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Effect of molecular structures and mobility on the thermal and dynamical mechanical properties of thermally cured epoxy-bridged polyorganosiloxanes

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Abstract

The effects of molecular structures and mobility on the thermal properties of epoxy-bridged polyorganosiloxanes have been investigated by solid-state ^{29}Si and ^{13}C solid state NMR in this study. Epoxy-bridged alkoxysilanes precursors with mono-(APDES), di-(APMDS), tri-(APTES) functional ethoxysilane terminal groups have been synthesized and thermally cured with or without the addition of catalysts to obtain epoxy-bridged polyorganosiloxanes. Three kinds of catalysts including acidic, basic, and organometalllic compounds have been used as the curing catalyst for the direct thermal curing of epoxy-bridged polyorganosiloxane precursors. The structures of epoxy-bridged polyorganosiloxanes with respect to the catalysts are quantitatively investigated. Acidic $BF_3 \cdot MEA$ shows the best catalytic effects on the formation of T^3 and D^2 structures in the epoxy-bridged polyorganosiloxanes from tri-functional epoxy-APTES and di-functional epoxy-APMDS precursors, but basic $NBu_4 \cdot OH$ has better enhancement on the formation of M^1 structure in the epoxy-bridged polyorganosiloxanes from mono-functional epoxy-APDES precursor. TEM spectra show that the epoxy-bridged polysilsesquioxanes of epoxy-APTES precursors exhibit polysilsesquioxanes nano domain around 45–55 nm under the catalysis of dibutyltindilaurate (DBTDL), but show bigger polysilsesquioxanes nano domain around 50–150 nm under the catalysis of basic tetrabutylammonium hydroxide ($NBu_4 \cdot OH$) in epoxy matrix after direct thermal curing process.

The coefficient of thermal expansion of the epoxy-bridged polyorganosiloxanes are affected by the functionality of terminated alkoxysilanes and the species of catalyst used during curing process. The epoxy-bridged polysilsesquioxanes of epoxy-APTES precursor possesses the lowest coefficient of thermal expansion compared with the other two epoxy-bridged polyorganosiloxanes from mono-, and di-functional epoxy-bridged polyorganosiloxanes precursors. There is no obvious T_g observed in the epoxy-bridged polysilsesquioxanes of epoxy-APTES precursor from the analysis of TMA and DMA. ^{13}C solid state NMR has been used to investigate the molecular motion behaviors of epoxy-bridged polyorganosiloxanes structures with respect to the changes in T_g and CTE. The $T_{1\rho}^H$ (the relaxation time of ^{13}C after the spin lock process) of the epoxy-bridged polysilsesquioxanes of epoxy-APTES precursor is longer than that of epoxy-APMDS precursor, which indicates that the molecular mobility of epoxy-bridged polysilsesquioxanes of epoxy-APTES is highly restricted due to the strong intermolecular interaction of nano hybrid network.
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Keywords: Molecular structure; Mobility; Epoxy-bridged polyorganosiloxanes

1. Introduction

Epoxy resin has been utilized in many applications such as composite materials, electronic materials, and insulation materials due to its excellent adhesion characteristics, good mechanical strength, and insulation property. However, they are challenged in recent years by the newly emerging request from the fast booming of electronic optical application [1]. There are many research works in studying the effect of polyorganosiloxane on the enhancement of thermal, optical, and mechanical properties of epoxy resin [2–4]. The properties of epoxy resin can be improved by the incorporation of inorganic structures to form functional hybrid structure. Silicon molecule is the most popular inorganic structure used for the design of organic–inorganic

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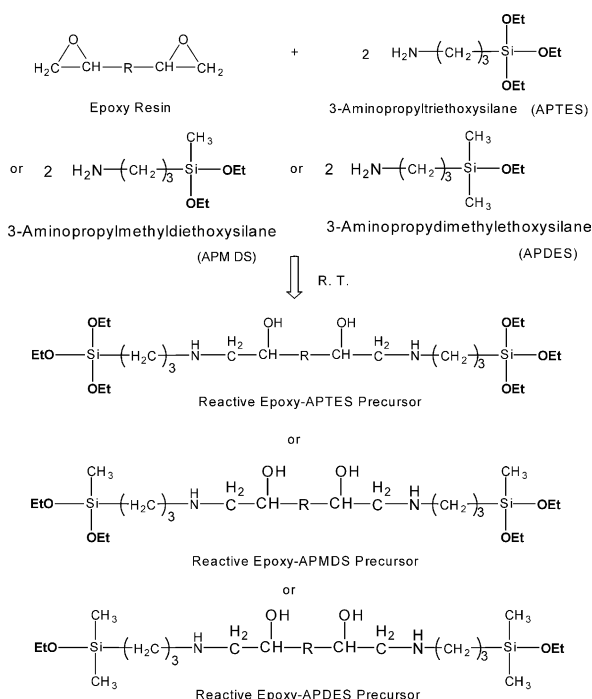
Scheme 1. Synthetic method of epoxy-bridged polyorganosiloxanes precursors with various types of terminated alkoxysilanes.

hybrid. There are several synthetic routes to prepare silicon–epoxy hybrid structures [5–8]. Polyorganosiloxane-epoxy hybrid system with polyhedral oligomeric polysilsesquioxanes (POSS) structure can be prepared from the sol–gel process of TEOS followed by the incorporation of epoxide group on the polyhedral terminal site. This type of epoxy terminated polyhedral oligomeric polysilsesquioxane can be crosslinked with various kinds of curing agent to form organic–inorganic epoxy-polyorganosiloxane hybrid network [9]. Hybrid structure from this synthetic method possesses nano size pore structure, which decreases the dielectric constant of epoxy resin. However, since the hybrid structure depends very much on the PH value of aqueous solution in sol–gel process and it takes a long time to complete the sol gel reaction, it is very difficult to utilize the sol gel process in traditional manufacturing process.

Organoalkoxysilanes has been considered as another effective starting compound to synthesize organic–inorganic hybrid. The synthesis and reaction kinetics between aminosilane with epoxy had been firstly reported by Serier [13,14]. The prepolymer from the reaction of aminotrialkoxysilane with epoxy has been synthesized and discussed by Serier. However, sol gel process was still used in the study to obtain the final hybrid structures. In order to improve the disadvantage in preparing epoxy-polyorganosiloxane hybrid system from sol gel process, a series of new epoxy-bridged polyorganosiloxanes have been prepared and cured through directly thermal curing in this study. Epoxy-bridged polyorganosiloxanes precursors of various alkoxysilane functionalities have been synthesized by

reacting aminoalkylalkoxysilanes with di-functional epoxy resins. The epoxy-bridged polyorganosiloxane precursors have been thermally cured with or without catalyst to form an organic–inorganic network with both good film strength and thermal stability. Different types of catalysts had been added to cure the precursor systems to study the thermal properties of epoxy-bridged polyorganosiloxanes. The structures of epoxy-bridged polyorganosiloxanes from different functional epoxy-bridged alkoxysilanes precursors are investigated in this study. Solid-state ^{29}Si and ^{13}C solid state NMR are also used to study the molecular motion behaviors with respect to the difference of T_g and CTE of cured epoxy-bridged polyorganosiloxane structures. Effects of catalysts on the structures of epoxy-bridged polyorgano-siloxanes during thermal curing process have also been discussed.

2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A (DGEBA) epoxy used in this study was supplied by the Nan Ya Plastics Co. Ltd. Taiwan, with an epoxide equivalent weight of 190 g/equiv. 3-Aminopropyltriethoxysilane (APTES, Z-6011, M.W. of 221.37) was purchased from Dow Corning, Co. Midland, Michigan, USA. 3-Aminopropylmthyldiethoxysilane (APMDS, M.W.: 191.34) was obtained from TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan. 3-Aminopropyldimthylethoxysilane (APDES, M.W.: 161.32) was provided by GELEST Inc., USA. Diaminopropane (DAP) was supplied from TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan. Dibutyltindilaurate, tetrabutylamonium hydroxide and boron trifluoride monoethylamine were obtained from TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan were used as catalysts for curing epoxy-bridged polyorganosiloxanes precursors.

2.2. Synthesis

2.2.1. Preparation of epoxy-bridged polyorganosiloxane precursors

Aminosilanes such as APTES, APMDS, or APDES were reacted, respectively, with stoichiometric amount of diglycidyl ether of biphenol-A (DGEBA) epoxy in a 100 ml single necked flask with a reaction molar ratio of 1:2 (n_{epoxy}: $n_{animosilane}$). The reaction mixture was mixed at room temperature with a magnetic stirrer for 5 h to complete the reaction of epoxide group with the amino group of aminosilanes. After 5 h of reaction, APTES, APMDS, or APDES terminated epoxy-bridged polyorganosiloxanes precursors were obtained as clear and low viscous liquid as shown in Scheme 1.
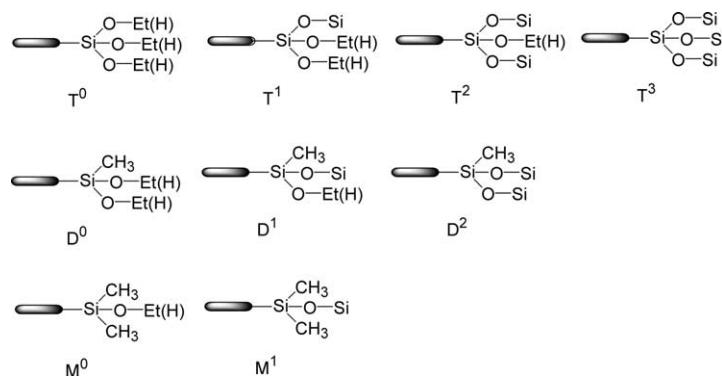
Scheme 2. Types of possible crosslinked hybrid structures of epoxy-bridged polyorganosiloxanes.

2.2.2. Curing of epoxy-bridged polyorganosiloxanes precursors

The obtained reactive epoxy-bridged polyorganosiloxanes precursors were mixed with 1 phr (part per hundred parts of epoxy resin) of catalysts such as dibutyltindilaurate (DBTDL), tetrabutylamonium hydroxide (NBu$_4$·OH); or boron trifluoride monoethylamine (BF$_3$·MEA) at room temperature, respectively. The mixture became clear and homogenous after 30 min of mixing and was poured into an aluminum pan of one square inch in diameter for further curing. The epoxy-bridged polyorganosiloxanes was obtained after being cured at 150 °C for 2 h. The epoxy-bridged polyorganosiloxanes structures of epoxy-APTES bridged polysilsesquioxanes, epoxy-APMDS bridged polyorganosiloxane, and epoxy-APDES bridged polyorganosiloxane were analyzed by ^{29}Si solid state NMR. Diaminopropane (DAP) was used in this study to cure with DGEBA epoxy under the same condition to obtain a comparative pure epoxy cured product. Thermal and mechanical properties of epoxy-bridged polyorganosiloxanes were compared with those of epoxy/DAP.

2.3. Morphology of epoxy-bridged polyorganosiloxanes

2.3.1. Scanning electron microscopy (SEM) and Si mapping analysis

The morphology of the fracture surface of the epoxy-bridged polyorganosiloxanes was examined using a scanning electron microscope (SEM; JEOL JSM 840A, Japan). SEM EDX mapping (JEOL JSM 840A, Japan) was used to analyze the distribution of Si atoms in cured nano hybrid network. The light points in the figures denoted the Si atoms.

2.3.2. Transmission electron microscopy (TEM)

Nano structure of epoxy-bridged polyorganosiloxanes was analyzed by transmission electron microscopy (TEM). The type of TEM used is JEOL-2000EX and its accelerated voltage is 200 kV. Cured epoxy-bridged polyorganosiloxanes were microtomed with Leica Ultracut Uct into 90 nm thick slices in a direction normal to the plane of the films. The slice samples were analyzed by TEM to observe the nano phase structures of the nano hybrid composite.

2.4. Characterization of epoxy-bridged polyorganosiloxanes

2.4.1. CP/MAS solid state ^{29}Si nuclear magnetic resonance (NMR) spectroscopy

High-resolution solid-state ^{29}Si NMR experiments were performed on a BRUKER DSX 400 MHz solid-state ^{29}Si NMR. The spectra of ^{29}Si CP/MAS NMR of epoxy-bridged polyorganosiloxanes were used to characterize the degree of condensation of cure hybrid networks by examining the contribution of various silicon species presented in the condensed materials.

2.4.2. CP/MAS solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy

High-resolution solid-state ^{13}C NMR experiments were performed on a BRUKER DSX 400 MHz solid-state ^{13}C NMR. The resonance frequencies were 399.53 and 100. 47 MHz for ^{1}H and ^{13}C, respectively. The ^{13}C cross polarization-magic angle spinning (CP/MAS) spectra were measured with 5.0 µs 90° pulse width; 2.0 s pulse delay time; 12.8 ms acquisition time; spectral width, 200 ppm; and 2048 scans. Proton spin-lattice relaxation times in rotating frame ($T_{1\rho}^{\mathrm{H}}$) were measured via carbon signal intensity using a 90°-τ-spin lock pulse sequence prior to the cross-polarization. All NMR spectra were taken at 300 K with a broadband decoupling, normal cross-polarization pulse sequence and a magic angle sample spinning frequency of 6.5 kHz.

2.5. Thermal analysis of epoxy-bridged polyorganosiloxanes

2.5.1. Thermal mechanical analysis (TMA)

Cured epoxy-bridged polyorganosiloxanes films of 2. 0 cm×0.3 cm in dimension were hanged under 0.05 N of tension force in the heating chambers of TMA (TA 2940, TA Instruments, Inc.) and heated to 200 °C under nitrogen
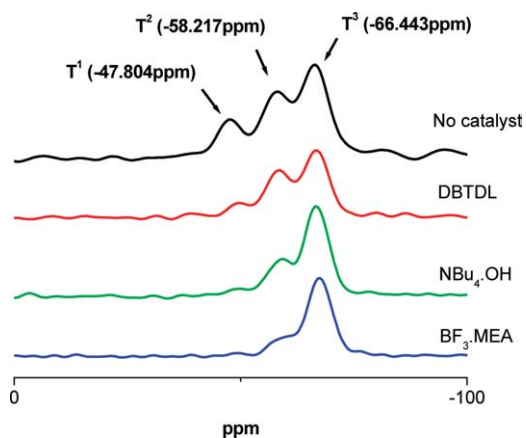
Fig. 1. ^{29}Si CP/MAS NMR spectra of epoxy-bridged polyorganosiloxanes from epoxy-APTES without and with DBTDL, NBu$_4$·OH and BF$_3$·MEA catalyst.

with a heating rate of 10 °C/min to measure their glass transition temperatures (T_g) and coefficient of thermal expansion (CTE).

2.5.2. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of cured epoxy-bridged polyorganosiloxanes were studied by DMA (TA 2940, TA Instruments, Inc.). Cured samples of $17.0 \times 6.6 \times 0.06$ mm^3 in dimension were mounted on a single cantilever clamp. The dynamic mechanical properties were measured from room temperature to 200 °C under nitrogen with a heating rate of 10 °C/min to observe their storage modulus and tan δ.

3. Results and discussion

3.1. Characterization of cured structure of epoxy-bridged polyorganosiloxanes

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

The structures of epoxy-bridged polyorganosiloxanes cured with or without catalysts have been characterized by ^{29}Si solid state NMR. Scheme 2 shows the types of possible crosslinked hybrid structures in this research.

The peaks of ^{29}Si NMR resonance of epoxy-APTES system networks lie between −45 and −70 ppm. As shown in Fig. 1, there are three types of silicon (−47.8 ppm, T^1; −58.2 ppm, T^2; −66.4 ppm, T^3) in epoxy/APTES system networks. No residual triethoxysilane resonance (T^0) is detected in structures of epoxy-bridged polyorganosiloxane from epoxy-APTES precursor, which indicates that the ethoxysilane group could be condensed to polysilsesquioxanes network during thermal curing process. As shown in Fig. 2, there are three types of epoxy-bridged polyorgano-siloxanes structures (−5.9 ppm, D^0; −14.5 ppm, D^1; −22.0 ppm, D^2) found in epoxy-APMDS system networks.
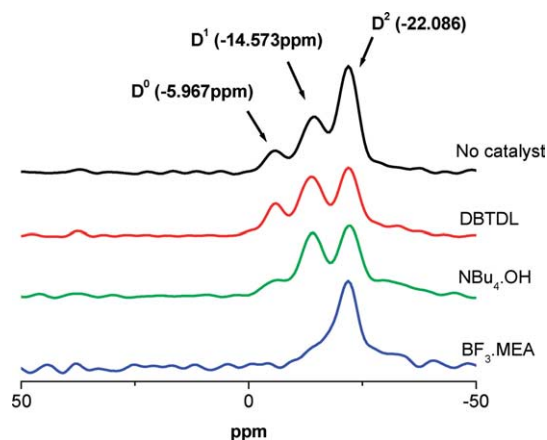

Fig. 2. ^{29}Si CP/MAS NMR spectra of epoxy-bridged polyorganosiloxanes from epoxy-APMDS without and with DBTDL, NBu$_4$·OH and BF$_3$·MEA catalyst.

Both of epoxy/APTES and epoxy/APMDS systems form crosslinking hybrid networks because there are tri-functional and di-functional reactive alkoxy groups on both ends of the synthesized bridged-alkoxysilanes. The peaks of ^{29}Si NMR resonances of cured epoxy/APDES networks located between 18 and 6 ppm as shown in Fig. 3. There are two types of silicon (16.5 ppm, M^0; 7.6 ppm, M^1) observed in epoxy/APDES system. Since the of epoxy/APDES system only possesses mono-alkoxysilane terminated reactive groups on both ends of molecules, only little crosslinking network is formed by the reaction of the hydroxyl groups in the middle chain with alkoxysilanes.

In order to understand the effect of catalyst on the cured structures of epoxy-bridged polyorganosiloxanes, it is necessary to calculate the degree of condensation of siloxane structures in the cured network. The degree of condensation can be explained by the percentage of every type of structures (T^n, D^n and M^n) according to the following
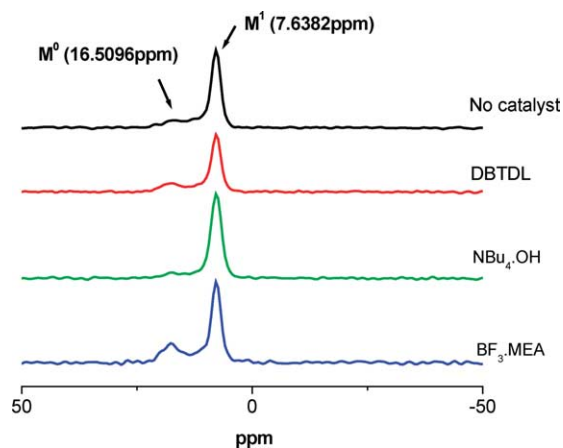

Fig. 3. ^{29}Si CP/MAS NMR spectra of epoxy-bridged polyorganosiloxanes from epoxy-APDES without and with DBTDL, NBu$_4$·OH and BF$_3$·MEA catalyst.

Table 1
Integrated ^{29}Si CP/MAS NMR of (a) T distributions in the epoxy-bridged polysilsesquioxanes from epoxy-APTES system, (b) D distributions in the epoxy-bridged polyorganosiloxanes from epoxy-APMDS system and (c) M distributions in the epoxy-bridged polyorganosiloxanes from epoxy-APDES

	Catalyst	T distribution			Degree of condensation (%)
		T^1 (%)	T^2 (%)	T^3 (%)	
(a) T distributions of epoxy-APTES system					
Epoxy-APTES	No catalyst	20.1	30.7	49.2	76.4
	DBTDL	11.4	35.4	53.2	80.6
	NBu$_4$.OH	8.2	25.9	65.9	85.9
	BF$_3$.MEA	4.4	17.2	78.4	91.4
	Catalyst	D distribution			Degree of condensation (%)
		D^0 (%)	D^1 (%)	D^2 (%)	
(b) D distributions of epoxy-APMDS system					
Epoxy-APMDS	No catalyst	12.1	31.0	56.9	72.4
	DBTDL	18.4	38.8	42.8	62.2
	NBu$_4$.OH	14.5	41.0	44.5	65.0
	BF$_3$.MEA	7.0	10.0	83.0	88.0
	Catalyst	M distribution			Degree of condensation (%)
		M^0 (%)		M^1 (%)	
(c) M distributions of epoxy-APDES					
Epoxy-APDES	No catalyst	23.0		77.0	77.0
	DBTDL	24.0		76.0	76.0
	NBu$_4$.OH	11.0		89.0	89.0
	BF$_3$.MEA	27.8		72.2	72.2

Note: Each data of distribution of T, D, and M are the mean average of three repeated measurement of ^{29}Si CP/MAS NMR spectra of each sample.

equations [10–11]:

Degree of condensation of T distribution

$$= [(1.0)(\% \text{ area } T^1) + (2.0)(\% \text{ area } T^2)$$
$$+ (3.0)(\text{area } T^3)]/3.0$$

Degree of condensation of D distribution

$$= [(1.0)(\% \text{ area } D^1) + (2.0)(\% \text{ area } D^2)]/2.0$$

Degree of condensation of M distribution

$$= [(1.0)(\% \text{ area } M^1)]/1.0(5-4)$$

When there is no catalyst used for the curing of epoxy-APTES system, the distribution of T^1, T^2, and T^3 structures in the epoxy-bridged polyorganosiloxanes from epoxy-APTES do not have obvious difference. The effect of curing catalysts on the degree of condensation of epoxy-APTES precursors is discussed as shown in Table 1(a). The epoxy-bridged polyorganosiloxanes of epoxy-APTES without curing catalyst shows the lowest degree of condensation. The highest degree of condensation of 91.4% appears when acidic curing catalyst of BF$_3$·MEA is used. The degrees of condensation are 80.6 and 85.9%, respectively, for the epoxy-bridged polyorganosiloxanes of epoxy-APTES under the catalysis of DBTDL and NBu$_4$·OH. The acidic catalyst,

BF$_3$·MEA, also shows the best catalytic effects on the condensation of di-functional alkoxysilane terminated precursor (epoxy-APMDS) as shown in Table 1(b). The highest condensation degree (88.0%) of the epoxy-bridged polyorganosiloxanes from epoxy-APMDS precursor has been found when BF$_3$·MEA is used as catalyst. However, basic and organometallic curing catalysts of both NBu$_4$·OH and DBTDL are found to have negative effect on the formation of polyorganosiloxanes during thermal curing reaction of epoxy-APMDS. On the contrary, when basic catalyst, NBu$_4$·OH, is used for the curing of mono-functional ethoxysilane terminated precursor (epoxy-APDES), the highest degree of condensation of epoxy-bridged polyorganosiloxanes appears as shown in Table 1(c). The degree of condensation of the epoxy-bridged polyorganosiloxanes from epoxy-APDES precursor under the catalysis of NBu$_4$·OH is (89.0%), whereas the degrees of condensation are 76.0 and 72.2% with DBTDL and BF$_3$·MEA, respectively. The acidic catalyst, BF$_3$·MEA, effectively enhances the formation of T^3 and D^2 distribution in the epoxy-bridged polyorganosiloxanes from epoxy-APTES and epoxy-APMDS precursors system, but basic tetrabutylammoniumhydroxide (NBu$_4$·OH) shows stronger catalytic effect in the formation of M^1 structure in the epoxy-bridged polyorganosiloxanes from epoxy-APDES. The structure distribution of the epoxy-bridged polyorganosiloxanes has strong correspondence to the curing catalysts used during curing reaction. Effective curing
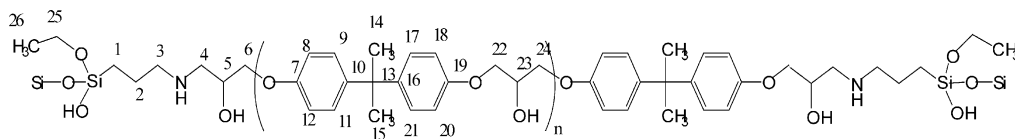
Scheme 3. Chemical structure epoxy-APTES.

Table 2
$T_{1\rho}^{H}$ spin lock relaxation time measured at 300 K of corresponding segmental motions of epoxy-APTES and epoxy-APMDS

Epoxy-APTES			Epoxy-APMDS		
δ (ppm)	Carbon	$T_{1\rho}^{H}$	δ (ppm)	Carbon	$T_{1\rho}^{H}$
			0.38	27	1.56
11.76	1	3.90	15.64	1	1.77
18.87	26	4.12	19.08	26	3.72
23.44	2	3.87	24.00	2	2.24
31.87	14, 15	3.25	32.10	14, 15	2.67
42.11	13	8.56	42.16	13	1.67
53.01	3, 4	4.39	53.31	3, 4	2.04
57.92	25	3.34	58.24	25	2.26
70.25	5, 6, 22, 23, 24	3.35	70.14	5, 6, 22, 23, 24	2.23
114.82	8, 12, 18, 20	3.33	114.57	8, 12, 18, 20	2.39
127.96	9, 11, 17, 21	3.45	127.99	9, 11, 17, 21	2.14
144.04	10, 16	4.95	144.11	10, 16	3.44
157.23	7, 19	5.56	157.34	7, 19	3.75

Unit of $T_{1\rho}^{H}$, ms.

catalyst for the formation of epoxy-bridged polyorganosiloxanes is also decided by the functionality of terminated alkoxysilane of the epoxy-bridged alkoxysilane precursors.

3.1.2. Study on the molecular motion of epoxy-bridged polyorganosiloxanes with ^{13}C solid state NMR

The ^{13}C solid state NMR is an effective analysis to observe the molecular motions of polymer structures. Nuclear magnetic resonance interactions can be modulated or averaged by molecular motions. The mobility of polymer chains with respect to the relaxation behavior can be investigated in NMR analysis. The changes of mobility of

Fig. 4. ^{13}C CP/MAS NMR spectra of epoxy-APTES (numbers are correlated to Scheme 3).

each atom would explain the movement of molecular chain. Since the thermal properties of polymers are decided by their molecule chain mobility, ^{13}C solid state NMR could be used in analyzing the relationship between thermal properties and molecular chain mobility of the thermal cured epoxy-bridged polyorganosiloxanes.

The relaxation time of ^{13}C in the rotating frame and laboratory frame are called $T_{1\rho}$ and T_{1}, respectively. $T_{1\rho}^{H}$ can be referred to the motion of molecules in mega hertz and the intensity of the magnetization of the ^{13}C can be expressed as below [12]:

$$M(\tau) = M_0 \exp(-\tau/T_{1\rho})$$

$T_{1\rho}$ can be calculated from the magnetization with various contact times (τ). $M(\tau)$ is the intensity at $t = \tau$ and M_0 is the intensity when τ equals to zero.

To study the molecular motion of epoxy-bridged polyorganosiloxanes, high resolution ^{13}C solid state NMR technique is utilized. The chemical shift position of each carbon in epoxy-APTES without catalyst and the spectrum of ^{13}C solid state NMR of epoxy-APTES are shown in Scheme 3 and Fig. 4. The chemical shift of each carbon in epoxy-APMDS without catalyst and the ^{13}C solid state NMR spectrum of epoxy-APMDS are shown in Scheme 4 and Fig. 5.

The spin lock relaxation time ($T_{1\rho}^{H}$) of epoxy-bridged polyorganosiloxanes from epoxy-APTES and epoxy-APMDS are calculated from the negative reciprocal of the slope of the logarithmic plots of the magnetization intensities corresponding to various contact times. As found in Table 2, the $T_{1\rho}^{H}$ of the carbon in epoxy-APTES
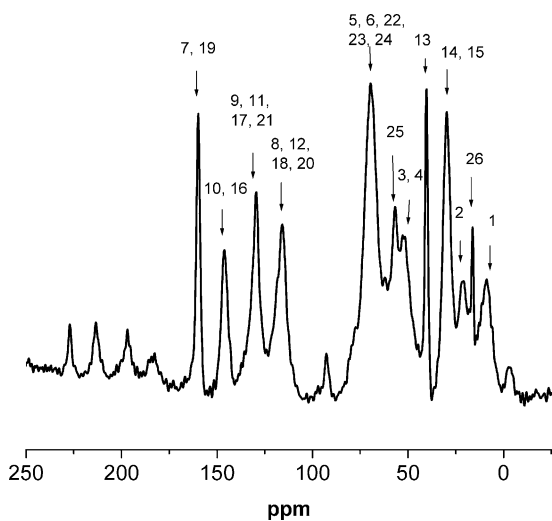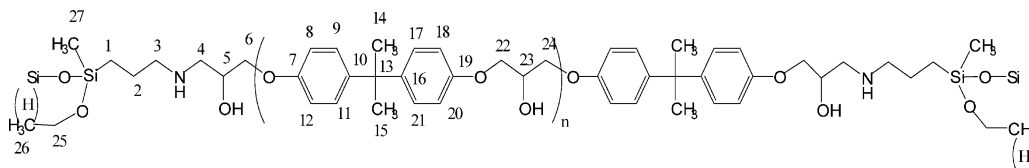
Scheme 4. Chemical structure of epoxy-APMDS.

Table 3
CTE 1 and CTE 2 of epoxy-APTES, epoxy-APMDS and epoxy-APDES without and with DBTDL, NBu$_4$·OH and BF$_3$·MEA catalyst, and epoxy/DAP

	Catalyst	CTE (ppm/°C)	
		CTE 1	CTE[a] 2
Epoxy-APTES	No catalyst	28	–
	DBTDL	96	–
	NBu$_4$·OH	73	–
	BF$_3$·MEA	28	–
Epoxy-APMDS	No catalyst	118	312
	DBTDL	115	348
	NBu$_4$·OH	142	248
	BF$_3$·MEA	108	526
Epoxy-APDES	No catalyst	183	1981
	DBTDL	234	931
	NBu$_4$·OH	110	837
	BF$_3$·MEA	181	801
Epoxy/DAP		169	316

[a] The CTE2 of epoxy-APTES is unable to obtain since cured epoxy-APTES shows no obvious T_g transition during thermal heating.

is 8.56 ms but is only 1.67 ms in epoxy-APMDS hybrid network. The $T_{1\rho}^H$ of the carbons in epoxy-APTES are longer than those of epoxy-APMDS, which indicates that the molecular relaxation in epoxy-APTES is slower and longer than those of epoxy-APMDS. Since the crosslinking density of the epoxy-bridged polyorganosiloxanes from tri-functional epoxy-APTES is higher than that from di-functional epoxy-APMDS system, the molecular motion of bending and rotation of carbon the epoxy-bridged polyorganosiloxanes from tri-functional epoxy-APTES is restricted stronger than that from epoxy-APMDS. The
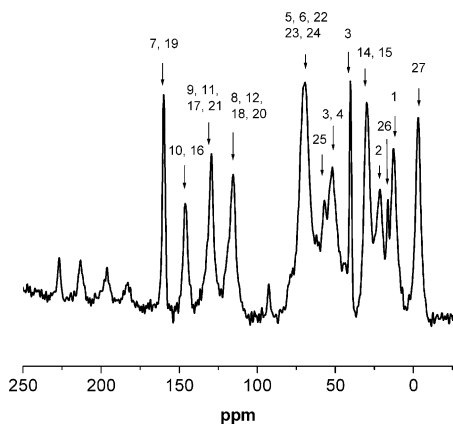
epoxy-bridged polyorganosiloxanes from tri-functional alkoxysilane shows stronger molecular interaction than the other two epoxy-bridged polyorganosiloxanes from di-functional epoxy-APDES and mono-functional epoxy-APMDS precursor due to the lower molecular motion of T structure in epoxy-bridged polyorganosiloxanes. The T structure in epoxy-bridged polyorganosiloxanes from trifunctional epoxy-bridged alkoxysilane could be observed to have nano scale domain as shown in Fig. 11.

3.2. Thermal properties of epoxy-bridged polyorganosiloxanes

3.2.1. Thermal mechanical analysis (TMA) of epoxy-bridged polyorganosiloxanes

Cured epoxy-bridged polyorganosiloxanes from epoxy-APTES, epoxy-APMDS, and epoxy-APDES precursors have been investigated on their thermal mechanical properties. It is found from TMA analysis that CTE1 (the coefficients of thermal expansion under T_g) of cured epoxy-bridged polyorganosiloxanes exhibit significant correspondence with the functionality of terminated alkoxysilane groups as shown in Fig. 6 and Table 3. The CTE1 of epoxy-bridged polyorganosiloxanes from tri-functional epoxy-APTES precursor shows the lowest CTE1 of 28 ppm/ °C among the three epoxy-bridged polyorganosiloxanes from precursors with different alkoxysilane functionalities. Comparisons on the CTE1 and CTE2 (the coefficient of thermal expansion at the temperature over T_g) of the cured materials from four different epoxy-APTES, epoxy-APMDS, epoxy-APDES and epoxy-DAP systems are shown Table 3. The more the functionality of alkoxysilane terminated epoxy-bridged
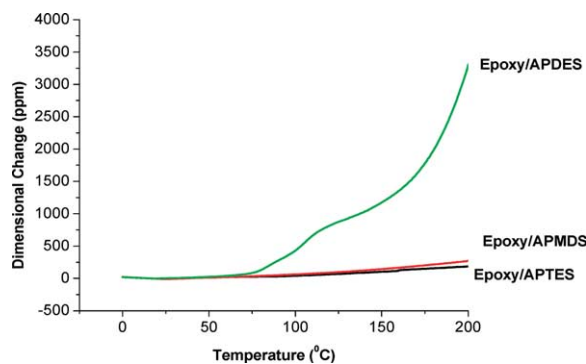

Fig. 5. ^{13}C CP/MAS NMR spectra of epoxy-APMDS (numbers are correlated to Scheme 4).

Fig. 6. TMA curves of epoxy-APTES, epoxy-APMDS and epoxy-APDES without catalyst.

Table 4
The T_g measured by TMA and DMA and the degree of condensation of epoxy-APMDS and epoxy-APDES systems

	Epoxy-APTES		Epoxy-APMDS			Epoxy-APDES			Epoxy-DAP	
	T_g by TMA (°C)	T_g by DMA (°C)	T_g by TMA (°C)	T_g by DMA (°C)	Degree of Condensation (%)	T_g by TMA (°C)	T_g by DMA (°C)	Degree of condensation (%)	T_g by TMA (°C)	T_g by DMA (°C)
No catalyst	–	–	111	151	72.4	81	90	77.0	63	80
DBTDL	–	–	92	133	62.2	60	72	76.0	–	–
NBu$_4$·OH	–	–	113	142	65.0	81	88	89.0	–	–
BF$_3$·MEA	–	–	115	146	88.0	67	76	72.2	–	–

T_g of epoxy/APTES was not able to be decided.

polyorganosiloxanes is used, the lower the coefficient of thermal expansion of the epoxy-bridged polysilsesquioxanes would be obtained. Since the structure interaction of the epoxy-bridged polysilsesquioxanes from epoxy-APTES is proven to be the strongest among the three kinds of precursors according to the above analysis of ^{13}C solid state NMR technique, the lowest CTE found in the epoxy-bridged polysilsesquioxanes from epoxy-APTES was due to strong molecular interaction of cured trifunctional terminated alkoxysilane. It is very interesting to find that the addition of catalyst during the thermal curing process does not show any enhancement in the decreasing of CTE of epoxy-bridged polyorganosiloxanes from epoxy-APTES, epoxy-APMDS, and epoxy-APDES precursors. Even the epoxy-APTES precursors with BF$_3$·MEA catalyst shows T^3 dominated phase in its cured epoxy-bridged polyorsilsesquioxanes, the CTE of epoxy-bridged polyorganosiloxanes from epoxy-APTES precursors under BF$_3$·MEA catalyst is still the same as that with catalyst.

The T_gs of the epoxy-bridged polyorganosiloxanes from precursors with various terminated alkoxysilane functionalities under different catalyst are listed in Table 4. It is found in Fig. 6 and Table 4 that there is no obvious glass transition (T_g) behavior in the epoxy-bridged polyorganosiloxanes from epoxy-APTES precursors under the analysis of TMA and DMA. Since the polyorganosiloxanes structure obtained from trifunctional terminated epoxy-APTES

precursor will inhibit the molecular relaxation of epoxy chain backbone as mentioned in the ^{13}C CP/MAS NMR analysis of Table 2, the free volume of molecular chain of the epoxy-bridged polyorganosiloxanes from epoxy-APTES precursors is highly restricted. Therefore, the T_g is not detectable when the sample is analyzed in TMA and DMA. The epoxy-bridged polyorganosiloxanes from di-functional epoxy-APMDS shows higher T_g of 111 °C than the T_g from the mono-functional epoxy-APDES of 81 °C. Since the structure of epoxy-bridged polyorganosiloxanes from epoxy-APMDS is expected to have higher crosslinking density than that from mono-functional epoxy-APDES, the T_g of epoxy-bridged polyorganosiloxanes from epoxy-APMDS is increased due to the lower molecular chain mobility. The enhancement of polyorganosiloxanes structures on thermal stability of the epoxy-bridged polyorganosiloxanes could be concluded as: $T > D > M$. In order to obtain epoxy-bridged polyorganosiloxanes with lower CTE and higher T_g, the formation of T structure is better than the formation of D or M structure. The addition of catalyst during the thermal curing process shows no effect on the increasing of T_gs of epoxy-bridged polyorganosiloxanes from epoxy-APTES, epoxy-APMDS, and epoxy-APDES precursors. There is no obvious difference in T_g between the epoxy-bridged polyorganosiloxanes with and without catalyst. The epoxy-bridged polyorganosiloxanes from mono-functional epoxy-APDES precursor shows almost the same level of CTE and T_g as the cured epoxy network from epoxy-DAP (diaminopropane) because the epoxy-bridged polyorganosiloxanes from mono-functional epoxy-APDES precursor is too linear to enhance the T_g and CTE. The CTE and T_g of the thermal cured epoxy-bridged polyorganosiloxanes are mainly decided by the functionalities of the terminated alkoxysilane of the precursors rather than the curing catalysts used.

3.2.2. Dynamic mechanic analysis (DMA) of epoxy-bridged polyorganosiloxanes

Dynamic mechanic analysis (DMA) has been used to investigate the thermal mechanic modulus changes of epoxy-bridged polyorganosiloxanes from various epoxy-bridged alkoxy silanes at high temperatures. The changes of storage modulus and tan δ with respect to temperatures of the epoxy-bridged polyorganosiloxanes has been detected
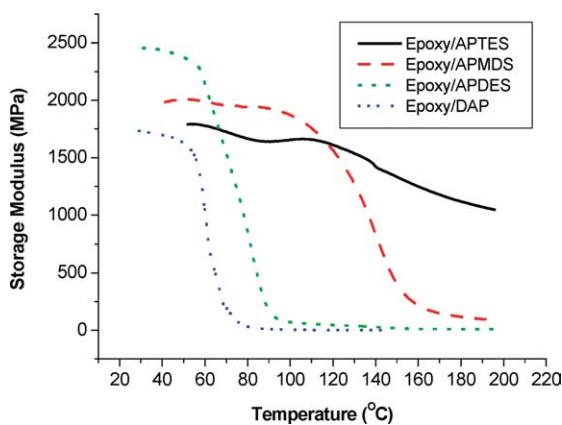

Fig. 7. (a) The storage modulus of epoxy-APTES, epoxy-APMDS, epoxy-APDES and epoxy/DAP in DMA analysis.
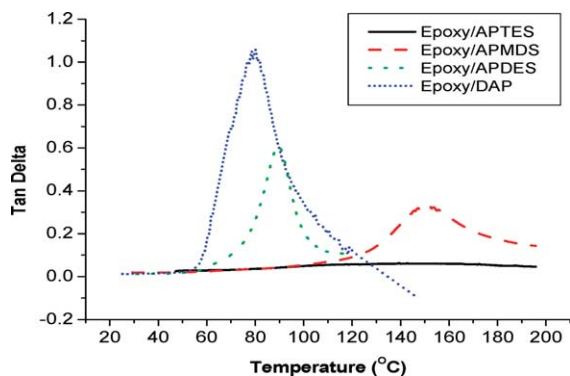
Fig. 8. The tan δ of epoxy-APTES, epoxy-APMDS, epoxy-APDES and epoxy-DAP in DMA analysis.

and compared with that of pure epoxy cured network of epoxy-DAP system as shown in Figs. 7 and 8. The storage modulus (E') of epoxy-bridged polyorganosiloxanes is found to be higher than that of pure epoxy-DAP due to the existence of inorganic polyorganosiloxanes in the cured network. The storage modulus of epoxy-bridged polysilsesquioxanes from epoxy-APTES, epoxy-APMDS, epoxy-APDES and epoxy-DAP precursors are 1789, 2004, 2374 and 1626 MPa, respectively, at 50 °C. When the temperature is raised to 170 °C, the elastic storage modulus of epoxy-bridged polyorganosiloxanes from epoxy-APTES still can maintain at 1175 MPa, but the elastic storage modulus of epoxy-bridged polyorganosiloxanes from epoxy-APDES and pure epoxy-DAP cured network have decreased to 9.9 and 6.9 MPa, respectively. Such kind of result indicates that the epoxy-bridged polyorganosiloxanes from epoxy-APTES retains higher thermal mechanical properties at high temperature due to the existence of high crosslinking polyorganosiloxanes in the hybrid network. It is interesting to find that the storage modulus, E', of epoxy-APDES is slightly higher than those of epoxy-APMDS and epoxy-APTES at $T < T_g$. However, the E' of epoxy-APTES is greatly higher than epoxy-APMDS and epoxy-APDES at $T > T_g$. Since the epoxy-bridged polyorganosiloxanes from epoxy-APTES could retain its storage modulus from room temperature to high temperature, there is no obvious transition temperature found during the analysis of DMA. Such kind of phenomenon is also coincident with the result observed in the analysis result of TMA. The restriction of the molecular motion will decrease the dissipation of energy

stored. Since the epoxy-bridged polyorganosiloxanes from epoxy-APTES shows the highest restriction on the molecular motion, its cured network could keep the storage modulus unchanged from low to high temperature. The T structure of epoxy-bridged polysilsesquioxanes creates higher rigidity in the hybrid structure than the D and M structures of both cured epoxy-APMDS and epoxy-APDES.

The glass of transition temperature (T_g) can also be observed from the peak temperature of tan δ as shown in the DMA of Fig. 8. Table 4 shows two kinds of T_gs of the cured epoxy-bridged polyorganosiloxane obtained from DMA and TMA analysis, respectively. Since the molecular motion of the epoxy-bridged polyorganosiloxanes is restricted during heating, the T_gs of the epoxy-bridged polyorganosiloxanes from epoxy-APMDS and epoxy-APDES decided by tan δ of DMA analysis are obviously higher than the T_gs measured in TMA analysis. Especially, the T_g of the epoxy-bridged polyorganosiloxanes from epoxy-APMDS measured by DMA is 30–40 °C higher than the T_g obtained from TMA analysis. The effect of polyorganosiloxanes structure on the free volume of epoxy-bridged polyorganosiloxanes is less than the chain backbone mobility during heating when the functionality of the terminated alkoxysilane is not high enough. The disappearance of T_g of epoxy-bridged polyorganosiloxanes from epoxy-APTES system is mainly caused by the formation of highly rigid polyorganosiloxanes phase in the cured hybrid network. It is also found that the addition of catalyst does not to have positive effect on the increasing of T_g in every system. On the contrary, the functionality of the alkoxysilanes dominates in determining the T_g of the cured hybrid networks.

3.3. Morphology of nano phase of epoxy-bridged polyorganosiloxanes

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have been used to observe the micro morphology of epoxy-bridged polyorganosiloxanes. It is found from the SEM Si mapping (Fig. 9) that the nano polyorganosiloxanes domains are well dispersed in epoxy-bridged polyorganosiloxanes matrix. The cured network of epoxy-bridged polyorganosiloxanes exhibits very uniform organic-inorganic hybrid structure. The distribution and density of nano polyorganosiloxanes domains are different with respect to various kind of catalysts used. The
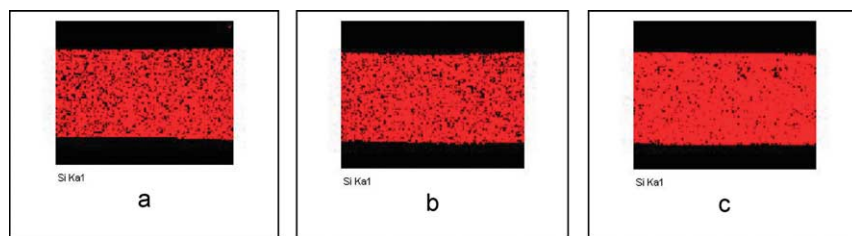

Fig. 9. Si mapping of epoxy-APTES nano hybrid composite systems cured under (a) no catalyst, (b) dibutyltin dilaurate catalyst, (c) tetra-ammonium hydroxide catalyst.
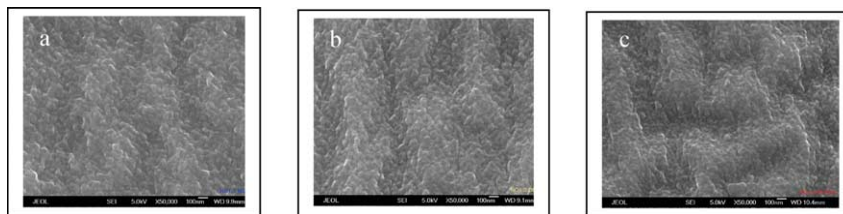
Fig. 10. SEM spectras of epoxy-APTES nano hybrid composite cured under (a) no catalyst, (b) dibutyltin dilaurate catalyst, (c) tetra-ammonium hydroxide catalyst. The scale bar represented 100 nm.

epoxy-bridged polysilsesquioxanes from epoxy-APTES cured with tetra-ammonium hydroxide catalyst shows the lowest density of nano polysilsesquioxanes domain. The SEM spectra of epoxy-bridged polysilsesquioxanes from epoxy-APTES cured with various kinds of catalysts are also shown in Fig. 10. It is found in the spectra that the nano polyorganosiloxanes domains are well distributed in the epoxy-bridged polyorganosiloxanes. The nano polyorganosiloxanes domains are further analyzed by TEM analysis. It is found in Fig. 11 that the epoxy-bridged polyorganosiloxanes of epoxy-APTES precursors exhibit polyorganosiloxanes nano domain around 45–55 nm in TEM spectra under the catalysis of dibutyltindilaurate, but has bigger polyorganosiloxanes nano domain around 50–150 nm under the catalysis of basic tetrabutylammonium hydroxide in epoxy matrix after direct thermal curing process. The polysilsesquioxanes nano domain is only found in the epoxy-bridged polyorganosiloxanes from epoxy-APTES. There is no polyorganosiloxanes nano domain appeared in TEM spectra of epoxy-bridged polyorganosiloxanes from epoxy-APDES and epoxy-APMDS precursors due to less crosslinking density of their epoxy-bridged polyorganosiloxanes structures.

4. Conclusions

Epoxy-bridged polyorganosiloxanes have been successfully prepared from direct thermal curing of epoxy-bridged polyorganosiloxanes precursors synthesized by reacting various kinds of aminoalkoxysilanes with di-functional epoxy resins. Three kinds of catalysts including dibutyltindilaurate (DBTDL), tetrabutylamonium hydroxide (NBu$_4$·OH), and boron trifluoride monoethylamine (BF$_3$·MEA) are used for the thermal curing of epoxy-bridged polyorganosiloxane precursors. Acidic BF$_3$·MEA shows the best catalytic effects on the formation of T^3 and D^2 structures in the epoxy-bridged polyorganosiloxanes from tri-functional epoxy-APTES and di-functional epoxy-APMDS precursors, but basic NBu$_4$·OH has better enhancement on the formation of M^1 structure in the epoxy-bridged polyorganosiloxanes from mono-functional epoxy-APDES precursor. The diameters polyorganosiloxanes nano domain have been proven to be affected by the catalysts used during direct thermal curing process of epoxy-APTES precursors.

Coefficient of thermal expansion of the cured epoxy-bridged polyorganosiloxanes would change with both of the functionality of terminated alkoxysilanes and the species of catalyst used during curing process. However, only the functionality of terminated alkoxysilanes would affect the T_g of the cured epoxy-bridged polyorganosiloxane. There is also no obvious T_g transition found in epoxy-bridged polyorganosiloxanes from epoxy-APTES system. Investigate on the molecular motion behaviors of epoxy-bridged polyorganosiloxanes structures with respect to the changes in T_g and CTE have discussed by explain ^{13}C solid state NMR. The $T_{1\rho}^H$ (the relaxation time of ^{13}C after the spin lock process) of cured epoxy-bridged polyorganosiloxanes from epoxy-APTES is longer than that of epoxy-APMDS, which indicates that the molecular mobility of epoxy-bridged polysilsesquioxanes from epoxy-APTES is restricted due to the strong molecular interaction between inorganic polysilsesquioxanes and organic epoxy molecules.
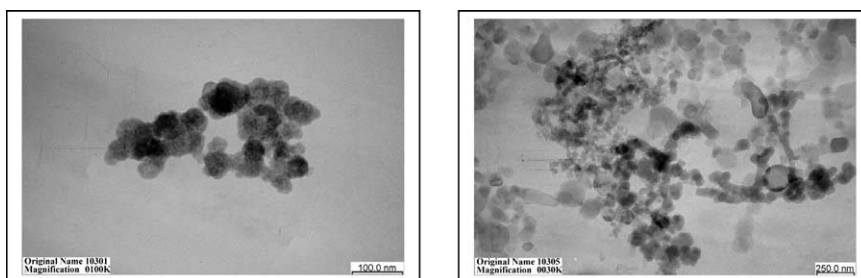
Fig. 11. TEM Spectra of epoxy-APTES nano hybrid composite system cured under (a) dibutyltin dilaurate, (b) tetra-ammonium hydroxide catalyst.

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References

[1] Wilkes GL, Drier B, Huang HH. Ceramers—hybrid materials incorporating polymeric oligomeric species into inorganic glasses utilizing a sol–gel approach. vol. 190 1985. p. 109 [Abstracts of Papers of the American Chemical Society].

[2] Baney RH, Itoh M, Sakakibara A, Suzuki T. Silsesquioxanes. Chem Rev 1995;95:1409.

[3] Provatas A, Matisons JG. Porosity in hexylene-bridged polysilsesquioxanes. Effects of monomer concentration. TRIP 1997;5:10.

[4] Lichtenhan JD. Aryl-bridged polysilsesquioxanes. A new class of microporous materials. Comments Inorg Chem 1995;17:115.

[5] Gozdz AS. Dialkylene carbonate-bridged polysilsesquioxanes. Hybrid organic–inorganic sol–gels with a thermally labile bridging group. Polym Adv Technol 1994;5:70.

[6] Li GZ, Wang L, Toghiani H, Daulton TL, Koyama K, Pittman Jr CU. Viscoelastic and mechanical properties of epoxy/multifunctional polyhedral oligomeric silsesquioxane nanocomposites and epoxy/ladderlike polyphenylsilsesquioxane blends. Macromolecules 2001; 34:8686–93.

[7] Kim GM, Qin H, Fang X, Sun FC, Mather PT. Hybrid epoxy-based thermosets based on polyhedral oligosilsesquioxane: Cure behavior and toughening mechanisms. J Polym Sci, Part B: Polym Phys 2003; 41(24):3299–313.

[8] Cabanelas JC, Serrano B, Gonzalez-Benito J, Bravo J, Baselag J. Morphology of epoxy/polyorganosiloxane reactive blends. Macromol Rapid Commun 2001;22:694–9.

[9] Choi J, Harcup J, Yee AF, Zhu Q, Laine RM. Organic/inorganic hybrid composites from cubic silsesquioxanes. J Am Chem Soc 2001; 11422:123.

[10] Liu F, Fu L, Wang J, Meng Q, Li H, Guo J, et al. Luminescent film with terbium-complex-bridged polysilsesquioxanesy. New J Chem 2003;27:233–5.

[11] Shea KJ, Loy DA, Webster O. Arylsilsesquioxane gels and related materials. New hybrids of organic and inorganic networks. J Am Chem Soc 1992;114:6700–10.

[12] Clauss J, Schmidt-Rohr K, Spiess HW. Determination of domain sizes in polymers. Acta Polym 1993;44:1.

[13] Serier A, Pascault JP, Thanh Lam My. Reactions in aminosilane-epoxy prepolymer systems 1. Kinetics of epoxy-amine reactions. J Polym Sci, Part A: Polym Chem 1991;29:209–18.

[14] Serier A, Pascault JP, Thanh Lam My. Reactions in aminosilane-epoxy prepolymer systems II. Reactions of alkoxysilanes groups with or without the presence of water. J Polym Sci, Part A: Polym Chem 1991;29:1125–31.