Structure and Characterization for Conterminously Linked Polymer of Short-Chain Epoxy Resin with Triallyl Isocyanurate and Bismaleimide

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ABSTRACT: The short-chain epoxy resin (SCER) was prepared direct from epichlorohydrin/bisphenol A (ECH/BPA). The resulted SCER and 4,4'-diaminodiphenyl sulfone (DDS) with various weight percent of triallyl isocyanurate/4,4'-bismaleimidophenylmethane (TAIC/BMI) were subsequently thermally coreacted to the corresponding high performance materials for high frequency application. They were characterized using potentiometry, Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), thermogravimetric analyses (TGA), dielectric analyzer, and scanning electron microscope (SEM). Dynamic mechanical analysis (DMA) of polymers showed only a T_g indicating a low en-

INTRODUCTION

Epoxy resins are commercially used in high-performance materials. They have been the most important class of thermosetting resin in industry for various applications, such as composite matrix, coating, potting compounds, laminates, encapsulant for semiconductor, insulating material for electric devices¹⁻⁶ and many others, because of its application versatility, processability, low cost, and performance. Through the proper selection of resin, modifier, and curing agent, the cured epoxy resin system can be tailored to specific performance characteristics. Among addition polyimides, bismaleimides (BMIs) are the most important system currently used for advanced material applications due to its high performance-to-cost ratio. Similar to other types of addition polyimides, unmodified BMI resins suffer from brittleness due to their high crosslinking densities; addition polyimides generally possess better thermal properties.

The diglycidyl ether of bisphenol A (DGEBA) has been the most usual epoxy resin system in industry because of its fluidity, physical strength after curing, tropy, amorphous state and formed a conterminously linked polymer. The morphology of polymers revealed no phase separation. The formation of polymer was in good agreement with the proposed molecular structure, and has enhanced good thermal, mechanical, and electric properties. Furthermore, with lower nitrogen content was achieved UL-94 V-0 rating. No fume and toxic gas emission were observed during burning test for this system. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2470–2480, 2006

Key words: short-chain epoxy resin; conterminously linked structure; morphology

and advantage. Curing of the most commonly used epoxy resin, DGEBA, with a variety of curing agents, was extensively reported in the literature.^{7–9} Recently, many studies on improving the flame retardancy of epoxy resins have been reported.^{10–14} In a fire, halogen of bromine and chlorine produces problems of smoke, toxicity, and corrosion.¹⁵ These considerations have led to the search for new flame retardants; nitrogen and phosphorus compounds incorporated into epoxy resins generate less toxic gas and smoke than halogen-containing compounds and also exhibit high flame retardancy. Some have achieved this goal with nitrogen or phosphorus content, and others have sacrificed thermal stability (e.g., lowering the glass transition temperature and the decomposition temperature.

Epoxy resins modified with bismaleimide through chemical reaction and physical blending have been reported to show good thermal mechanical and flame retardant properties.^{16–18} Additionally, the use of a reactive compound triallyl isocyanurate to improve the particulate morphology of polymer.¹⁹ In this study, we synthesized low molecular weight short-chain epoxy resin (SCER), and is further cured and mixed with various weight percent for coreactive mechanisms of trially isocyanurate and bismaleimide. This study explores the relationship between the structures and properties of the polymers. In addition, the object of this work was to produce high frequency materials with high glass transition temperature, low dielectric constant and

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dissipation factor for multilayer circuit board and semiconductor encapsulation applications.

EXPERIMENTAL

Materials

Epichlorohydrin (ECH), 2,2-bis(4-hydroxy phenyl) propane or bisphenol A (BPA), 4,4'-bismaleimidophenylmethane (BMI), triallyl isocyanurate (TAIC), and 4,4'-diaminodiphenyl sulfone (DDS) were purchased from Aldrich (Milnaukee, WI). 1-Methoxy-2-hydroxy propane and methyl isobutyl ketone (MIBK) were purchased from Ferak (Berlin, Germany). Triphenyl-phosphine (Ph₃P) was obtained from TCI (Tokyo, Japan), and was used as a curing accelerator. All the reaction chemicals and solvents were reagent grade or were purified by standard methods before use.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on 8100-type spectrometer (Japan) with KBr pellets, and spectra in the optical range of 400–4000 cm⁻¹ were obtained by averaging 32 scans at a resolution of 4 cm⁻¹. The epoxy equivalent weight (EEW) of the epoxy resin was determined by the HClO₄/potentiometric titration method²⁰ in which the solution was used as a titrant, and the end points were detected by the first derivative of the potential versus the volume of the titrant. Differential scanning calorimeter (Perkin-Elmer DSC-7, USA) measurements

were used in this study. Samples of approximately 5-10 mg in weight were sealed in hermetic aluminum pans and scanned in the calorimeter with a heating rate of 10°C/min from 30 to 300°C under N₂ atmosphere, and the glass transition temperature (T_{q}) values were taken as the change of the specific heat in the heat flow curves, and peak baseline was determined from the horizontal straight method. For dynamic scanning, calibration of the calorimeter was conducted for the heating rate using an indium standard. Dynamic viscoelastic properties were studied on a Perkin-Elmer 7 (USA) series thermal analysis with a DMA mode between 50 and 350°C with a heating rate of 5°C/min at a frequency of 1 Hz. A temperature/time scan in a three-point bending mode was chosen, and the dimensions of the specimen were $15 \times 5.5 \times 1.5 \text{ mm}^3$, according to ASTM Standard D790-95a: the distance of the support span was 10 mm. The elastic modulus, E' and the tan δ were determined. The coefficient of thermal expansion (CTE) was measured in the thermal mechanical analysis (TMA) mode of a Perkin-Elmer 7 instrument in accordance with ASTM Standard E831-86: a specimen 2 mm in thickness was used at a heating rate of 5°C/min, and the CTE values were calculated from the slope in front of T_g . Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA-7 (USA) thermal analyzer using a heating rate of 20°C/min in N₂ at a purge pressure of 25 psi within the temperature range of 100-600°C. Moisture uptake was obtained with a difference in mass. Samples (1 cm \times 1 cm \times 1 mm) of each cured resin disk





Scheme 1 Synthesis short-chain epoxy resin.

were immersed in hot water (about 90°C) for 5 h (until equilibrium saturation). The quantity of water absorbed as a result of the value was determined by weight differences before and after immersion. Before each weighing measurement, the samples were wiped to remove surface water and weighed immediately. A new value of the water absorbed is checked with the one obtained earlier and the same iterative procedure can be repeated until the value to within 1% deviation is achieved.

The dielectric constants and dissipation factor were determined by the bridge method with a RF Impedance

/material Analyzer (Japan) at 1 MHz or 1 GHz, 1 V, and 25°C in a N₂ by the two parallel plate mode. The specimens (1 cm \times 1 cm \times 1–3 mm) were subjected to vacuum pretreatment of 1–3 mmHg at 100°C for 8 h to eliminate the absorbed water. A Hitachi S 4200 scanning electron microscope (Japan) was employed to examine the morphology of samples fractured cryogenically in liquid nitrogen. The fracture surfaces were vacuum-coated with gold. The UL-94 vertical test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with a test specimen bar of 127 mm length, 12.7 mm width, and about 1.27 mm



Scheme 2 Curing reaction and structure of SCER/DDS.



Figure 1 DSC scans for (I) SCER/DDS, (II) TAIC/BMI and (III) TAIC/BMI-Ph₃P.

thickness. The LOI was determined with an Atlas Limiting Oxygen Index Chamber (USA), according to the standard procedure (ASTM D-2863-77) with a test specimen bar of 7–15 cm in length, 6.5 ± 0.5 mm in width, and 3.0 ± 0.5 mm in thickness.

Synthesis of Short-Chain Epoxy Resin (SCER)

To a 250-mL four-necked, round-bottomed flask, equipped with a heating mantle, stirrer, thermometer, and a Dean-Stark trap with reflux condenser, were charged with 11.40 g (0.05 mol) of bisphenol A, 46.25 g (0.5 mol) of epichlorohydrin (ECH), and 20 mL of 1methoxy-2-hydroxy propane. After stirring at a temperature and atmospheric pressure to thoroughly mix the contents, the temperature was raised to 65°C, and the pressure was reduced to 160 mmHg absolute. To the resulting solution was continuously added 25 mL of a 40 wt % sodium hydroxide solution at a constant rate via a metering pump over a period of 3 h while maintaining the reaction temperature at 65°C under a reduced pressure. During the addition of the NaOH, the water was removed from the system by codistilling with epichlorohydrin and solvent; in the meantime, distilled epichlorohydrin and solvent were returned to the system. On completion of the addition, the reaction mixture was maintained at 65°C for an additional 30 min, and the resulting mixture was washed with deionized water. The organic phase was finally rotary evaporated at 190°C under full vacuum for 3 h to remove the excess ECH and solvent. The residue was extracted with methyl isobutyl ketone, the extract was washed five times with deionized water, and the methyl isobutyl ketone (MIBK) was distilled off at 190°C to yield the liquid epoxy resin. Epoxy equivalent weight 176 (cal.: 170); Elemental analysis Calcd. for $C_{21}H_{24}O_4$: C, 74.12%; H, 7.06%. Found: C, 73.89%; H, 7.29%. IR (KBr) cm⁻¹: 912 (oxirane ring). The reaction is shown in Scheme 1.

The SCER cured and coreactive with various weight percent of trially isocyanurate/bismaleimide

The SCER/DDS (mole ratio = 2/1) and TAIC/BMI (mole ratio = 2/3) at an equivalent amount with 0.2% Ph₃P were mixed together [eqs. (1) and (2)] and taking 10 wt %

$$\frac{n(\Sigma x_i M_i)_{\text{TAIC/BMI}}}{n(\Sigma x_i M_i)_{\text{TAIC/BMI}} + W_{\text{SCER/DDS}}} = 0.1$$
(1)

$$m(\Sigma x_i M_i) = W_{\text{SCER/DDS}}$$
(2)

where, *n* or *m* is the mole, x_i is the mole fraction of component *i*, M_i is the molecular weight of component *i*, $W_{\text{SCER/DDS}}$ is the weight of SCER/DDS. If the mixture (20 g) was charged with 11.73 g of SCER and 8.27 g of DDS, then about 0.704 g of TAIC and 1.518 g of BMI were added to the aforementioned epoxy resin, i.e., 10 wt %. They were mixed with a stoichiometric (equal equivalent) amount of agent and Ph₃P poured into a hot aluminum mold, and the resin was cured in an oven at 160°C for 1 h, at 200°C for 2 h, 250°C for 3 h, and then postcured at 300°C for 1 h to obtain a cured specimen. All other composition polymers were prepared analogously.

UL-94V and LOI flame-retardant test

The UL-94V test determines the upward-burning characteristics of a solid. Five sample bars suspended vertically over surgical cotton ignited by a Bunsen



Figure 2 The homopolymerization of TAIC (a) intramolecular reaction and (b) intermolecular interaction.



Figure 3 The homopolymerization of BMI.

burner, two ignitions with 10 s burning time were applied to each sample bar. The LOI value can be used as an indicator to evaluate the flame retardant of polymers. The LOI is defined as the minimum fraction of oxygen in an oxygen–nitrogen mixture that is just sufficient to sustain combustion of the specimen after ignition. Thus, the flame-retardant properties of these polymers were further confirmed by the LOI measurement.

RESULTS AND DISCUSSION

Synthesis of SCER and analysis

In the direct process, a calculated excess of epichlorohydrin governs the degree of polymerization. However, preparation of the higher molecular weight species is subject to practical limitation. In the preparation SCER, an excess amount of epichlorohydrin (mole ratio: 10/1) was used to minimize high molecular weight species. Hence, the typical product contained ~97% by weight of the monomer (i.e., short-chain) SCER as shown in Scheme 1, where the degree of polymerization was nearly zero ($n \rightarrow 0$).

The structure of polymer

Curing reaction

Reaction of an epoxy group with a primary amine initially produces a secondary alcohol and amine. The secondary amine, in turn, reacts with an epoxy group to give a tertiary amine and two secondary hydroxyl groups. No competitive reaction is detectable between a secondary hydroxyl group in the backbone and an epoxy group. However, with excess epoxy, the secondary hydroxyl groups formed gradually add to the epoxide groups to afford ether. In general, primary amines react twice as fast as secondary amines²¹ and the reaction is shown in Scheme 2. The DSC traces of SCER/DDS cured resins are shown in Figure 1-I, the onset temperature at about 126°C. The results of the melting of DDS (mp: 175-177°C) was not observed fusion peak in the DSC scan, because the DDS was already dissolved in the hot of liquid SCER.



Figure 4 The copolymerization of TAIC/BMI.



Figure 5 Michael addition of bismaleimide with amine, to produce polyaspartimide.

TAIC/BMI coreaction

Matsumoto et al.^{22–25} have been concerned with the elucidation of the specific polymerization behavior of TAIC (Fig. 2). This results from the increased one horn (intermolecular) reaction of TAIC concentration on the linear polymer chains, and two horns revealed somewhat limited reactivity (hindrance effect). The most important curing reaction of BMI resins has been their homopolymerization²⁶ elevated temperatures. BMI resins generally show DSC exothermic peak temperature around 245°C.²⁷ The maleimide group can undergo a variety of chemical reaction, and the reactivity of the double bond is a consequence of the electron withdrawing nature of the two adjacent carbonyl

groups, which create a very electron-deficient double bond, and therefore is susceptible to homopolymerization (Fig. 3). The copolymerization of TAIC/BMI have been shown to be quite complex. The coreaction can yield combinations of chain extension, branching, and much less crosslinking depending on the cure path and cure state. Figure 1 summarizes the preparation of the TAIC extended with BMI resins. The onset temperature of an equivalent mix of TAIC/BMI around 243°C by DSC is shown in Figure 1-II. However, for the TAIC/BMI-Ph₃P system, (Fig. 1-III) the onset polymerization peak was shifted to the lower temperature (~161°C). This can be ascribed to the likelihood that a very small quantity of accelerator (Ph₃P) can have a marked effect on the rate of polymerization, and the



Figure 6 The interaction of molecular chain (a) Secondary amine-TAIC/BMI, (b) secondary alcohol-TAIC/BMI, and (c) hydrogen bonding between carbonyl group (in TAIC) and hydroxyl/amine group (in epoxy or polyaspartimide).



Figure 7 Infrared spectra of EP and EPTB30.

predominant reaction is chain extension of the double bond between the allyl and maleimide, with negligible reaction between the BMI monomers (higher reaction temperature), and the quick dissolution in DMSO of the heated (around 200°C) TAIC/BMI suggested that the reactions of allyl and maleimide groups of chain extended copolymer with the residual double bonds (TAIC or BMI) and homopolymerization were probably negligible (steric effect) as shown in Figure 4.

The interaction of SCER/DDS, BMI/DDS, and TAIC/BMI

The section treats cases in which whole polymer chains are linked together to form for larger nonlinear polymer structures. Stated mathematically, the probability of finding a sequence...*ABC*...of combination units A, B, C..., which can be written

$$P(\cdots ABC \cdots) = P(A) P(B) P(C) = \prod_{i} P(i)$$
$$i = A, B, C \cdots (3)$$

where, the P(A), P(B), P(C) and so forth are the unconditional probabilities of the occurrence of the various units. For eq. (3), the P(A) is SCER/DDS, P(B) is BMI/DDS, and P(C) is copolymer of TAIC/BMI. Since the initial state was supplied by the reactive-functionality, the chain formation might be postulated as a shift in the equilibrium for the polymer toward epoxy resin (EP, i.e., SCER/DDS, nonlinear structure), polyaspartimide^{28–30} (PAI, i.e., BMI/DDS, linear structure as illustrated in Fig. 5), and TAIC/BMI copolymer (TAIC/BMI, linear structure) that constitute a competing reaction each other. A possible route to formation the polymer is interaction by the attack of nitrogen (amine) or oxygen (alcohol) with simultaneous or



Figure 8 DSC scans for EP-TAIC/BMI, the corresponding TAIC/BMI compositions are from bottom to top (10, 20, 30, 40, and 50).



- + very few BMI remain free and homopolymerization can occurs
- + a few secondary amines, in turn, react with an epoxy to give tertiary amine or to afford an ether

Figure 9 Schematic drawing of the final molecular structure showing the products of the epoxy resin with TAIC/BMI mix system after heating.

subsequent loss of the proton on nitrogen or oxygen to form the long chain, as illustrated in Figure 6. The infrared spectra (Fig. 7) of EP and EPTB30 showed some of the characteristic differences observed in the optical range. The IR spectrum of EP exhibited absorption at 3200–3600 cm⁻¹ associated with the secondary hydroxyl groups and 3000–3500 cm⁻¹ for the secondary amine of the epoxy resin. However, the ether (1100 cm⁻¹) can also undergo polymerization by reaction of the secondary hydroxyl group with the epoxy. The Michael addition product compared to the spectrum of BMI are as follows: there is a medium intensity band at maleimide double bonds at 1634 cm⁻¹, which might be due to NH bending, suggesting the formation of a succinimide^{31,32} group;



Figure 10 Idealized structure of a conterminously linked polymer, constituted by a mutual combination of these polymers; chemically bonded together; \triangle : EP (SCER/DDS), \square : TAIC/BMI-EP, \Diamond BMI/DDS-EP, \bigcirc : TAIC/BMI/DDS, and fine dot line: hydrogen bonding.



Figure 11 Scanning electron micrographs in study systems at various weight percent of TAIC/BMI (a) EP (SCER/DDS), (b) EPTB10, (c) EPTB30, and (d) EPTB50.

characteristic maleimide double bond at 695 cm⁻¹ (in EPTB30) had part disappeared and a board band at 3370 cm⁻¹ for NH stretching confirmed the addition reaction of the imide ring. Moreover, they had a multipeaks in the range of 1100–1780 cm⁻¹, which the interaction of double bond (allyl group) with secondary amine or alcohol, and yield the structure of Ar-NR2 (1380 cm⁻¹), R–O–R (1100 cm⁻¹) and free BMI, imide ring (1725, 1780 cm⁻¹), they were showed a strong or medium intensity band, respectively, (in Fig. 7, bottom). Furthermore, the DSC scans of these compositions had a broad

exothermic peak and shifted to the higher temperature with increasing TAIC/BMI content, which the reaction can coexist combinations of chain extension, branching, and crosslinking as shown in Figure 8. From the above discussion, the main molecular structure showing the products of the epoxy resin with TAIC/BMI mix system after heating includes linear and nonlinear structures in the polymer chains. The reaction is depicted in Figure 9. The resulting structure of the epoxy resin with TAIC/BMI, along with the possible products and/or un-reacted species, in the tempera-

 TABLE I

 Thermal, Physical, and Mechanical Properties of Polymers

Polymer	$T_{\rm g}$ (°C) DMA	MA (%)	CTE (ppm)	T_d (°C) (5 wt % Loss in N ₂)	Char Yield (%) at 600°C	Storage Modulus (Gpa)
EP	186	2.40	65.24	412	22.1	2.04
EPTB10	171	2.33	50.57	407	21.6	1.97
EPTB20	180	1.96	46.01	410	27.4	2.06
EPTB30	191	1.25	42.32	413	28.6	2.15
EPTB40	195	0.49	41.36	416	29.4	2.18
EPTB50	202	0.45	41.09	418	32.5	2.20

MA, moisture absorption; CTE, coefficient of thermal expansion.

ture regime from 100 to 300°C, mostly the all reaction are completed. A conterminously linked polymer, constituted by a mutual combination of these polymers; chemically bonded together, in addition, the intermolecular interaction hydrogen bonding of polymer chains, as shown in Figure 10, hence all polymers were found only a glass transition temperature. To provide a structure and property comparison of the morphology evolution of the polymers observed in this discussed as above, the fractured surface of the samples at various compositions were also examined by scanning electron micrographs. Figure 11 shows SEMs of EP, EPTB10, EPTB30, and EPTB50 and also similar morphology of the other's polymers. The fracture surface all revealed a simple plane, with no visible phase domains or boundaries.

Structure and properties of polymers

The thermal properties of the polymer were investigated by TGA, DSC, and DMA as shown in Table I. The results of the TGA analyses showed an excellent thermal stability of the prepared polymers. The 5 wt %losses in N2 atmosphere were 407-418°C and the chair yields at 600°C in the range of 22–33%. The results suggest a high thermal stability of the special coreaction structure. No endothermic peaks above their glass transition temperatures were observed in DSC scans, which may be attributed to the amorphous molecular structure for all polymers. Moreover, they exhibited pretty high glass transition temperature. The T_g increased with the content of TAIC/ BMI, and this may resulted from the increased in the concentration of pendant and stiff (isocyanurate) structure of polymer chains. The coefficients of thermal expansion (CTEs) were in the range of 41.09-65.24 ppm, in general, the epoxy resin, which contained hard structure showed low CTE values. The moisture uptake of polymers in various compositions was investigated and the results of EPTB systems exhibited somewhat limited moisture absorption with increasing TAIC/BMI content. Although the molecular structure of EPTB systems was similar, the equivalent weight of oxirane groups reduced with increasing TAIC/BMI content, which led to the hydroxyl (because the epoxy ring to react) group content

TABLE II Electrical Properties of Polymers

	Dielectric	constant	Dissipation factor	
Polymer	1 MHz	1 GHz	1 MHz	1 GHz
EP	3.65	3.30	0.042	0.017
EPTB10	3.48	3.24	0.031	0.013
EPTB20	3.37	3.15	0.027	0.012
EPTB30	3.26	2.96	0.025	0.011
EPTB40	3.15	2.94	0.020	0.0095
EPTB50	3.09	2.82	0.017	0.0082

TABLE III UL-94 Test and LOI Measurement of Polymers

Polymer	N (%)	Drip	Fume	UL-94 Grade	LOI
EP	4.5	Yes	Heavy	V-2	26.3
EPTB10	5.1	No	Heavy	V-2	26.8
EPTB20	5.7	No	Heavy	V-2	29.2
EPTB30	6.3	No	Slight	V-1	29.6
EPTB40	6.9	No	No	V-0	30.1
EPTB50	7.6	No	No	V-0	31.4

decreases. The storage modulus of EPTB systems at 120°C are 1.97–2.20 Gpa, and the value increased with the increase in TAIC/BMI content.

Electrical properties of the materials are shown in Table II. Dielectric constant and dissipation factor values of polymer were noticeably low, especially, at high frequency. Owing to the introduction of a bulky and stiff isocyanurate group dangling from the main chain, the pendant structure provides a high free volume (or lower polarity), and resulted in the reduction of the dielectric constant and energy dissipation. Furthermore, the flame-retardant properties of EPTB systems were further examined by measuring the UL-94V test and LOI. Table III summarizes the results. Except EPTB30–50, the V-0, V-1 rating can be achieved for only nitrogen-containing polymers. The LOI values of the polymers are shown in Table, and the neat epoxy resin, the LOI values are 26. When 5.1–7.6 wt % nitrogen is added with total content, the LOI values are increased by 26 to over 30%.

CONCLUSIONS

A series of polymer containing pendant isocyanurate and bismaleimide were prepared from epoxy resin (SCER/DDS) with TAIC/BMI, so that the relationship could be studied between the structure and properties. These polymers provided an excellent physical property, such as thermal stability, mechanical/electric properties, and flame-retardant properties, which meet the essential requirements for high frequency electrical laminate application. The material formation is actually a very complex situation, which includes the intramolecular or intermolecular competition between crosslinking and coreaction, while the reaction can yield combination of epoxy resin (crosslinking, nonlinear structure), polyaspartimide (chain extension, linear structure), and TAIC/ BMI copolymer (branching, linear structure) depending on the heating path. DSC scans of all materials showed only one T_g , which indicated that the polymers are a random conterminously linked structure and the morphology was in good agreement with the proposed molecular structure. Furthermore, no fume and toxic gas emission were observed during burning test for this system.

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