

Synthesis and characterization of imide ring and siloxane-containing cycloaliphatic epoxy resins

Zhiqiang Tao, Shiyong Yang, Jiansheng Chen, Lin Fan *

Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Beijing 100080, China

Received 7 July 2006; received in revised form 25 October 2006; accepted 17 January 2007

Available online 30 January 2007

Abstract

A novel imide ring and siloxane-containing cycloaliphatic epoxy compound 1,3-bis[3-(4,5-epoxy-1,2,3,6-tetrahydrophthalimido)propyl]tetramethyldisiloxane (BISE) was synthesized from 1,3-bis(3-aminopropyl)tetramethyldisiloxane and tetrahydrophthalic anhydride by a two-step procedure, which was then thermally cured with alicyclic anhydrides hexahydro-4-methylphthalic anhydride (HMPA) and hexahydrophthalic anhydride (HHPA), respectively. As comparison, a commercial available cycloaliphatic epoxy 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ERL-4221) cured with the same curing agents was also investigated. The experimental results indicated that the BISE gave the exothermic starting temperature higher than ERL-4221 no matter what kind of curing agents applied, implying the reactivity of the former is lower than the latter. The fully cured BISE epoxy resins have good thermal stability with thermal decomposition temperature at 5% weight loss of 346–348 °C in nitrogen, although they gave the relatively low glass transition temperatures due to the presence of flexible propyl and siloxane segments in the epoxy backbone. The BISE epoxy resins exhibited good mechanical and dielectric properties as well as low water absorption. The improved dielectric properties and the reduced water absorption of BISE epoxy resins are attributed to the low polarity as well as the hydrophobic nature of siloxane segment in the epoxy backbone.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Imide ring; Siloxane; Cycloaliphatic epoxy; Resin; Synthesis

1. Introduction

In recent years, an important trend in developing advanced semiconductor devices is miniaturization, aiming at high density and complex functionality of electronic products [1]. The polymer materials applied in the future microelectronic packaging must

meet the following properties: (1) high purity, to exhibit good reliability; (2) low coefficient of thermal expansion (CTE), to reduce the internal stress; (3) high thermal stability and low water absorption, for better solder resistance; and (4) low dielectric constant and dissipation factor [2–5].

Cycloaliphatic epoxy resins have long been applied in a variety of industrial applications, such as paints, coatings, inks, reactive diluents, vacuum-pressure impregnation of coils, encapsulation of electronic circuit elements and printed circuit-board

* Corresponding author. Tel.: +86 10 62564819; fax: +86 10 62569562.

E-mail address: fanlin@iccas.ac.cn (L. Fan).

coatings because of their good heat and chemical resistance, superior mechanical and electrical properties, as well as excellent processability [6–10]. Unlike aromatic epoxies, the cycloaliphatic epoxies are highly resistant to ultraviolet light and more durable for outdoor applications because of no strong UV chromophore groups in their structure. Moreover, the cycloaliphatic epoxies are essentially free of chloride because they are synthesized by the peracid epoxidation of olefins rather than the condensation of epichlorohydrin with phenols. Therefore, the cycloaliphatic epoxy resins are suitable for the applications in the microelectronic packaging, in which even very low levels of chloride can cause corrosion of microcircuits [11]. Despite the many aforementioned advantages of cycloaliphatic epoxy resins, certain properties, such as thermal and mechanical properties, electrical insulating properties as well as moisture resistance, should be improved to satisfy the demand of advanced microelectronic packaging.

It is known that siloxane-containing polymer materials possess numerous unique properties, including good flexibility, high thermal resistance, excellent electrical insulating properties, good moisture resistance and low surface tension [12, 13]. Recently, several investigations have been conducted on epoxy resins modified with siloxane segments. Park and coworkers [14] reported that the flexibility of bisphenol A diglycidyl ether epoxy resins cured with a siloxane-containing curing agent ETSO-DDM could be improved with the increasing of ETSO content in the epoxy network. Kuo and coworkers [15] described their research on epoxy-siloxane copolymers blended with bisphenol A diglycidyl ether and their results confirmed that the thermal stability could be improved as the siloxane segments incorporated into the epoxy resin. Lin and coworkers [16] studied a siloxane- and imide-modified epoxy cured with a siloxane-containing dianhydride and found the cured epoxy resin has good thermal stability with similar thermal behavior in both nitrogen and air atmospheres. Ho and Wang [17] reported their work on modification of epoxy resin with siloxane-containing phenol aralkyl epoxy resin for electronic encapsulation application. Their results suggested that the devices encapsulated by the polysiloxane-modified epoxy molding compound have excellent resistance to the thermal shock cycling test and have resulted in an extended lifetime for the devices, which attributed to the effective reduction of flexural modulus and coefficient

of thermal expansion of cured epoxy molding compound.

Aiming at preparation the cycloaliphatic epoxy resins with excellent electrical insulating properties combined with good thermal and mechanical properties, in the present research, a novel imide ring and siloxane-containing cycloaliphatic epoxy compound 1,3-bis[3-(4,5-epoxy-1,2,3,6-tetrahydrophthalimido)propyl]tetramethyldisiloxane (BISE) was synthesized by the imidization and epoxidation reactions [18], in which the low polar and hydrophobic siloxane segment was introduced to the monomer backbone in order to improve the dielectric properties and the moisture resistance, meanwhile, the rigid imide ring was also combined to ensure the good thermal stability. The novel cycloaliphatic epoxy was thermally cured with alicyclic anhydrides hexahydro-4-methylphthalic anhydride (HMPA) and hexahydrophthalic anhydride (HHPA), respectively, and their thermal stability, mechanical properties, electrical and dielectric properties, as well as the water absorption were investigated. Furthermore, the epoxy resins based on the commercial available cycloaliphatic epoxy 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ERL-4221) cured with the same curing agents were also prepared and their properties were discussed in comparison with the cured BISE epoxy resins.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was purchased from Beijing Chemical Reagents Co., China; which was dried and distilled prior to use. Pyridine, acetic anhydride, petroleum ether and methylene chloride were purchased from Beijing Chemical Reagents Co., China and used as received. 3,4-Epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (trade name ERL-4221) was purchased from Aldrich and used as received. Tetrahydrophthalic anhydride (THPA), hexahydro-4-methylphthalic anhydride (HMPA), hexahydrophthalic anhydride (HHPA) and *m*-chloroperoxybenzoic acid (*m*-CPBA, content 70%) were purchased from Acros Organics and used as received. 1-Cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN) was purchased from Shikoku Chemicals Corp. and used as received. 1,3-Bis(3-aminopropyl)tetramethyldisiloxane was prepared in our laboratory according to the method previously reported in literature [19].

2.2. Monomer synthesis

2.2.1. 1,3-Bis[3-(1,2,3,6-tetrahydrophthalimido)-propyl]tetramethyldisiloxane (**1**)

A 500 ml three-necked flask equipped with a mechanical stirrer, a water condenser, and a nitrogen inlet tube was fitted with a mixture of 1,3-bis(3-aminopropyl)tetramethyldisiloxane (20.00 g, 80.48 mmol) and anhydrous THF (60 ml). The mixture was stirred at room temperature for 10 min in nitrogen, followed by addition of the tetrahydrophthalic anhydride (24.49 g, 161.00 mmol) in portions during 20 min. A yellow solution was obtained after the mixture was stirred at room temperature for 12 h under a nitrogen atmosphere. To which a mixture of acetic anhydride and pyridine (200 ml, 3:2 v/v) was added under stirring and then reacted at ambient temperature for 2 h and at 60 °C for another 4 h. The yellow crystals were gained after the solution was vacuum distilled to remove the residue solvent followed by cooled to room temperature, which was collected and washed with petroleum ether and water. The yellowish powder of compound **1** was obtained after dried in vacuum. Yield: 33.30 g (80%). m.p.: 80 °C (determined by DSC). ¹H NMR (CDCl₃, δ, ppm): 0.01 (s, 12H); 0.35–0.39 (t, 4H); 1.41–1.49 (m, 4H); 2.15–2.58 (m, 8H); 3.01–3.03 (t, 4H); 3.37–3.40 (t, 4H); 5.81–5.87 (m, 4H). FTIR (KBr, cm⁻¹): 3450, 3046, 2956, 2869, 1770, 1700 (imide group), 1354 and 1067 (Si–O–Si linkage) and 696 cm⁻¹. MS: (EI, *m/e*, % relative intensity): 501 (M–15, 12); 324 (M–192, 100). Elem. Anal. Calcd. for C₂₆H₄₀N₂O₅Si₂: C, 60.43%; H, 7.80%; N, 5.42%. Found C, 60.36%; H, 7.81%; N, 5.51%.

2.2.2. 1,3-Bis[3-(4,5-epoxy-1,2,3,6-tetrahydrophthalimido)propyl]tetramethyldisiloxane (**BISE**)

A 500 ml three-necked flask equipped with a thermometer, an addition funnel and a mechanical stirrer was first cooled with an ice bath for 10 min. It was then charged with *m*-chloroperoxybenzoic acid (28.62 g, 116.10 mmol) and 200 ml of methylene chloride. After the mixture was cooled to 0 °C, a solution of compound **1** (25.00 g, 48.38 mmol) in 100 ml of methylene chloride was added dropwise over 2 h. After the mixture was stirred at 0 °C for 10 h, it was filtered and washed with 10% of sodium sulfite aqueous solution, 10% of sodium bicarbonate aqueous solution, and deionized water to neutrality. The organic phase was dried over anhydrous sodium sulfate, and then the solvent was removed by vac-

uum distillation to yield crude product. The product was purified by recrystallization from a mixed solvent of petroleum ether and methylene chloride (2:1 v/v). Yield: 12.64 g (48%). m.p.: 166 °C (determined by DSC). EEW: 275 g/equiv (determined by HCl/acetone titration method). ¹H NMR (CDCl₃, δ, ppm): 0.02 (s, 12H), 0.49–0.53 (t, 4H), 1.53–1.61 (m, 4H), 2.10–2.77 (m, 8H), 2.73–2.75 (m, 4H), 3.14–3.15 (t, 4H), and 3.41–3.47 (t, 4H). FT-IR (KBr, cm⁻¹): 3446, 3026, 2956, 2923, 2861, 1769, 1700 (imide group), 1351, 1076 (Si–O–Si linkage) and 948 cm⁻¹ (oxirane ring). MS: (EI, *m/e*, % relative intensity): 533 (M–15, 6); 340 (M–208, 100). Elem. Anal. Calcd. for C₂₆H₄₀N₂O₇Si₂: C, 56.90%; H, 7.35%; N, 5.10%. Found C, 56.81%; H, 7.33%; N, 5.05%.

2.3. Curing procedure of epoxy resins

The imide ring and siloxane-containing cycloaliphatic epoxy **BISE** and a commercial cycloaliphatic epoxy **ERL-4221** were cured with anhydrides **HMPA** and **HHPA**, respectively. The chemical structures of epoxies and curing agents are shown in [Table 1](#). The reactant compositions were mixed in a 1:0.8 molar ratio of epoxy to anhydride at room temperature and 1.0 wt% of **2E4MZ-CN** was added as a curing accelerator. The mixture was stirred at 170 °C until a homogeneous solution was obtained. The curing cycles are listed in [Table 2](#), which were determined by DSC tracing of the respective epoxy/curing agent compositions. After curing, samples were allowed to cool slowly to room temperature in order to prevent cracking.

2.4. Characterization

¹H NMR spectra was record with a Bruker MSL-400 (300 MHz) NMR spectrometer using CDCl₃ as solvent. FT-IR spectra were obtained using a Perkin–Elmer 782 Fourier transform infrared spectrophotometer. Mass spectra were recorded by an AEI MS-50 mass spectroscopy. The EEW of epoxy resin was determined by the HCl/acetone titration method. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on a Perkin–Elmer 7 series thermal analysis system in nitrogen at a heating rate of 20 °C min⁻¹. Dynamic mechanical analysis (DMA) was carried out a Perkin–Elmer 7 series thermal analysis system in nitrogen using at a heating rate of 5 °C min⁻¹. Mechanical properties were performed with 60 ×

Table 1
Chemical structures of the epoxies and curing agents

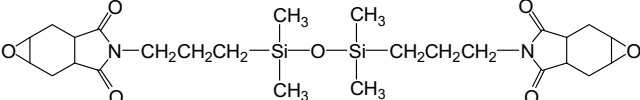
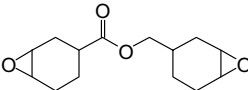
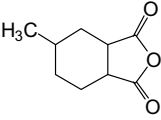
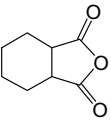
Component	Abbreviation	Chemical structure
Epoxy	BISE	
	ERL-4221	
Curing agent	HMPA	
	HHPA	

Table 2
Curing cycles of epoxy resins

Sample	Curing temperature (°C)	Curing time (h)	Postcure temperature (°C)	Postcure time (h)
BISE/HMPA	180	2	200	2
BISE/HHPA	170	2	190	2
ERL-4221/HMPA	150	2	190	2
ERL-4221/HHPA	140	2	180	2

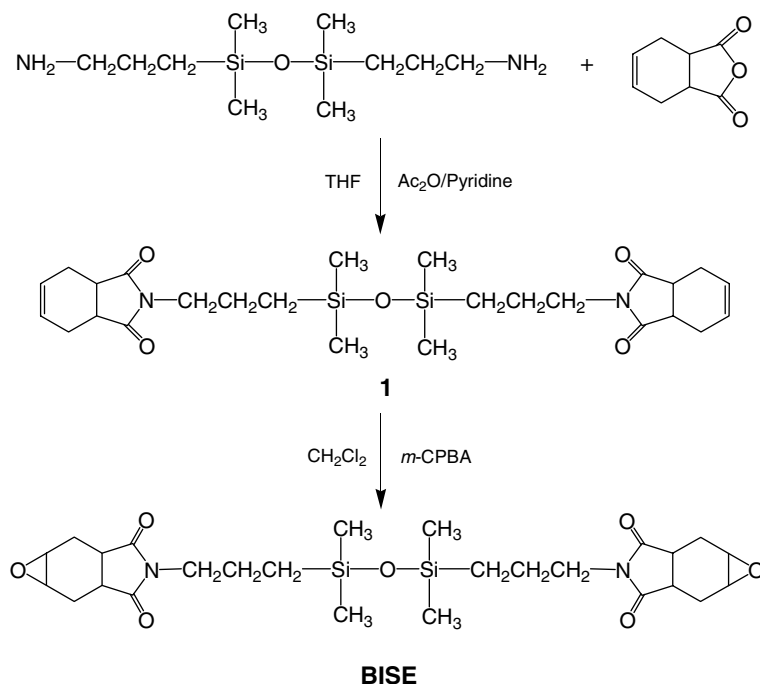
15 × 3 mm specimens in accordance with GB1449-87 using an Instron 3365 Tensile Apparatus. The electrical properties were measured on a Hewlett-Packard 4284A Precision LCR meter. The dielectric constant and dissipation factor were determined by the bridge method with an LKI-1 capacitance meter at a frequency of 1 MHz at 25 °C. Water absorptions were determined by weighing the changes of the cured epoxy samples (Φ 50 mm × 3 mm) before and after immersion in water at 25 °C for 24 h.

3. Results and discussion

3.1. Synthesis

The novel imide ring and siloxane-containing cycloaliphatic epoxy BISE was synthesized through a two-step procedure as shown in Scheme 1. Firstly, siloxane-containing diamine was reacted with tetrahydrophthalic anhydride by chemically imidization with the mixture of acetic anhydride and pyridine in THF to yield imide ring and siloxane-containing

cyclohexene (compound 1). Then, the compound 1 was oxidized by *m*-chloroperoxybenzoic acid, in which the unsaturated cyclohexenyl ring was epoxidized to give the imide ring and siloxane-containing cycloaliphatic epoxy BISE. The chemical structures of these compounds were confirmed by ¹H NMR, FT-IR, elemental analysis and MS. Fig. 1 shows the ¹H NMR spectra of compound 1 and BISE in CDCl₃, respectively. All the signals corresponding to the proposed structures were observed. In the ¹H NMR spectrum of compound 1 (Fig. 1a), the methyl protons of siloxane (H₁) were observed at 0.01 ppm. The propyl protons H₂ and H₃ showed in the region of 0.35–0.39 and 1.41–1.49 ppm, respectively. The propyl protons adjacent to the imide rings (H₄) and the protons on imide rings (H₅) shifted to the downfield because of the electron drawing effect of carboxyl group, which were observed in the range of 3.37–3.40 and 3.01–3.03 ppm, respectively. The protons on the double bonds of the cyclohexenyl rings (H₇) appeared at 5.81–5.87 ppm and the other protons in the cyclo-



Scheme 1. Synthesis of imide ring and siloxane-containing cycloaliphatic epoxy compound BISE.

hexenyl rings (H_6) showed in the range of 2.15–2.58 ppm. In the 1H NMR spectrum of BISE (Fig. 1b), the resonance signals assigned to the protons H_1 – H_6 showed no significant changes as compared with those of compound 1. However, the signal at 5.81–5.87 ppm for the double-bond protons in the cyclohexenyl rings of compound 1 disappeared. The signal attributed to the protons in the oxirane ring was observed at 2.73–2.75 ppm.

Fig. 2 shows the FT-IR spectra of compound 1 and BISE, in which the absorptions for the asymmetric and symmetric C=O stretching vibrations of imide groups can be observed at 1770 and 1700 cm^{-1} , respectively. The characteristic absorptions for Si–O–Si linkage of siloxane were also detected in the region of 1050–1100 cm^{-1} . Moreover, in the FT-IR spectrum of BISE, the absorptions at 3046 and 696 cm^{-1} related to the double bond in the cycloaliphatic rings of compound 1 disappeared completely. The absorption bands of deformation of the oxirane ring appeared at 948 cm^{-1} and the absorption due to the CH_2 stretching vibration of terminal epoxide exhibited at 3027 cm^{-1} .

The elemental analysis results of compound 1 and BISE are listed in Table 3, which were in good agreement with the calculated values. In the mass

spectrum of BISE the characteristic peaks at 533 (M–15, lost a methyl group) and 340 (M–208, cleaved in Si– CH_2 linkage) were detected. The epoxy equivalent weight (EEW) of BISE was determined to be 275 g/equiv by titration, which was close to the theoretical value of 274 g/equiv. These results confirmed that pure BISE compound was obtained.

3.2. Thermal curing behavior

The thermal curing behavior of the epoxy and curing agent compositions were investigated by DSC. Significant caution was taken during the DSC study of the polymerization reactions to obtain homogeneous mixture of the epoxy resin and curing agents. The reactivity of the epoxies can be studied directly from the exothermic starting temperature. It is well known that a curing agent exhibited a lower exothermic starting temperature under the same set of curing condition is more reactive toward the epoxy resins. Fig. 3 showed the DSC thermograms for the curing procedure of BISE and ERL-4221 with HMPA and HHPA, respectively. The endothermic peaks around 130 °C were observed only in BISE system, which attributed to the melting course of the BISE and anhydride mixture. The exothermic

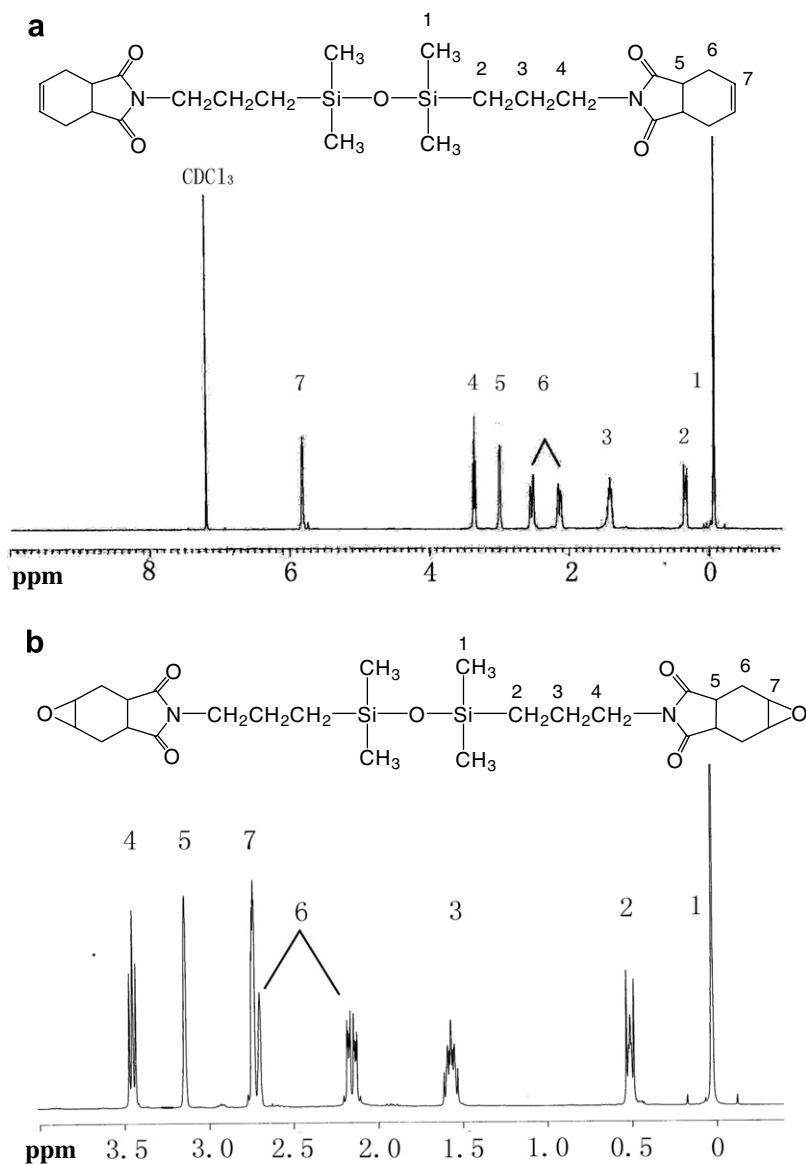


Fig. 1. ^1H NMR spectra of compound 1 (a) and BISE (b) in CDCl_3 .

peaks were detected around 200–210 °C for BISE and ERL-4221 system. As comparing with the reactivities of these epoxy resins, we found that the BISE exhibited the exothermic starting temperature higher than the ERL-4221, which suggested the chemical reactivity of the former is lower than the latter. We suspect that it may be related to the reduction of electron density in the oxirane ring because of the electron acceptor character of the imide rings, which is unfavorable for the electrophilic attack of the anhydride curing agents. In addition, for both of

BISE and ERL-4221 epoxies, the exothermic starting temperatures for HMPA curing system are slightly higher than those of HHPA curing system, which revealed that the chemical reactivity of HHPA toward cycloaliphatic epoxies BISE and ERL-4221 is higher than that of HMPA. It might be attributed to electron-donating effect of methyl group in the HMPA, which might increase the electron density of the anhydride and subsequently reduced the electrophilic addition on the oxirane ring of epoxies.

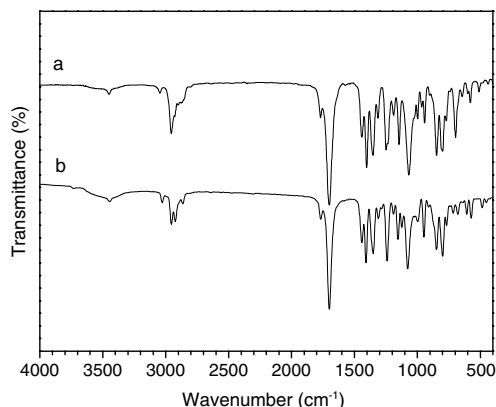


Fig. 2. FT-IR spectra of compound 1 (a), and BISE (b).

3.3. Thermal properties

The thermal stability of fully cured BISE and ERL-4221 was evaluated by thermal gravimetric analysis (TGA) and the results are shown in Fig. 4. It was found that the cured epoxy resins did not lose any original weight before the scanning temperature reached up to 300 °C, implying that they have good thermal stability below 300 °C. The decomposition temperature at 5% of weight loss (T_5) for BISE/HMPA and BISE/HHPA epoxy resins were at 346 and 348 °C and that for ERL-4221/HMPA and ERL-4221/HHPA epoxy resins were at 351 and 343 °C, respectively (Table 4). As the scanning temperature rose to 360 °C, the TGA curves of these epoxy resins exhibited a dramatic decreasing. However, we found that the BISE epoxy resins exhibited a relative slow weight decreasing tendency in comparison with ERL-4221 epoxy resins, which suggested that the former have better thermal stability than the latter. The residual weight retention at 450 °C for the BISE/HMPA and BISE/HHPA was 30.2% and 29.9%, respectively, whereas that for the ERL-4221/HMPA and ERL-4221/HHPA was 1.0% and 1.4%, respectively. The improved thermal stability of BISE epoxy resins might be attributed to the presence of the thermal stable imide rings and Si–O–Si linkages in the polymer backbone.

Table 3
Elemental analysis of monomers

Monomer	Molecular formula	C (%)		H (%)		N (%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
Compound 1	C ₂₆ H ₄₀ N ₂ O ₅ Si ₂	60.36	60.43	7.81	7.80	5.51	5.42
BISE	C ₂₆ H ₄₀ N ₂ O ₇ Si ₂	56.81	56.90	7.33	7.35	5.05	5.10

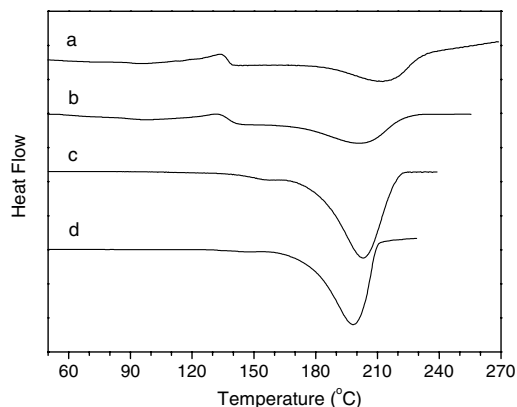


Fig. 3. DSC thermograms of the curing procedure of epoxy resins; (a) BISE/HMPA; (b) BISE/HHPA; (c) ERL-4221/HMPA, and (d) ERL-4221/HHPA.

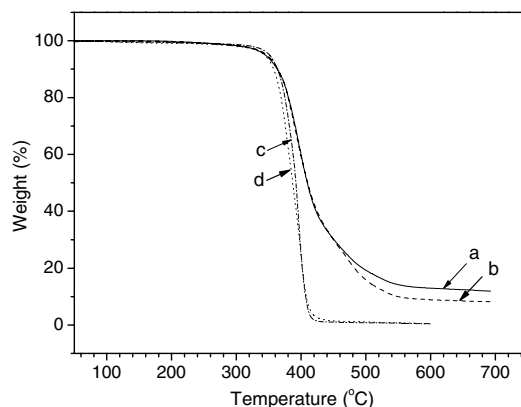


Fig. 4. TGA thermograms of the cured epoxy resins; (a) BISE/HMPA; (b) BISE/HHPA; (c) ERL-4221/HMPA, and (d) ERL-4221/HHPA.

Table 4
Thermal properties of the cured epoxy resins^a

Sample	T_5 (°C)	T_{10} (°C)	R_w (%)
BISE/HMPA	346	364	30.2
BISE/HHPA	348	365	29.9
ERL-4221/HMPA	351	363	1.0
ERL-4221/HHPA	343	357	1.4

^a T_5 : decomposition temperature at 5% of weight loss; T_{10} : decomposition temperature at 10% of weight loss; R_w : residual weight retention at 450 °C.

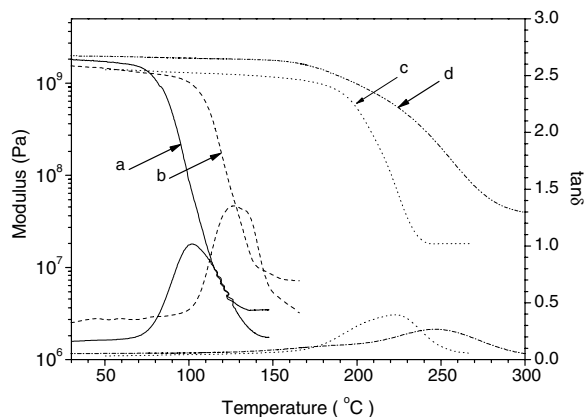


Fig. 5. DMA curves of the cured epoxy resins; (a) BISE/HMPA; (b) BISE/HHPA; (c) ERL-4221/HMPA, and (d) ERL-4221/HHPA.

Table 5
DMA analysis of the epoxy resins

Sample	T_g (°C)	Storage modulus (GPa)	
		50 °C	$T_g + 40$ °C
BISE/HMPA	102	1.72	0.004
BISE/HHPA	127	1.45	0.007
ERL-4221/HMPA	222	1.40	0.018
ERL-4221/HHPA	246	1.96	0.044

The dynamic mechanical analysis of these cycloaliphatic epoxies was carried out to get more details about their thermal properties. DMA curves of the cured epoxy resins are shown in Fig. 5 and the data are summarized in Table 5. The glass transition temperatures (the peak temperature of the loss tangent) of BISE/HMPA and BISE/HHPA are 102 °C and 127 °C, respectively, which are much lower than that of ERL-4421/HMPA (222 °C) and ERL-4421/HHPA (246 °C). The low glass transition temperature of BISE epoxies is considered to be due to the existence of the flexible propyl and siloxane segments in the epoxy backbone. The storage moduli of these epoxy resins at low temperature (50 °C) show no obvious difference, which are in the range of 1.40–1.96 GPa. However, the storage moduli of BISE/HMPA and BISE/HHPA at rubbery region ($T_g + 40$ °C) were as low as 0.004 and 0.007 GPa, respectively, which attributed to the flexible propyl and siloxane segments in the polymer structure. While the ERL-4221 epoxy resins gave the storage moduli at rubbery region about ten times of the BISE epoxy resins, which are 0.018 and 0.044 GPa for ERL-4221/HMPA and ERL-4221/HHPA, respectively. It is well known that the crosslink den-

sity is proportionate to the storage modulus at $T_g + 40$ °C according to rubber elasticity theory [20]. Therefore, the ratios of crosslink densities for BISE/HMPA:BISE/HHPA and ERL-4221/HMPA:ERL-4221/HHPA are 1.0:2.1 and 1.0:2.4, respectively. It is suggested that the cycloaliphatic epoxies cured with HHPA have the higher crosslink density than the corresponding epoxies cured with HMPA. This result also can be confirmed by the T_g of these epoxies determined by DMA, in which the glass transition temperatures of BISE/HHPA and ERL-4221/HHPA are 25 °C and 24 °C higher than those of the corresponding epoxies cured with HMPA. In addition, from the DMA curves of the cured BISE epoxy resins, it is found that both loss tangent ($\tan\delta$) and storage modulus (E') curves of these epoxy resins displayed a single transition course implying good compatibility of the system. Furthermore, no phase separation phenomena was observed in the SEM micrograph of fracture surface of the cured BISE/HMPA epoxy resin (Fig. 6), which also suggested the homogeneity and good compatibility of the cured BISE/HMPA.

3.4. Mechanical and dielectric properties

The mechanical properties of cured epoxy resins were investigated. As comparing the results listed in Table 6, we found that the cured imide rings and siloxane-containing cycloaliphatic BISE epoxy resins have the mechanical properties as good as the commercial cycloaliphatic epoxy resins derived from ERL-4221. The flexural strength and the flexural modulus of these epoxies are ranged at 63–

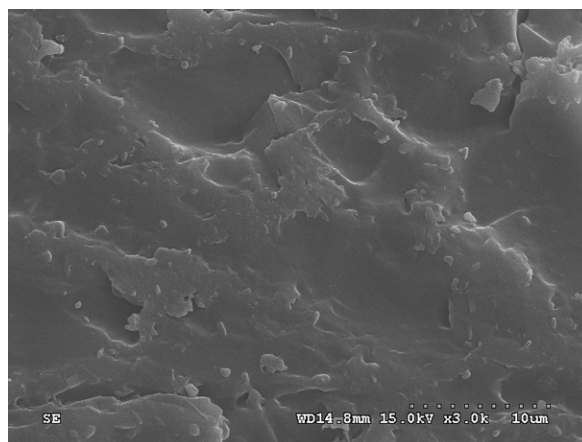


Fig. 6. SEM micrograph of fracture surface of the cured BISE/HMPA epoxy resin.

Table 6
Mechanical properties of the epoxy resins

Sample	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Tensile modulus (GPa)
BISE/HMPA	63	3.35	33	1.44
BISE/HHPA	83	2.68	31	1.21
ERL-4221/HMPA	81	2.95	36	1.35
ERL-4221/HHPA	88	2.52	31	1.46

Table 7
Electrical and dielectric properties of the cured epoxy resins and their water absorption^a

Sample	ρ_v (Ω cm)	ρ_s (Ω)	ϵ_r	$\tan \delta$	Water absorption (%)
BISE/HMPA	2.3×10^{16}	7.3×10^{16}	3.2	2.4×10^{-3}	0.48
BISE/HHPA	3.3×10^{16}	3.1×10^{16}	3.3	4.8×10^{-3}	0.50
ERL-4221/HMPA	7.9×10^{16}	2.0×10^{16}	3.6	6.9×10^{-3}	0.54
ERL-4221/HHPA	5.4×10^{16}	4.2×10^{16}	3.6	7.5×10^{-3}	0.55

^a Water absorption: immersion in water at 25 °C for 24 h; ρ_v : volume resistivity; ρ_s : surface resistivity; ϵ_r : dielectric constant at 1 MHz at 25 °C and $\tan \delta$: dissipation factor.

88 MPa and 2.52–3.35 GPa, respectively. The tensile strength and tensile modulus of these resins are in the region of 31–36 MPa and 1.21–1.46 GPa, respectively.

The electrical and dielectric properties of the cured epoxy resins are shown in Table 7. The volume resistivities (ρ_v) and surface resistivities (ρ_s) of the epoxy resins are at the level of 2.3 – 7.9×10^{16} Ω cm and 2.0 – 7.3×10^{16} Ω , respectively. The dielectric constants (ϵ_r) and the dielectric dissipation factors ($\tan \delta$) at 1 MHz were measured in the range of 3.2–3.6 and 2.4 – 7.5×10^{-3} , respectively. In comparison, the cured BISE epoxy resins exhibited lower dielectric constants and dissipation factors than the commercial ERL-4221 epoxy resins cured with the corresponding curing agents. The improved dielectric properties of the cured BISE epoxies may be attributed to the presence of the low polarity dimethylsiloxane segments in the epoxy backbone [21].

3.5. Water absorption

In actual service, microelectronic packaging materials are subject to varying conditions of humidity and temperature. Unfortunately, moisture has a detrimental effect, especially at elevated temperature, on the mechanical properties and electrical insulating performance of epoxy resins [22,23]. Table 7 summarizes the water absorption of the cured epoxy resins, in which the water absorption was determined by immersing the dried samples (Φ

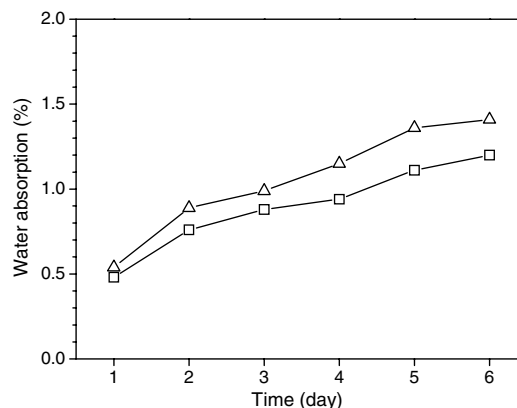


Fig. 7. Water absorption of the cured epoxy resins; (□) BISE/HMPA, and (△) ERL-4221/HMPA.

50 mm × 3 mm) in water at room temperature for 24 h, followed by weighing. The cured BISE epoxy resins gave the water absorptions slightly lower than the ERL-4221 epoxy resins. For instance, the water absorptions of BISE/HMPA and BISE/HHPA are 0.48% and 0.50%, respectively, whereas the ERL-4221 cured with the corresponding curing agents are 0.54% and 0.55%, respectively. Fig. 7 depicts the changes of water absorption of these epoxy resins according to the time. It was found that these epoxy resins showed the water absorptions increased with the time prolongation. After the samples immersed in water for 6 days, the water absorptions of BISE/HMPA and ERL-4221/HMPA increased to 1.20% and 1.41%, respectively. In addition, the results also clearly revealed that the siloxane-containing epoxy resins exhibited lower water

absorption than that of nonsiloxane-containing epoxy resins due to the presence of the hydrophobic nature of the siloxane segment. Because of free rotatability and polarization of the Si–O bond, the siloxane chain is able to align itself accordingly resulting in hydrophobic properties [13].

4. Conclusions

A novel imide ring and siloxane-containing cycloaliphatic epoxy compound BISE was successfully synthesized by a two-step procedure, which was then thermally cured with alicyclic anhydrides HMPA and HHPA. The reactivity and the properties of the fully cured BISE epoxy resins were investigated and compared with the cured commercial cycloaliphatic epoxy ERL-4221. The experimental results indicated that the BISE gave the exothermic starting temperature higher than ERL-4221 no matter what kind of curing agents applied, implying the reactivity of the former is lower than the latter. The fully cured BISE epoxy resins have good thermal stability with thermal decomposition temperature at 5% weight loss of 346–348 °C in nitrogen, although they gave the relatively low glass transition temperatures due to the flexible propyl and siloxane segments in the epoxy backbone. The BISE epoxy resins exhibited good mechanical properties with the flexural strengths of 63–82 MPa and tensile strengths of 31–33 MPa. As comparing with the commercial ERL-4221 epoxy resins, the cured BISE epoxy resins exhibited improved dielectric properties with the dielectric constants of 3.2–3.3, the dielectric dissipation factors of $2.4\text{--}4.8 \times 10^{-3}$ and the lower water absorptions of 0.48–0.50%. The improvement in dielectric properties and the moisture resistance may be attributed to the low polarity as well as the hydrophobic nature of siloxane segment in the epoxy backbone.

References

- [1] Show JM. Overview of polymers for electronic and photonic applications. In: Wang CP, editor. *Polymers for electronic and photonic applications*. New York: Academic Press; 1993.
- [2] Lin CH, Chiang JC, Wang CS. Low dielectric thermoset. I. Synthesis and properties of novel 2,6-dimethyl phenoldicyclopentadiene epoxy. *J Appl Polym Sci* 2003;88:2607–13.
- [3] Li H, Wang L, Jacob K, Wong CP. Syntheses and characterizations of thermally degradable epoxy resins III. *J Polym Sci Part A: Polym Chem* 2002;40:1796–807.
- [4] Moon KS, Choi HD, Lee AK, Cho KY, Yoon HG, Suh KS. Dielectric properties of epoxy-dielectrics-carbon black composite for phantom materials at radio frequencies. *J Appl Polym Sci* 2000;77:1294–302.
- [5] Lin LL, Ho TH, Wang CS. Synthesis of novel trifunctional epoxy resins and their modification with polydimethylsiloxane for electronic application. *Polymer* 1997;38:1997–2003.
- [6] Stevens JJ. *Epoxy resin technology*. New York: Interscience; 1968.
- [7] Lee SM. Electrical and electronic applications. In: May CA, editor. *Epoxy resins*. New York-Basel: Marcel Dekker; 1988.
- [8] Kinjo N, Ogata M, Nishi K, Kaneda A. Epoxy molding compounds as encapsulation materials for microelectronic devices. *Adv Polym Sci* 1989;88:1–48.
- [9] Xie MR, Wang ZG, Zhao YF. Synthesis and properties of a novel, liquid, trifunctional, cycloaliphatic epoxide. *J Polym Sci Part A: Polym Chem* 2001;39:2799–804.
- [10] Xie MR, Wang ZG. Synthesis and properties of a novel cycloaliphatic epoxide. *Macromol Rapid Commun* 2001;22:620–3.
- [11] Wang LJ, Wong CP. Epoxy-additive interaction study of thermal reworkable underfills for flip-chip applications. In: *Proceedings of 49th Electronic Components and Technology Conference*, San Diego, CA: 1999. p. 34–42.
- [12] Shih WC, Ma CC. Tetrafunctional aliphatic epoxy I: synthesis and characterization. *J Appl Polym Sci* 1998;69:51–8.
- [13] Kricheldorf HR, editor. *Silicon in polymer synthesis*. Berlin Heidelberg: Springer-Verlag; 1996.
- [14] Park SJ, Jin FL, Park JH, Kim KS. Synthesis of a novel siloxane-containing diamine for increasing flexibility of epoxy resins. *Mater Sci Eng A* 2005;399:377–81.
- [15] Hou SS, Chung YP, Chan CK, PL Kou. Function and performance of silicone copolymer. Part IV. Curing behavior and characterization of epoxy-siloxane copolymer blended with diglycidyl ether of bisphenol-A. *Polymer* 2000;41:3263–3272.
- [16] Li HT, Chuang HR, Wang MW, Lin MS. Synthesis, properties and pyrolysis of siloxane- and imide-modified epoxy resin cured with siloxane-containing dianhydride. *Polym Int* 2005;54:1416–21.
- [17] Ho TH, CS Wang. Modification of epoxy resin with siloxane containing phenol aralkyl epoxy resin for electronic encapsulation application. *Eur Polym J* 2001;37:267–74.
- [18] Batog AE, Petko IP, Penczek P. Aliphatic-cycloaliphatic epoxy compounds and polymers. *Adv Polym Sci* 1999;144:49–115.
- [19] McGrath JE, Dunson DL, Mecham SJ, Hedrick JL. Synthesis and characterization of segmented polyimide-polyorganosiloxane copolymers. *Adv Polym Sci* 1999;140:61–105.
- [20] Tobolsky AV. *Properties and structure of polymers*. New York: Wiley; 1960.
- [21] Zhu PK, Li ZB, Wang Q, Feng W, Wang LX. Synthesis and characterization of photosensitive copolysiloxaneimides. *J Appl Polym Sci* 1997;64:1463–8.
- [22] Morgan RJ, O'Neal JE. Durability of epoxies. *Polym Plast Technol Eng* 1978;10:49–116.
- [23] Browning CE. PhD dissertation, University of Dayton, Dayton, OH, 1976.