

Synthesis and Characterization of a Liquid Crystalline Epoxy Containing Azomethine Mesogen for Modification of Epoxy Resin

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ABSTRACT: A novel liquid crystalline epoxy monomer, 1,1'-bis [4-(2,3-epoxypropoxyphenyleneinimethyl)]-2,2'-dimethylbiphenylene (BMPE) was synthesized and characterized by infrared (IR) and Nuclear magnetic resonance (NMR) spectroscopy. The effect of BMPE content on mechanical and thermal properties of its blends with Diglycidyl Ether of Biphenol A (DGEBA) was investigated. BMPE presented a Schlieren texture in the range of 150 to 215°C as observed by differential scanning calorimeter (DSC) and polarizing optical microscope (POM). The improvement of mechanical properties of DGEBA modi-

fied with BMPE was achieved without sacrificing thermal resistance. Scanning electronic microscopy (SEM) graphs of fracture surfaces of the cured blends showed that microfibrillar-like structure formed in the cured blends, which would be a result of self-oriented alignment of azomethine mesogen component. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1861–1868, 2007

Key words: synthesis; epoxy monomer with azomethine mesogen; thermal and mechanical properties; microfibrillar-like structure; blends

INTRODUCTION

Epoxy resins have good thermal, electrical, and mechanical properties; however, the major drawback of epoxy resins is that they are brittle materials having fracture energy of about two orders of magnitude lower than engineering thermoplastics.^{1,2} Hence, modification of epoxy resins to impart fracture toughness has been the subject of intense research interest.

In recent years, liquid crystalline thermosets attract much attention because of enhanced properties such as anisotropic orientation, high modulus and tensile strength, and low coefficient of thermal expansion. Many research groups have studied the synthesis, curing behavior, and mechanical properties of liquid crystalline thermosets.^{3–19} Various liquid crystalline thermosets with different mesogenic units and reactive end functional groups have been prepared. Epoxy resins with aromatic stilbene structure were investigated by many research groups. Mallon et al. studied liquid crystalline epoxy (LCE) resins with aromatic ester unit in the main chain.¹⁵ Ober et al. synthesized symmetric twin LCE resins.¹⁶

In addition, biphenol epoxy resin,^{17,18} azine epoxy resin,¹⁰ and binaphthyl epoxy resin¹⁹ were studied by many research groups. Among these materials LCE resins have gained considerable interest due to their advantages like controllable curing rate, high thermal and chemical resistance and good mechanical properties. However, few articles have been published on epoxy resins with azomethine mesogens. In 1989, Mikroyannidis²⁰ reported synthesis of epoxy derivatives of bis(azomethine)s without flexible spacers, curing by 4,4'-sulfonyl dianiline, and thermal stability of the resulting polymers. Later, Mormann et al.²¹ reported synthesis of azomethine-linked aromatic mesogenic epoxies with methyl and methoxy substituents, and the phase behavior. Recently, E-Joon Choi reported synthesis of azomethine epoxies and the curing behavior with diamine.^{6,22} According to their results, aromatic azomethine LC epoxy resins have advantages of high mesomorphic properties and can be obtained by easy process with high yield.^{4,23}

In the present article, three LCE monomers containing azomethine mesogenic unit were concerned. We report the synthesis and characterization of a novel LCE monomer, 1,1'-bis [4-(2,3-epoxypropoxyphenyleneinimethyl)]-2,2'-dimethylbiphenylene (BMPE). The curing behavior and morphologies of its blends with DGEBA were investigated, and the effects of BMPE content and curing temperature on thermal and mechanical properties are discussed.

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EXPERIMENTAL

Materials

Diglycidyl ether of Bisphenol A (DGEBA) was supplied by Dow Chemical (DER331, with epoxide equivalence weight (EEW) in the range of 182–192 g/eq). Curing agents [diaminodiphenylmethane (DDM mp = 93°C), *p*-phenylene diamine (PDA mp = 143°C), diaminodiphenylsulfide (DDS mp = 178°C) and diaminodiphenylether (DDE mp = 193°C)] and other chemicals (Sinopharm Chemical Reagent) for synthesis of LCE resin were used as purchased. The solvents were pretreated according to general process before use.

Instruments

Infrared (IR) spectra were recorded on a Magna 550 Fourier transform infrared (FTIR) spectrometer using samples in KBr pellets. The 500-MHz ¹H NMR was obtained with a Bruker 500 MHz NMR spectrometer with CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal standard. Dynamic study of curing behavior was undertaken with Pyris1 type differential scanning calorimetry (DSC) calorimeter (Perkin-Elmer), which was heated from room temperature up to 300°C at a heating rate of 10°C/min, in a nitrogen atmosphere. Pure indium was used as a standard for calorimetric calibration. A small quantity of the sample (8–12 mg) was used for the DSC studies in aluminum cell. An identical empty cell was taken as reference.

Transition temperature of LCE was characterized by a polarized optical microscope (POM) and DSC. POM (Olympus BH-2) was equipped with a hot stage connected to a self-made temperature control unit. Thermogravimetric analyses (TGA) were performed from room temperature to 800°C on powdered samples with masses between 8 and 15 mg using a Pyris 1 Thermogravimetric Analyzer (Perkin-Elmer) at a heating rate of 10°C/min in a nitrogen atmosphere.

The morphologies of the cured blends were observed under a scanning electron microscope (SEM) (Tescan TS 5163 MM) at 20 kV accelerating voltage. The sample was fractured in liquid nitrogen, then mounted on a sample holder using an electrically conductive paint as an adhesive and coated with a thin gold layer by plasma sputtering to avoid a charging effect due to nonconductivity of the polymer.

Tensile strength data was obtained by using an Instron 1121 static tensile test device according to ASTM D 170B standard.

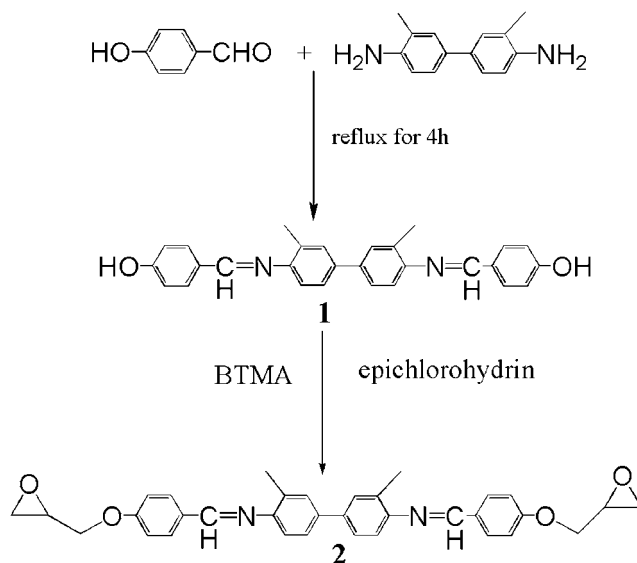
Synthesis

In this work, three kinds of LCE monomer containing azomethine mesogen were synthesized: 1,1'-

bis[4-(2,3-epoxypropoxyphenyleneinimethyl)]-2,2'-dimethylbiphenylene (BMPE), *N,N'*-bis[4-(2,3-epoxypropoxy) benzylidene]-1,4-phenylenediamine (BPE) and *N,N'*-bis[4-(2,3-epoxypropoxy) benzylidene]-2-methyl-1,4-phenylene-diamine (MPE). Synthesis of BMPE was shown in Scheme 1. The similar procedure was used for the other two monomers.²⁴

Synthesis of *N,N'*-bis [4-(4-hydroxyphenylimino-methyl)]-2,2'-dimethylbi-phenylene (1) 4-hydroxybenzaldehyde (12.2 g, 0.1 mol) and 4,4'-diaminobimethyl phenylene (10.6 g, 0.05 mol) were dissolved in 100 mL of ethanol in a 250 mL round-bottomed flask. A catalytic amount of 4-toluenesulfoic acid in 20 mL ethanol was added dropwise to the flask and the mixture was stirred and refluxed for 6 h. The resulting mixture was evaporated under reduced pressure to yield a yellow solid, which was washed thoroughly with diethylether and dried under vacuum, 18.9 g of yellow crystal (mp 284°C, yield: 90%) was obtained. IR (KBr, cm⁻¹): 3405, 2926, 2870, 1603, 1572, 1411, 1301, 1166. ¹H NMR [CDCl₃/TMS, (ppm)]: 8.34 (2H, s), 7.89 (4H, d), 7.46 (4H, s), 7.01(6H, d), 5.01 (2H,s), 2.45 (6H, s).

Synthesis of *N,N'*-bis[4-(2,3-epoxypropoxyphenyleneinimethyl)]-2,2'-dimethylbiphenylene (2) 18.9 g of 1 (0.045 mol) was dissolved in 90 mL epichlorohydrin (mol ratio 40 : 1). After heating at 110°C for 1 h with stirring, the solution became clear and then benzyltrimethylammonium (BTMA) was added as a catalyst. The resulting mixture keeps refluxing for another 2 h. Epichlorohydrin was removed by distillation, the residual solid was washed by water and dried at 60°C under vacuum. A yellow solid product was obtained (mp 150°C, Yield: 91%). The (EEW)²⁵ of BMPE was 264 g/eq (according to testing method²⁵, theoretical value: 266 g/eq). IR (KBr, cm⁻¹): 2926,



Scheme 1 Synthetic scheme of BMPE.

TABLE I
The Composition of DER331/BMPE Blends

Blend code	DER331 (weight)	BMPE (weight)
Neat	100	0
BMPE-5	95	5
BMPE-10	90	10
BMPE-15	85	15
BMPE-20	80	20

2870, 1603, 1572, 1411, 1301, 1166, 851. ^1H NMR [CDCl_3/TMS , (ppm)]: 8.34 (2H, s), 7.89 (4H, d), 7.20 (2H, s), 7.01(4H, d), 6.80(4H,d), 4.36 (2H, dd), 3.90 (2H, dd), 3.38(2H,m),2.92(2H, dd), 2.78(2H, dd), 2.45(6H,s).

Curing of BMPE and its blends with DER331

Stoichiometric amounts of BMPE and diamine were dissolved in chloroform and removed with the solvent under reduced pressure at room temperature. The curing reaction of the samples was examined with DSC. In this work, the composition of four blends and neat epoxy cured by DDS was listed in Table I.

To evaluate thermal and mechanical properties of the blends, the cured samples were obtained as follows: the preweighed BMPE, DER331 were poured into a beaker, and stoichiometric amounts of the diaminodiphenylsulfone (DDS) were added at 120°C . The mixture was stirred over a period of 5 min. After that it was poured into a polished steel mold, and then the mixture was cured for 4 h at 160°C , and postcured for 4 h at 200°C .

RESULTS AND DISCUSSIONS

Mesomorphic phase transition of BPE, MPE, and BMPE

Mesomorphic phase transition of BPE, MPE, and BMPE was studied by DSC and POM. Table II

shows the comparison of liquid crystalline transition temperature of three kinds of LC epoxy monomer. Apparently, the substitute has a pronounced effect on the liquid crystalline transition temperature. As one can see, BPE displays the transition at 193°C , which is the highest among three monomers. While methyl group on the mesogen of MPE results in a decrease of 63°C of liquid crystalline transition temperature to 130°C . Interestingly, introduction of methyl group to biphenol mesogen deduces a nematic transition temperature at 150°C for BMPE molecules, which is much higher than MPE. It is reasonable that the rigidity of biphenol mesogen would surely increase the transition temperature.

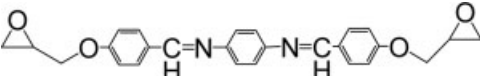
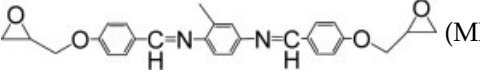
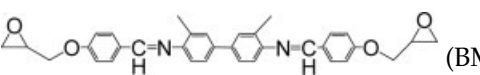
As MPE has been well studied in previous research work and BPE shows poor solubility in ordinary organic solvents, such as acetone, chloroform, toluene, etc. Owing to the better solubility of BMPE in organic solvents and its good compatibility with DER331, it would be expected that BMPE has well processing properties for industrial usage. In this work, modification of DER331 with BMPE was especially focused.

Characterization, mesogenicity of BMPE, and its reactivity with diamine

The molecular structure of BMPE was identified by means of IR and NMR techniques. BMPE exhibits characteristic absorption peaks at the band 1603 cm^{-1} , which was assigned to stretching vibration of the azomethine group. Vibration bands of methyl group appeared at near 2900 cm^{-1} , while epoxy group of BMPE appeared at 851 cm^{-1} . Figure 1 showed the ^1H NMR spectrum, in which the peak assignments corresponded to the structure was also included. The protons in an epoxy ring were found at 2.5–3.8 ppm and a proton in the azomethine moiety appeared at 8.4 ppm.

BMPE showed a nematic birefringent pattern in the temperature range of 150 to 215°C . The optical

TABLE II
Comparison of Liquid Crystalline Transition Temperatures of LC Monomers

Liquid crystalline epoxy monomers	LC transitions*
 (BPE)	k 193°C n 257°C i
 (MPE)	k 130°C n 228°C i
 (BMPE)	k 150°C n 215°C i

*k ~ n: from crystal to nematic; n ~ i: from nematic to isotropic.

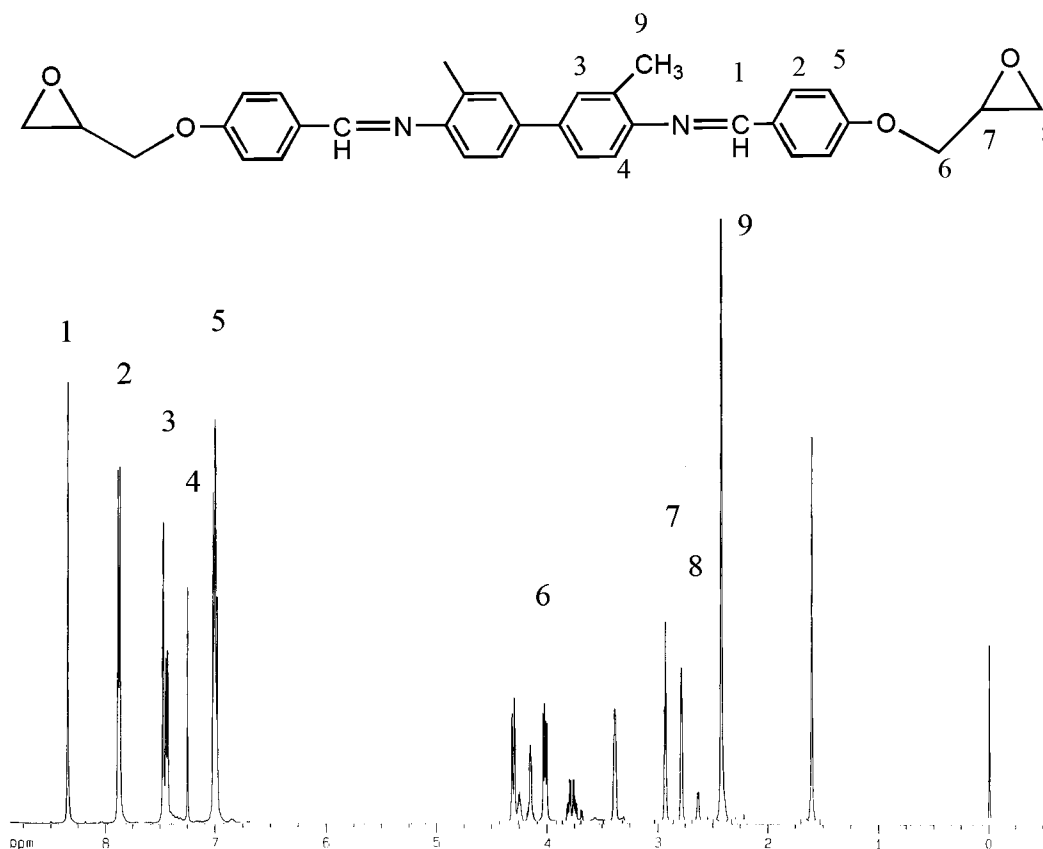
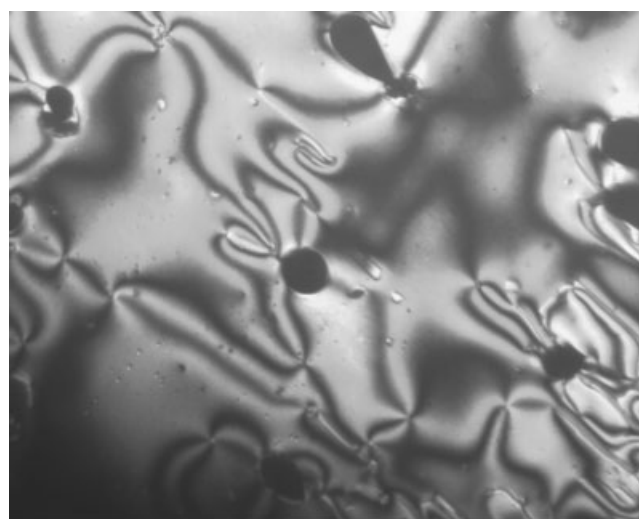


Figure 1 ^1H NMR spectra of BMPE.

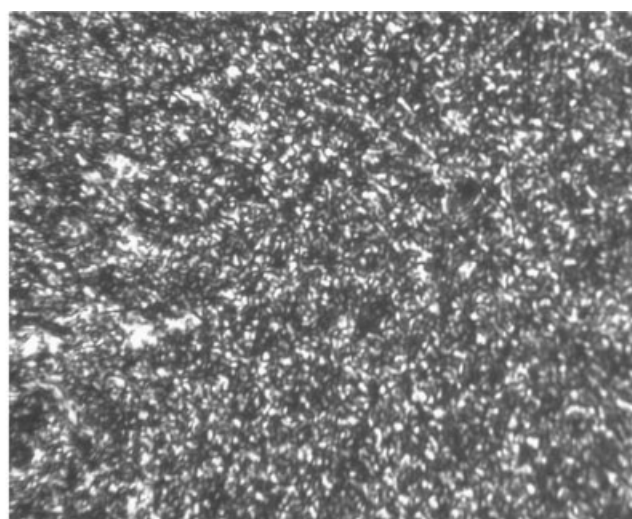
micrograph of BMPE was shown in Figure 2(a), in which it was observed at 160°C as an example. The fluid displayed flow birefringence when pressure was applied on the cover slip during POM observation. This flow birefringence remained after releasing

pressure on the cover slip. At higher temperature above 215°C , the flow birefringence disappeared and fluid displayed isotropic.

In the liquid crystalline state, BMPE shows a typical Schlieren texture. However, the mesogenic group



(a)



(b)

Figure 2 Cross-polarized optical microscopy of BMPE: (a) BMPE at 160°C ($320\times$ magnification); (b) BMPE cured by DDS at 160°C ($200\times$ magnification).

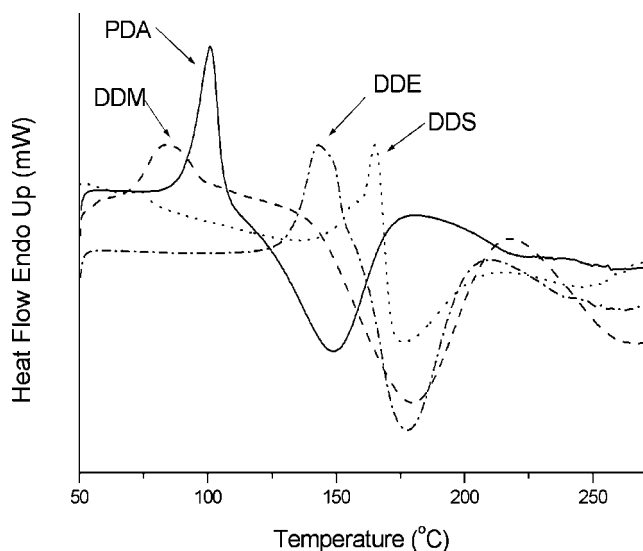


Figure 3 DSC scans of BMPE cured with various diamines.

in liquid crystalline monomer is not sufficient to show mesogenicity during cure process. Therefore, the properties of curing agents or thermal story during curing play an important role in formation and maintenance of mesogenicity. To select a proper curing agent, the reactivity of BMPE with diamines was examined by using DSC. Diaminodiphenylmethane (DDM, mp = 93°C), *p*-phenylene diamine (PDA, mp = 143°C), diaminodiphenylsulfide (DDS, mp = 178°C) and diaminodiphenylether (DDE, mp = 193°C) were used as curing agents. Figure 3 showed the DSC scans of BMPE cured with various diamines. Upon heating DSC curves of unreacted mixtures show melting endotherms, and a subsequent cure exotherm. Among the four mixtures with the diamines, PDA reacts with BMPE at the lowest temperature. BMPE reacts with DDM more slowly than with PDA. If the curing reaction is followed immediately with melting, BMPE would melt completely into the nematic mesophase before a substantial degree of crosslinking had occurred. While DDS shows eutectic behavior with BMPE and meantime the eutectic temperature match the transition temperature of nematic mesophase of BMPE, then, BMPE reacted with DDS at 160°C can form its mesophase in the cured networks. Therefore, the DSC results suggest that the curing reaction is not only related to the melting point of hardeners, it also depends on the nematic mesophase transition temperature of LC epoxy. Figure 2(b) shows mesogenicity in the network of BMPE cured by DDS at 160°C.

In this work, DDS was taken as curing agent to study the cure of the BMPE and its blends with DER331.

Curing behavior of BMPE/DER331 with DDS

The isothermal DSC of the blends of DER331/BMPE content ranged from 5 to 20% were shown in Figure 4 (Cure reaction at 160°C as an example). It indicates that the curing reaction rate increases with increment of BMPE content, which suggests that the addition of BMPE accelerates the curing reaction of epoxy blends. Similar results were also reported by Carfagna et al.²⁶ that curing rate of LC epoxy can be accelerated when LC epoxy was cured in a mesomorphic structure.

Morphologies of the cured blends of BMPE and DER331

Figure 5 shows the morphology of fractured surfaces of the blends. Morphology of BMPE presented microfiber structures. Moreover, it displays that the microfibers of BMPE-5 [Fig. 5(a)] are less and shorter than that of BMPE-10 [Fig. 5(b)], which is similar with the result observed by CK Ober et al.¹¹: A macroscopically fibrillar or grooved fracture surface was observed in the crack fracture of LCE based thermoset. In this case, the formation mechanism of microfiber like structure could be as follows: before the curing reaction, BMPE molecular dispersed well in DER331 resin because of good miscibility of DER331 and BMPE. However, the curing reaction results in self-oriented alignment of BMPE molecules in the blend due to its rigidity of azomethine mesogen component, and then microfibers was formed, followed by skin-core structure with DER331 wrapped the microfibers in the cured epoxy as shown in Figure 5. The detailed investigations of the formation mechanism of microfibers in the cured blends of

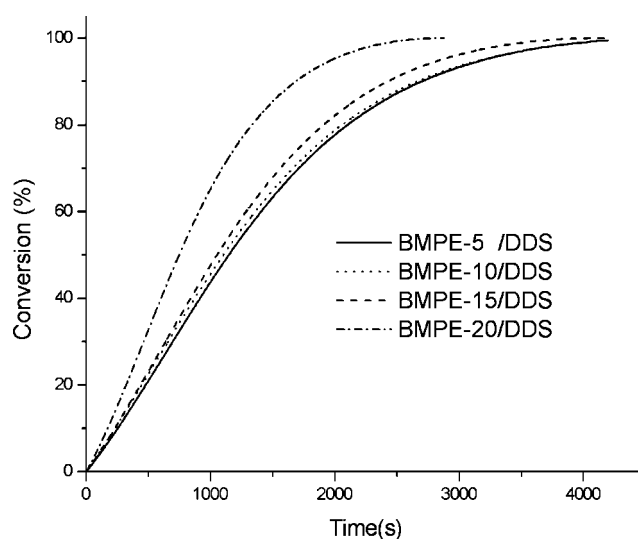


Figure 4 The conversion versus cured time for BMPE/DER331/DDS system (isothermal cured at 160°C).

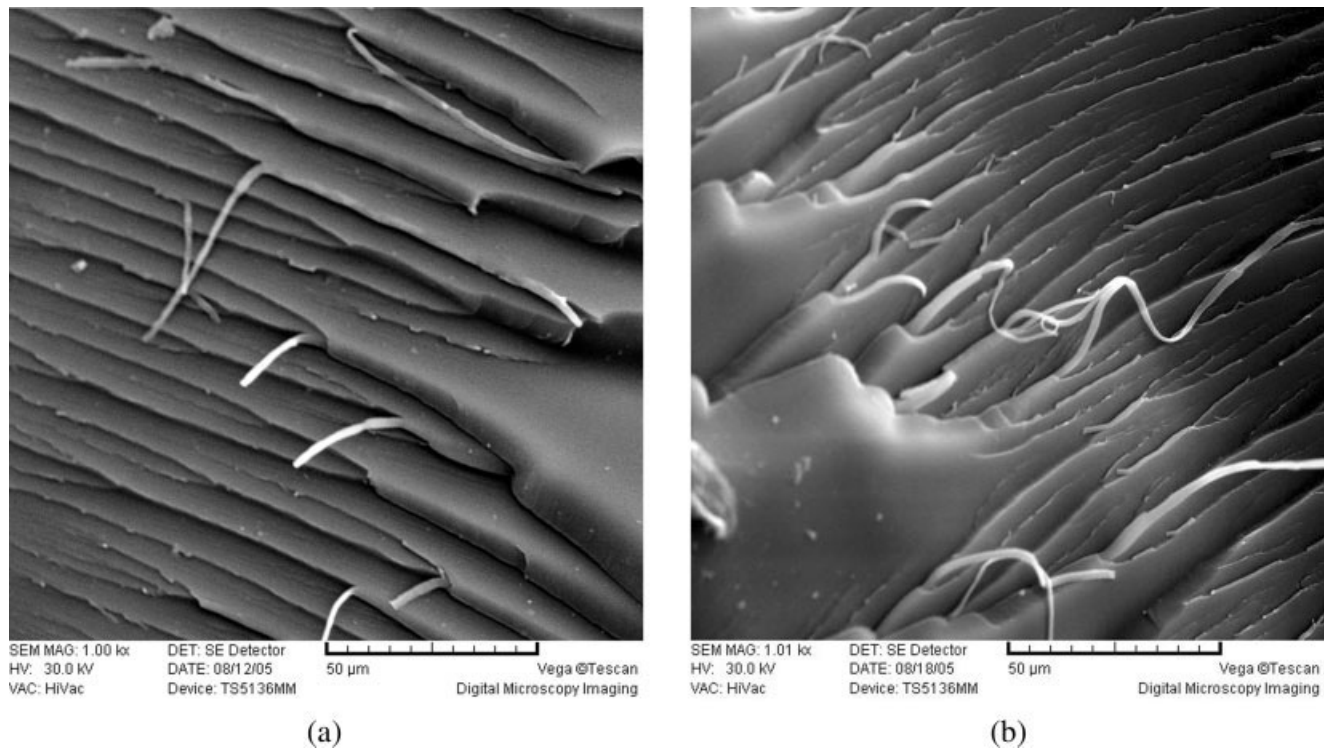


Figure 5 SEM graphs of BMPE/DER331 cured by DDS at 160°C for 4 h: (a): BMPE (5%) b) BMPE(10%).

DER331 with BMPE are ongoing and will be reported later.

Glass transition temperature of blends

T_g of cured blends was evaluated by means of DSC, all blends were cured at 160°C and postcured at 200°C for 4 h. DSC curve of the cured blends showed no exothermic peak, which indicated the completion of the curing reaction. Dynamic DSC curves of the cured DER331/BMPE blends are depicted in Figure 6.

From the DSC curves, the glass transition temperatures of the cured blends of DER331/BMPE were obtained. T_g of cured blends increases with the increment of BMPE content in the range of 182°C up to 213°C. While T_g of neat DER331/DDS is 182°C and T_g of BMPE/DDS is 213°C. It was reported that the glass transition temperature of the epoxy resin's blends with azomethine mesogens increased by introducing the tetramethyl biphenyl²⁷ and biphenyl¹⁷ to the epoxy resin network, which indicates that the incorporation of BMPE increased the glass transition temperature of the cured blends of epoxy.

Thermogravimetric analysis of blends

The thermal degradation behaviors of BMPE and DER331 system were studied using TGA at a heating

rate of 10°C/min in a nitrogen atmosphere. Figure 7 shows the TGA scan of BMPE-10/DDS and DER331/DDS system. The two samples were cured at 160°C for 4 h and 200°C for 4 h. As far as we know, thermal stability parameters, including initial decomposed temperature (IDT) and temperatures of maximum rate of degradation (T_{max}) of the blends can be determined from the DTG curves, which showed IDT of the blends commences near at 360°C and T_{max} at 410°C. It elucidates that the incorpora-

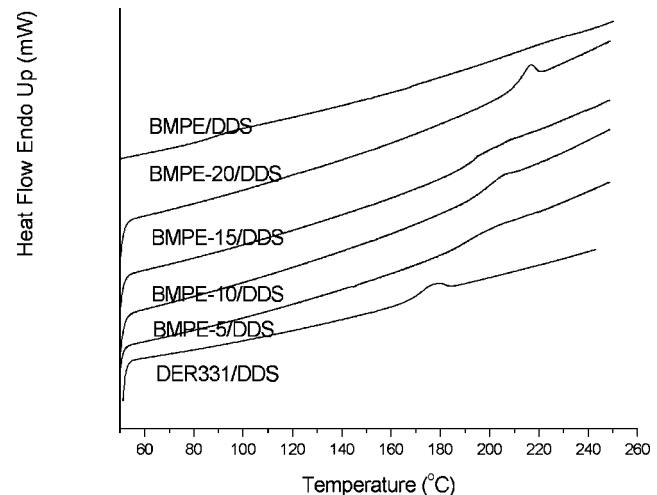


Figure 6 Glass transition temperatures of DER331/BMPE blends cured at 160°C for 4 h and postcured at 200°C for 4 h.

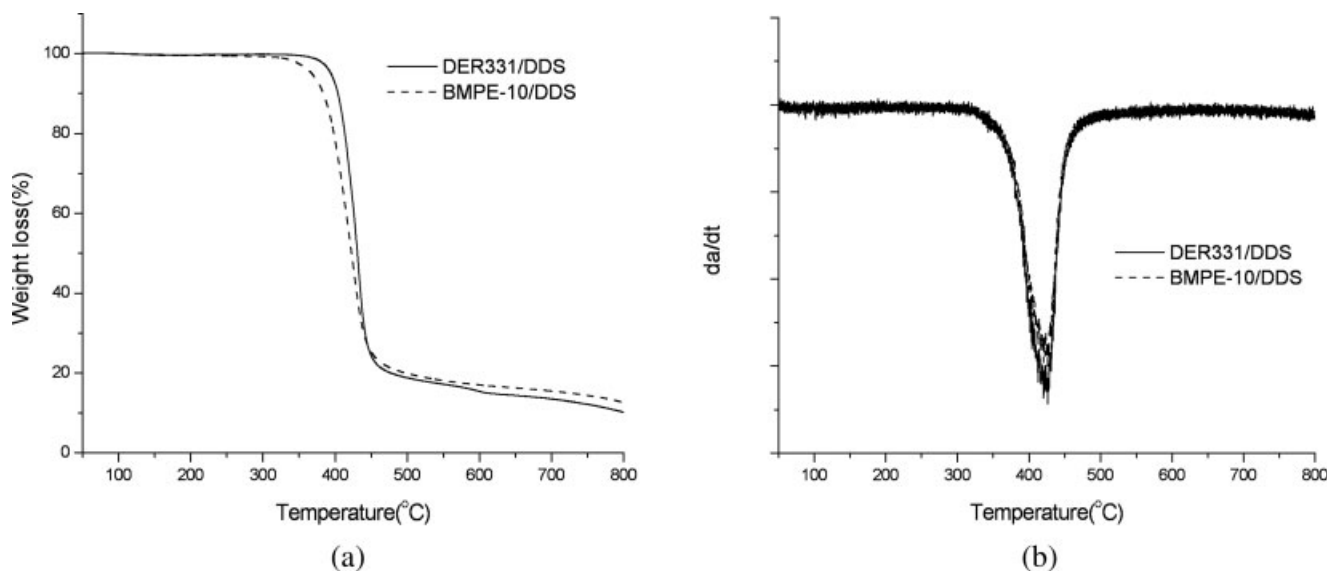


Figure 7 (a) TGA and (b) DTG thermograms of BMPE-10 cured at 160°C for 4 h and postcured at 200°C for 4 h.

tion of BMPE into the epoxy network does not affect the thermal stability of this system.

Mechanical properties

The effect of content of BMPE on tensile properties of the cured blends was studied. From Table III, tensile strength and elongation at break of the blends increase with the increment of BMPE content, tensile strength and elongation of BMPE-20 improved 38 and 90% compared with neat one respectively.

As shown in Figure 5(b), the microfibrils terminated at the tip of fracture segments and hindered the crack propagation, it can benefited the improvement of tensile strength. Thus, the increase of mechanical properties could be related to formation of the microfibrils in the epoxy networks. Hence, the improvement of mechanical properties with increasing BMPE could be attributed to the increase of the mesogenic concentration in the blends of DER331/BMPE. The similar result was also found by C. Farren, which indicated that the increasing mesogen content leads to increase intermolecular interactions between the polymer chains and hence reduced

micro-Brownian motion and reduced free volume. Although macroscopically isotropic, the degree of order at the microdomain level can be related to the network physical properties.³

CONCLUSIONS

In this work, a novel LCE monomer BMPE can be easily prepared with high yield. The effect of BMPE content on the curing behaviors, thermal and mechanical properties of DER331/BMPE blends were investigated. The improvement of mechanical properties of DER331 modified with BMPE was achieved without reducing thermal resistance: tensile strength and elongation of BMPE-20 increased 38 and 90% respectively, and the glass transition temperature increased 28°C compared with the DER331/DDS blend. The results illustrated that improvement of physical properties of epoxy resin could be related to formation of self-oriented alignment of BMPE and microfibrils formation in the network of cured epoxy resin. Therefore, it has potential application for modification of epoxy resin.

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TABLE III
Effect of BMPE content on the mechanical properties of DER331/BMPE blends cured at 160°C for 4 h and postcured at 200°C for 4 h

	Tensile strength (Mpa)	Elongation at break (%)
DER331/DDS	52.3	2.1
BMPE-5	58.1	2.5
BMPE-10	66.5	3.5
BMPE-15	67.3	3.5
BMPE-20	72.2	4

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