDL) or tetrabutylammonium hydroxide (NBu_4OH) at room temperature, respectively. After 30 min of mixing, the mixture becomes clear and homogeneous. The curing behavior of the clear mixture was investigated by dynamic DSC analysis. The clear precursor mixtures were poured into a one inch square aluminum pan and cured directly at 150°C for 2 h to obtain cured products of 1.5–2.0 mm in thickness to investigate the final properties of cured hybrid network. The cured structures of epoxy-APTES-bridged polyorganosiloxane (epoxy/APTES), epoxy-APMDS-bridged polyorganosiloxane (epoxy/APMDS), and epoxy-APDES-bridged polyorganosiloxane (epoxy/APDES) were analyzed by using FTIR and ²⁹Si Solid State NMR to study their changes in functional groups and the crosslinked structures. Diaminopropane (DAP) was also mixed with DGEBA epoxy at equal equivalent ratio and cured under 150°C for 2 h to compare with the properties of cured network of epoxy-bridged polyorganosiloxanes precursors. The thermal properties of cured epoxy/DAP were compared with those of cured epoxy-bridged polyorganosiloxanes precursors.

Thermal analysis

The curing behaviors of epoxy-bridged polyorganosiloxanes precursors obtained were analyzed by DSC (TA 2000, TA Instruments, Inc) under nitrogen with



Scheme 1

10°C/min of heating rate from room temperature to 250°C. Reactive precursors and cured organic-inorganic materials of about 10 mg were placed in the furnace chamber of TGA (TA 2000, TA Instruments, Inc) and heated to 800°C under nitrogen with a heating rate of 20°C/min to compare the thermal degradation temperatures and char yields. Cured organic-inorganic hybrid films with the dimensions of 2.0 × 0.3 cm² were hanged under 0.05N of tension force in the heating chambers of TMA (TA 2940, TA Instruments, Inc.) and heated to 200°C under nitrogen with

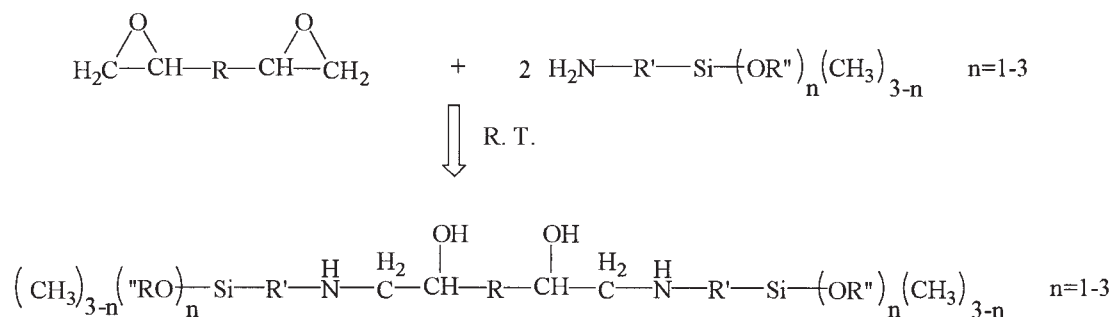
a heating rate of 10°C/min to observe their T_g s and coefficient of thermal expansion (CTE).

RESULTS AND DISCUSSION

Synthesis of epoxy-bridged polyorganosiloxanes precursors

Characterization of reactive precursors structures by FTIR

Since the amino group of aminosilane possesses stronger reactivity toward epoxide group than the alkoxide



Scheme 2

group of aminosilane, the reaction between aminosilane and epoxy group will form an alkoxy silane-terminated reactive precursor as shown in Scheme 2.²

As shown in Figure 1, the absorption peaks of epoxide group at 913 cm^{-1} of FTIR spectra decrease gradually with reaction time and finally disappear after 5 h of reaction time. The reaction is completed after 5 h of reaction. Since the absorption peaks of ethoxysilane ($-\text{Si}-\text{OC}_2\text{H}_5$) at 820–910, 1060, and 1180 cm^{-1} show no changes after reaction, the reactive alkoxy silane on both end of epoxy-bridged polyorganosiloxanes precursors are proved to exist after reaction. There are absorption peaks around 3200 cm^{-1} , which show the formation of hydroxy groups after the reaction of amine with epoxide group. The amino groups in aminosilanes react with epoxide group very rapidly at room temperature.

Characterization of reactive precursors structures by ^1H NMR

The terminated alkoxy groups in the epoxy-bridged polyorganosiloxanes precursors after reaction have

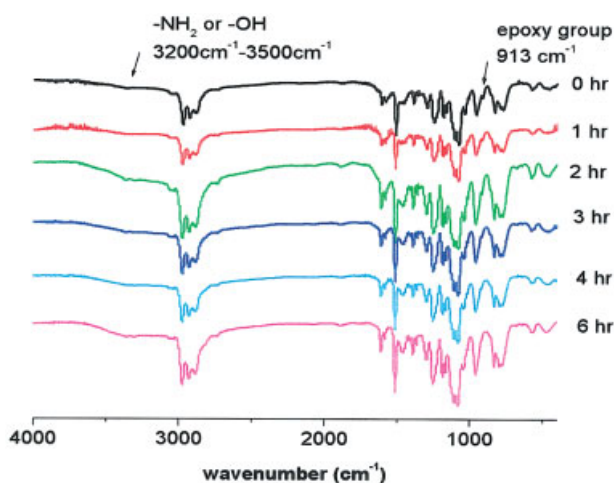


Figure 1 Changes of FTIR spectra of epoxy-APTES with respect to various reaction times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

been characterized by the analysis of ^1H NMR. The chemical shifts at δ 3.81 in Figure 2 show that the terminated ethoxy groups still exist in the structures of epoxy-bridged polyorganosiloxanes precursors.

Studies on the curing behaviors of epoxy-bridged polyorganosiloxanes precursors

DSC (Differential Scanning Calorimeter) analysis has been used to observe the curing behaviors of epoxy-bridged polyorganosiloxanes precursors. It can be found from Table I that the reactive epoxy-APTES precursor shows a maximum exothermal peak temperature at 120°C . The reactive epoxy-APTES bridged polyorganosiloxanes precursor can be thermally cured below 150°C in a conventional epoxy curing process. Trifunctional epoxy-APTES-bridged polyorganosiloxane precursor shows the highest T_{peak} of 120°C among the three kinds of bridged polyorganosiloxanes precursors studied. As shown in Figure 3, the epoxy-bridged mono-, di-, and triethoxysilane start to cure at 60°C and reach their maximum exothermal peak temperatures between 110 and 120°C . The curing temperatures of the bridged-silane precursors do not have much dependence on the functionalities of the terminated ethoxy groups. The heats of curing of the three kinds of bridged polyorganosiloxanes precursors were also measured, as summarized in Table I.

Characterization of cured structures of epoxy-bridged polyorganosiloxanes

Determination of cured structures of epoxy-bridged polyorganosiloxanes with ^{29}Si solid state NMR

Epoxy-bridged polyorganosiloxanes precursors, with or without catalysts, were thermally cured at 150°C for 2 h to obtain transparent solid films with a thickness of 1–2 mm. The cured structures of bridged polyorganosiloxanes have been characterized by ^{29}Si .¹⁵ In cured epoxy/APTES hybrid network, it was found that the spectra of ^{29}Si solid state NMR of cured network with catalysts show obvious differences with that of cured network without catalyst as shown in

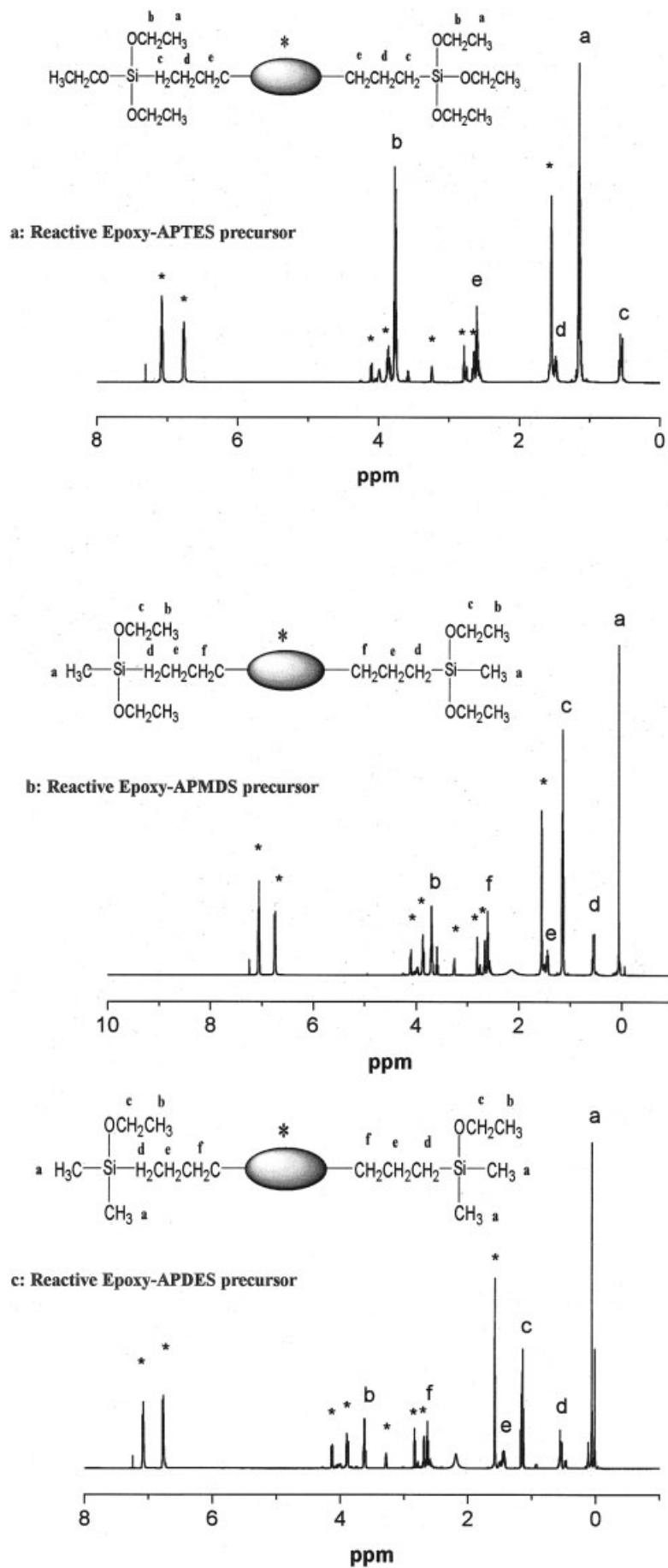


Figure 2 ^1H NMR spectra of (a): reactive epoxy-APTES precursor, (b): reactive epoxy-APMDS precursor, (c): reactive epoxy-APDES precursor.

TABLE I
DSC Analysis on the Curing Condition of Precursors

Properties	Precursor		
	Epoxy-APTES	Epoxy-APMDS	Epoxy-APDES
T_{peak} (°C) ^a	124.4	106.2	107.7
ΔH (kJ/mol) ^b	110.2	107.8	94.2
ΔH (kJ/mol per —OEt) ^c	18.4	27.0	47.1

The samples are measured with a heating of 10°C/min under nitrogen.

^a Maximum exothermal temperature during curing process.

^b Heat of curing per molar precursor.

^c Heat of curing per ethoxysilane equivalent.

Figure 4(a). The T^1 shift, δ , -46.104 ppm, disappeared when the catalyst DBTDL was added to the precursor as catalyst. T^1 shift, δ -46.104 ppm, and T^2 shift, δ -59.916 ppm, disappeared when NBu_4OH was used as catalyst in the curing of reactive epoxy-APTES precursors. The cured structures of the epoxy/APTES strongly depend on the quantity and the species of catalyst used. The ^{29}Si solid state NMR spectra of cured epoxy/APMDS is also observed to be affected by the catalyst used during curing. It can be found from Figure 4(b) that the D^1 and D^2 shift became stronger when DBTDL and NBu_4OH were added. The D^0 shift decays significantly when NBu_4OH is used in the curing process. There is a broad shift peak at the right shoulder of D^2 shift in the NBu_4OH -catalyzed epoxy/APMDS spectra. This indicates that the structure, cured with DBTDL catalyst, is different from that without catalyst. It is also very interesting to find that there is no obvious difference in the ^{29}Si NMR spectra of epoxy/APDES cured without and with catalyst of DBTDL. The addition of catalyst to the reactive epoxy-APTES precursors shows a significant influence on the cured structure. However, the effects

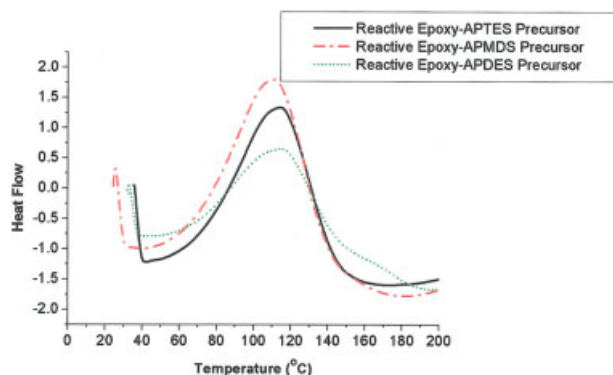
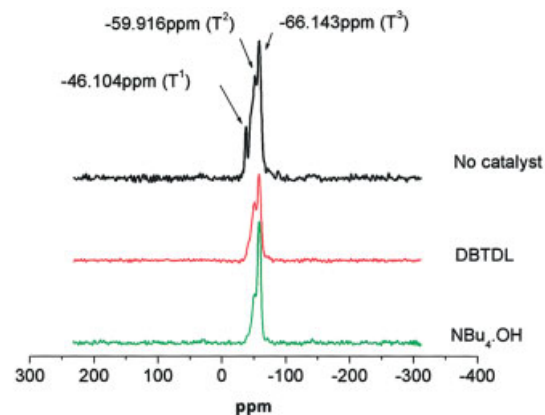
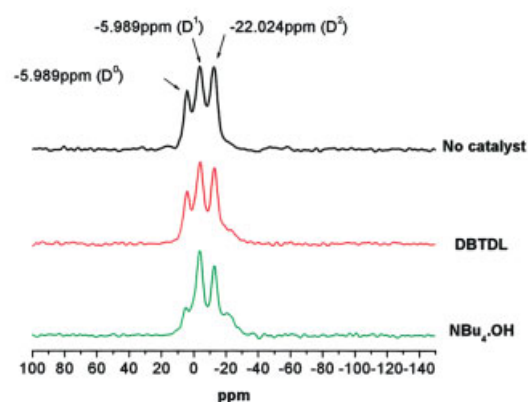


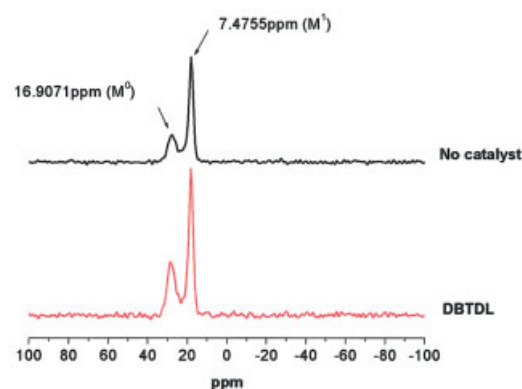
Figure 3 DSC analysis on the curing behaviors of epoxy-APTES precursor, epoxy-APMDS precursor, and epoxy-APDES precursor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



a: Epoxy/APTES



b: Epoxy/APMDS



c: Epoxy/APDES

Figure 4 ^{29}Si -NMR spectra of cured epoxy-bridged polyorganosiloxanes precursors with or without catalysts. (a) ^{29}Si -NMR spectra of epoxy/APTES with no catalyst, DBTDL, and NBu_4OH , (b) ^{29}Si -NMR spectra of epoxy/APMDS with no catalyst, DBTDL, and NBu_4OH , and (c) ^{29}Si -NMR spectra of epoxy/APDES with no catalyst and DBTDL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

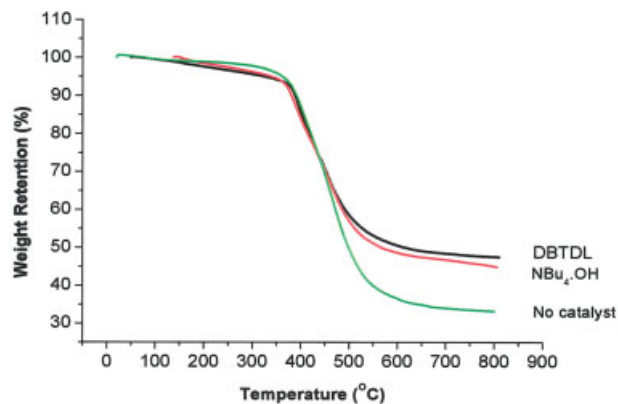


Figure 5 Comparison of TGA analysis among epoxy/APTES cured with DBTDL, NBu_4OH , and without catalyst. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

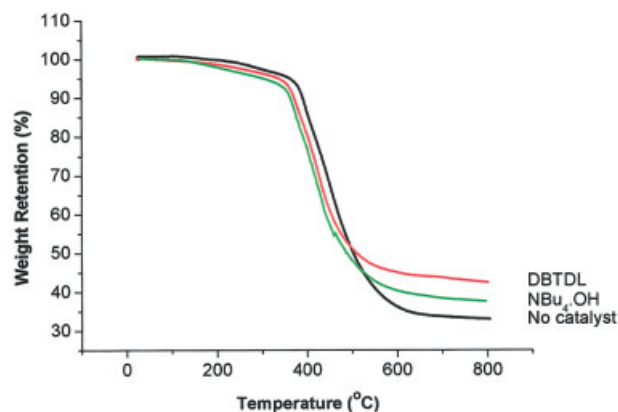


Figure 6 Comparison of TGA analysis among epoxy/APMDS cured with DBTDL, NBu_4OH , and without catalyst. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the catalysts exhibit insignificant effect on the cured structure of epoxy-APMDS precursor and epoxy-APDES precursor.¹⁶

Thermal properties of cured epoxy-bridged polyorganosiloxanes by direct curing process

Analysis on the thermal resistance of cured epoxy-bridged polyorganosiloxanes

The epoxy-bridged polyorganosiloxanes precursors are able to form tough and transparent films after a thermal curing process. Their thermal properties were investigated by thermal gravimetric analysis (TGA) and thermal mechanical analysis (TMA). The effect of catalyst on the thermal stability of cured epoxy-bridged polyorganosiloxanes was also analyzed and compared. In the epoxy/APTES-cured network, it was found that the addition of catalyst such as DBTDL and NBu_4OH enhanced the thermal stability of cured network. As shown in Figure 5 and Table II, the T_{d10} (decomposition temperature at 10% weight loss) of cured network with catalysts is 30°C higher than that of cured network without catalyst. When DBTDL and

NBu_4OH were used to catalyze the thermal curing of epoxy/APTES precursor, there was no obvious difference both in char yield and T_{d10} between the two catalytic systems. However, high T_{d50} (decomposition temperature at 50% weight loss) of around 500–600°C are found in the hybrids of epoxy/APTES cured without or with catalyst. When epoxy/APTES precursor was thermally cured with the addition of DBTDL or NBu_4OH , high T_{d50} s were found to reach 613.6 and 563.6°C which are 50°C higher than the T_{d50} of epoxy/APTES cured without catalyst, as shown in Table I. The char yield of network cured with catalyst is also higher than that of network cured without catalyst. The addition of catalyst to epoxy/APTES will increase the thermal stability of the cured hybrid structure.

When the epoxy/APMDS precursor is thermally cured without catalyst, or with catalysts of DBTDL and NBu_4OH , there is no obvious difference in the T_{d10} and T_{d50} as shown in Figure 6. However, cured hybrids of epoxy/APMDS with DBTDL and NBu_4OH catalysts show higher char yield than that of cured epoxy/APMDS without catalyst. It is also observed in Figure 7 that the effects of catalyst on the thermal

TABLE II
Data of TGA Analysis on the Cured Epoxy-Bridged Polyorganosiloxanes

Cured system	Catalyst	Cured condition	T_{d10} (°C)	T_{d50} (°C)	Char yield (%)
Epoxy/APTES	No catalyst	150°C, 4 h	351.9	500.0	39.30
	DBTDL	150°C, 2 h	391.0	613.6	50.73
	NBu_4OH	150°C, 2 h	380.7	563.6	44.87
Epoxy/APMDS	No catalyst	150°C, 4 h	388.7	509.9	33.00
	DBTDL	150°C, 2 h	371.3	518.8	42.47
	NBu_4OH	150°C, 2 h	390.6	491.1	37.56
Epoxy/APDES	No catalyst	150°C, 4 h	353.8	418.2	8.70
	DBTDL	150°C, 2 h	332.0	395.5	16.48
	NBu_4OH	150°C, 2 h	364.3	436.3	11.34
Epoxy/DAP	—	150°C, 2 h	377.4	400.0	11.33

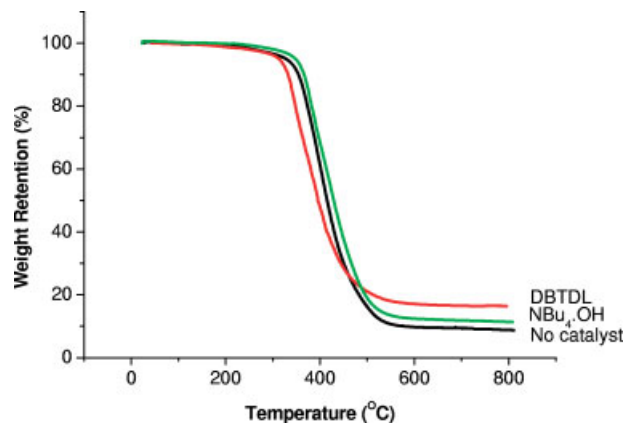


Figure 7 Comparison of TGA analysis among epoxy/APDES cured with DBTDL, NBu_4OH , and without catalyst. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

degradation temperature and char yield of cured epoxy/APDES are not so clear as shown in cured hybrid of epoxy/APTES and epoxy/APMDS system. DAP (diaminopropane)-cured epoxy network has been prepared to compare with the cured epoxy-bridged polyorganosiloxanes systems on the thermal properties. It is found from Figure 8 that the cured epoxy-bridged polyorganosiloxanes systems exhibit higher char yield than that of DAP cured epoxy system, except for the cured epoxy/APDES system. The order of the char yield among the cured epoxy-bridged polyorganosiloxanes systems is as follows: epoxy/APTES (50%) > epoxy/APMDS (42%) > epoxy/APDES (16%). The little difference in char yield between epoxy/APDES and epoxy/DAP system may be due to the reason that epoxy/APDES only possesses mono functional-terminated ethoxysilane group, which contains less

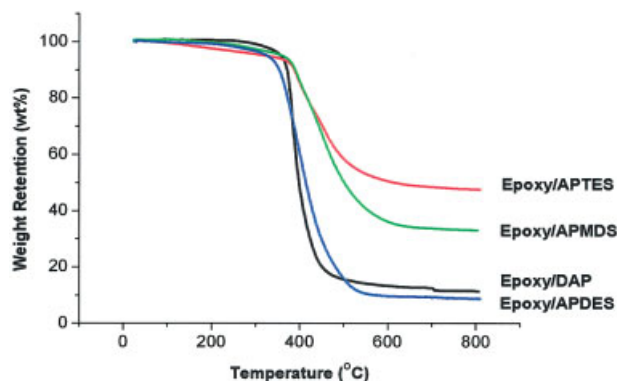


Figure 8 Comparison of thermal resistance among cured epoxy-bridged polyorganosiloxanes and cured epoxy/DAP system. The curves of epoxy/APTES and epoxy/APMDS are cured with DBTDL. The curves of epoxy/APDES and epoxy/DAP are cured without catalyst. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

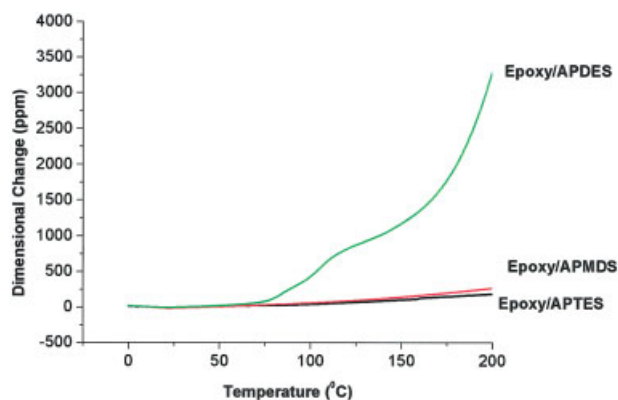


Figure 9 Comparison of TGA analysis among epoxy/APMDS cured with DBTDL, NBu_4OH , and without catalyst. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

crosslinking density than that of epoxy/APTES and epoxy/APMDS. Meanwhile, the cured hybrids of epoxy/APTES and epoxy/APMDS precursors exhibit high T_{d50s} , 613.6 and 518.8°C, respectively, as shown in Figure 8. The T_{d50s} of epoxy/APTES and epoxy/APMDS are 100°C higher than those of epoxy/APDES and epoxy/DAP. The greater the functionality of terminated-alkoxysilane group in the chain ends of bridged-epoxy precursors, the higher will be the thermal resistance obtained in the cured structure. Table II summarizes the data of TGA analysis of all the cured epoxy-bridged polyorganosiloxanes systems and cured epoxy/DAP system with or without catalyst.

TMA analysis of cured network

It is also very obvious, in the TMA analysis, that the T_g s and CTE of cured epoxy-bridged polyorganosiloxanes systems exhibit significant correspondence to the functionality of terminated-alkoxysilane groups. As

TABLE III
TMA Analyses on the T_g and CTE of Cured Products of Epoxy/DAP System, and Epoxy/APTES, Epoxy/APMDS, and Epoxy/APDES with No Catalyst or with Catalyst of DBTDL and NBu_4OH

Cured system	Catalyst	T_g (°C)	CTE before T_g ($\mu\text{m}/\text{m}^\circ\text{C}$)
Epoxy/APTES	No catalyst	—	27.5 ^a
	DBTDL	—	95.7 ^a
	NBu_4OH	—	73.1 ^a
Epoxy/APMDS	No catalyst	92	115.0
	DBTDL	111	118.0
	NBu_4OH	113	142.0
Epoxy/APDES	No catalyst	81	183.0
	DBTDL	60	234.0
Epoxy/DAP	—	63	169.4

^a CTE is measured from room temperature to 120°C.

shown in Figure 9 and Table III, trifunctional epoxy-bridged polyorganosiloxane, epoxy/APTES, shows no obvious glass transition after thermal curing at 150°C for 2–4 h. The APTES-cured hybrid exhibits the lowest coefficient of thermal expansion (CTE) among the three kinds of epoxy-bridged polyorganosiloxanes. The order of CTE of cured hybrid of the three kinds of alkoxy-silane-terminated epoxy-bridged polyorganosiloxanes is as follows: APTES (27.5 $\mu\text{m}/\text{m}^\circ\text{C}$) > APMDS (115 $\mu\text{m}/\text{m}^\circ\text{C}$) > APDES (183 $\mu\text{m}/\text{m}^\circ\text{C}$). It is very interesting to find that trifunctional epoxy-bridged polyorganosiloxanes, cured without catalyst, exhibited lower CTE of 27.5 $\mu\text{m}/\text{m}^\circ\text{C}$ than that of trifunctional epoxy-bridged polyorganosiloxanes cured with catalysts of dibutyltindilaurate (DBTDL), 95.7 $\mu\text{m}/\text{m}^\circ\text{C}$, and tetrabutylammonium hydroxide (NBu_4OH), respectively, 73.1 $\mu\text{m}/\text{m}^\circ\text{C}$. It seems that the cured structures of trifunctional epoxy-bridged polyorganosiloxanes without catalyst possesses higher molecular interaction than those cured hybrids with catalyst. However, the catalysts will play an important role in cured hybrid of difunctional epoxy-bridged polyorganosiloxanes system. The addition of DBTDL or NBu_4OH catalyst will help the epoxy/APMDS system to overcome the stereo hindrance during curing process; consequently, the T_g of epoxy/APMDS system with catalyst is 20°C higher than that of epoxy/APMDS system without catalyst. Catalysts will help the epoxy/APMDS precursor to form a cured hybrid with stronger molecular interaction. Difunctional alkoxy-silane-terminated epoxy-bridged polyorganosiloxane system (epoxy/APMDS) shows higher T_g s (90–110°C) than that of monofunctional alkoxy-silane-terminated epoxy-bridged polyorganosiloxane (epoxy/APDES), which has T_g around 60–80°C as shown in Table III. The incorporation of alkoxy-silane group in the chain network will enhance the thermal stability of cured epoxy structure. The cured products of epoxy-bridged polyorganosiloxanes show higher T_g and lower CTE than the cured product of epoxy cured by DAP, as shown in Table III. The cured product of epoxy/APDES system shows the same level of CTE as that of epoxy/DAP system, since there is no strong molecular interaction in the cured hybrid structure of monofunctional epoxy/APDES.

CONCLUSIONS

A series of novel epoxy-bridged polyorganosiloxanes precursors with different kinds of alkoxy-silane functionality have been synthesized in this study by reacting aminoalkoxy-silanes with difunctional epoxy resins. FTIR, ^1H NMR, and ^{29}Si NMR have been success-

fully used to characterize the structures of the synthesized epoxy-bridged polyorganosiloxanes precursors. Direct thermal curing of the epoxy-bridged polyorganosiloxanes precursors is proved to be effective to obtain high thermal stability of epoxy-siloxane hybrid. The addition of catalysts shows significant enhancement in increasing the thermal decomposition temperature (T_{d50} s) of cured network of trifunctional epoxy-bridged polyorganosiloxane (epoxy/APTES). High T_{d50} s of 613.6 and 518.8°C in the cured hybrids of epoxy/APTES and epoxy/APMDS precursors are also observed, respectively. There is no obvious glass transition in the analysis of TMA for cured hybrid of trifunctional epoxy-bridged polyorganosiloxane (epoxy/APTES). The epoxy-bridged polyorganosiloxanes with trifunctional aminoalkoxy-silane shows the lowest CTE (22 $\mu\text{m}/\text{m}^\circ\text{C}$) among the three kinds of epoxy-bridged polyorganosiloxanes studied. The thermal stability of cured epoxy-bridged polyorganosiloxanes has been proved to have high dependence on the functionality of terminated alkoxy-silanes in epoxy-bridged polyorganosiloxane precursors.

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