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Synthesis and curing of liquid crystalline epoxy resins based on 4,4′-biphenol

Jun Yeob Lee[a], Jyongsik Jang[a,*], Seung Sang Hwang[b], Soon Man Hong[b] and Kwang Ung Kim[b]
[a]*Department of Chemical Technology, College of Engineering, Seoul National University, Shinlimdong 56-1, Seoul, Korea*
[b]*Polymer Processing Laboratory, Korea Institute of Science and Technology(KIST), P. O. Box 131, Cheongryang, Seoul, Korea*
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Two liquid crystalline epoxy (LCE) resins based on biphenol mesogen, BP1 and BP2, were synthesized to produce a highly heat-resistant liquid crystalline network, and the curing behaviour of them was investigated using diaminodiphenylsulfone (DDS) and diaminodipheylester (DDE) as curing agents. The curing rate and heat of curing of LCE resins were measured with dynamic and isothermal DSC. The curing reaction of BP2 based on aromatic ester was faster than that of BP1, and the degree of cure was vice versa. A densely cross-linked BP2 network showed a much higher glass transition temperature (≈280°C) and elastic modulus than other epoxy resins reported up to now. BP2 formed a liquid crystalline network on curing with DDS and DDE, while BP1 showed a liquid crystalline network on curing with DDE. The liquid crystalline phase of the resulting network was maintained up to decomposition temperature (<300°C). © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: liquid crystalline epoxy resin; biphenol mesogen; curing)

INTRODUCTION

Liquid crystalline thermosets (LCT) have been widely investigated in many research groups because of their unique properties, e.g. anisotropic orientation, low coefficient of thermal expansion and liquid crystalline phase development during curing. LCT can be prepared by many routes. It can be made through the self-cross-linking reaction of LC monomer or non-LC rigid rod monomer [1]. The reaction between LC monomer and non-LC curing agent, or LC curing agent can yield LCT [2–5]. In addition, the curing reaction of non-LC rigid rod monomer with non-LC curing agent is also a method to produce LCT [6]. In recent years, it has been reported that non-LC rigid rod oligomer can form a LCT through the cross-linking reaction with non-LC curing agent [7].

A number of different LCTs which have aromatic mesogenic groups and reactive end-functional groups have been reported. Among these LCTs, liquid crystalline epoxy resins (LCE) are being intensively investigated. Many research groups reported the synthesis, curing behaviour, phase behaviour and thermal properties of various LCE resins. In addition, anisotropic mechanical properties of oriented LCE were also studied by Jahromi *et al.* [8]. The curing behaviour of LCE was dependent on the structure of the aromatic mesogenic group and the length of the flexible spacer which decouples the reactive end-functional group from the rigid rod mesogenic group. The liquid crystalline phase of cured LCE was controlled by the length of flexible spacer and aspect ratio of the mesogenic group. Long rigid rod mesogenic group improves the thermal properties of LCE and raises the thermal transition temperature of LCE. Flexible spacer lowers the curing temperature and enhances the mesophase stability of LCE. However, flexible spacer was detrimental to the thermal stability and mechanical properties of cured LCE. Therefore, long mesogenic unit and short flexible spacer are required to produce high heat resistant LCE.

In this paper, we described the synthesis and curing of LCE resins based on the biphenol mesogenic group to prepare a highly heat resistant liquid crystalline network. A biphenol group which has a high aspect ratio offers good thermal properties and mesophase stability. The influence of chemical structure of mesogenic group and curing agent on the curing behaviour of LCE was investigated, and the liquid crystalline phase of the LCE network was monitored according to curing temperature. The mechanical and thermal properties of a biphenol-based heat resistant LCE network were also examined.

EXPERIMENTAL

Synthesis

Two liquid crystalline epoxy resins based on biphenol were synthesized. The synthetic scheme of two LCEs is illustrated in *Figure 1*.

4,4′-Di(2,3-epoxypropyloxy) biphenyl (BP1)

*4,4′-Di(2-propenyloxy) biphenyl (***1a***).* A mixture of biphenol (37.2 g, 0.2 mol), 3-bromopropene (26 ml, 0.30 mol) and K_2CO_3 (70 g, 0.5 mol) was added to 400 ml of acetone and then refluxed for 24 h. The solid was filtered and acetone evaporated. The remaining solid was washed successively with 5% Na_2CO_3 solution, excess water and 200 ml of cold ethanol. After drying, a white powder was obtained. Yield: 81% (43 g). ^1H n.m.r.(DMSO-d_6): δ 4.70

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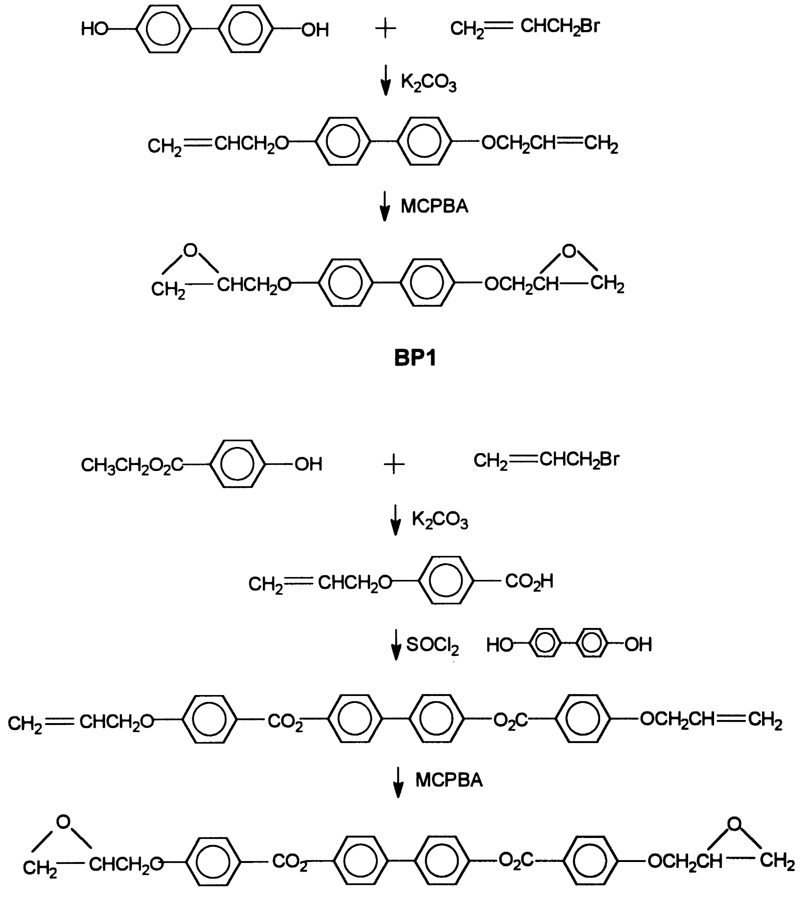
[*] To whom correspondence should be addressed



BP1

BP2

Figure 1 Synthetic scheme of biphenol-based liquid crystalline epoxy resins

(4H, d, -O-CH_2-), 5.32 (4H, dd, CH_2=CH-), 6.04 (2H, m, -CH=CH_2), 6.96 (4H, d, aromatic), 7.48 (4H, d, aromatic).

4,4′-Di(2,3-epoxypropyloxy) biphenyl (BP1). This compound was prepared according to the procedure proposed by Broer *et al.*[2]. Diallyl monomer **1a** (27 g, 0.1 mol) was oxidized with 3-chloroperoxybenzoic acid. Yield: 74% (22 g). T_m: 156°C. ^{1}H n.m.r. ($CDCl_3$): δ 2.79 (2H, dd, CH_2 of epoxy), 2.92 (2H, dd, CH_2 of epoxy), 3.39 (2H, m, CH of epoxy), 3.94 (2H, dd, CH_2 of glycidyl), 4.27 (2H, dd, CH_2 of glycidyl), 6.94 (4H, d, aromatic), 7.48 (4H, d, aromatic).

4,4′-Biphenyl-di[4-(2,3-epoxypropyloxy)benzoate] (BP2)

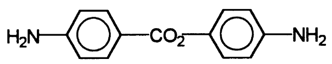
*4-(2-propenyloxy)benzoic acid (***2a***).* The synthesis of **2a** is described in a previous paper [9]. Yield: 50% (58 g). T_m: 170°C.

*4,4′-Biphenyl-di[4-(2-propenyloxy)benzoate] (***2b***).* A mixture of **2a** (21 g, 0.11 mol) and $SOCl_2$ (29 ml, 0.4 mol) was refluxed for 2 h. Excess $SOCl_2$ was evaporated and 80 ml of pyridine poured into the solution. After addition of biphenol (10.2 g, 0.055 mol) the mixture was reacted for 2 h in an ice bath and 24 h at room temperature. The mixture was poured into the 1000 ml acidified aqueous solution. The solid was filtered and washed with 500 ml of 5% Na_2CO_3 aqueous solution and 500 ml of water. After drying, the solid product was recrystallized from ethyl acetate. Yield: 86% (24 g). ^{1}H n.m.r. (DMSO-d_6): δ (ppm) 4.70 (4H, d, -O-CH_2-), 5.34 (4H, dd,-CH_2=CH-), 6.04 (2H, m, -CH=CH_2-), 7.14 (4H, d, aromatic), 7.36 (4H, d, aromatic), 7.77 (4H, d, aromatic), 8.10 (4H, d, aromatic).

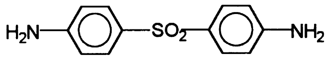
4,4′-Biphenyl-di[4-(2,3-epoxypropyloxy)benzoate] (BP2). BP2 was prepared according to the procedure for the synthesis of BP1. Diallyl monomer **2b** (15.3 g, 0.030 mol) was oxidized with 3-chloroperoxybenzoic acid, and pure product was obtained after recrystallization from ethylacetate/isopropanol. Yield: 65%(10.6 g). T_{KS}: 113°C; T_{SN}: 163°C; T_{NI}: 243°C. ^{1}H n.m.r. ($CDCl_3$): δ (ppm) 2.83 (2H, dd, CH_2 of epoxy), 2.93 (2H, dd, CH_2 of epoxy), 3.42 (2H, m, CH of epoxy), 4.13 (2H, dd, CH_2 of glycidyl), 4.34 (2H, dd, CH_2 of glycidyl), 7.13 (4H, d, aromatic), 7.35 (4H, d, aromatic), 7.76 (4H, d, aromatic), 8.09 (4H, d, aromatic).

Curing of epoxy resins

Two LCE resins synthesized in this experiment were cured using diaminodiphenylsulfone (DDS) and diaminodiphenylester (DDE) as curing agents. Chemical structures of DDS and DDE are shown in *Figure 2*. DDS was supplied by Aldrich Chem. and DDE was synthesized by catalytic reduction of 4-nitrophenyl 4-nitrobenzoate. T_m of DDS was 175°C and that of DDE was 182°C. The mole ratio of curing agent to LCE was fixed at 0.45. The curing mixtures were prepared by dissolving LCE resins and curing agent in chloroform/acetone-mixed solvent and removing the solvent under reduced pressure at room temperature. The mixture of BP1 and DDS will be called BPS1, and that of BP2 and DDS, BPS2. The mixture of BP1 and BP2 with DDE will be designated BPE1 and BPE2, respectively.



diaminodiphenylester (DDE)



diaminodiphenylsulfone (DDS)

Figure 2 Chemical structures of curing agents

Characterization

A differential scanning calorimeter (DuPont 910 DSC) was used for the study of dynamic and isothermal curing behaviour of LCE resins synthesized in this experiment. Isothermal curing temperature was varied from 140 to 240°C and isothermal curing time was fixed at 2 h. The sample was inserted into the DSC cell after equilibrium at the isothermal temperature. The heating rate of the dynamic experiment was 10°C/min. The liquid crystalline phase of the LCE monomer and cured thermoset was observed with a Leitz optical microscope equipped with a Mettler FP82 hot stage and FT80 central processor with a magnification of 200. A dynamic mechanical thermal analyzer (DMA, Rheometris, MK III) was used to measure the glass transition temperature and dynamic elastic modulus of cured LCE network. Data were collected in bending mode at a frequency of 1 Hz and heating rate was 5°C/min. The coefficient of thermal expansion (CTE) of the cured LCE network was measured with DMA in compression mode according to ASTM D 3386.

RESULTS AND DISCUSSION

Thermal behaviour of epoxy monomers

The synthetic scheme of BP1 and BP2 is outlined in *Figure 1*. BP1 showed T_m at 156°C (lit. 159°C [3], 140–142°C[10], 153°C [11]) and did not display any liquid crystalline phase on heating. A smectic-like liquid crystalline phase appeared only on cooling from the isotropic phase. The synthesis of BP1 was also reported by Mormann and Brocher [3], Su [10] and Carfagna *et al.* [11]. They synthesized BP1 from a direct reaction between 4,4′-biphenol and epichlorohydrin in the presence of sodium hydroxide. However, their results do not coincide each other. Carfagna *et al.* [11] observed a monotropic liquid crystalline phase on cooling from the isotropic state and suggested that a highly ordered smectic liquid crystalline phase existed on supercooling. Su [10] proposed that BP1 exhibited a smectic birefringent pattern at 135°C. However, the T_m of BP1 synthesized by them is too low (140–142°C) compared to the results reported by other groups. In contrast to the results by these groups, Mormann and Brocher [3] insisted that no liquid crystalline phase would be detected on cooling from isotropic melt. They thought that the birefringence pattern displayed after cooling was caused by the crystallization of BP1. However, BP1 showed a viscous flow on cooling from the isotropic phase, which implied that the birefringence pattern observed was due to the ordered smectic liquid crystalline phase. BP2 showed three transitions on heating at 113, 163 and 243°C. The transition at 113°C was caused by smectic transition, that at 163°C was nematic transition and that at 243°C corresponds to isotropization. The excellent mesophase stability of BP2 is attributed to the high aspect ratio of the mesogenic unit.

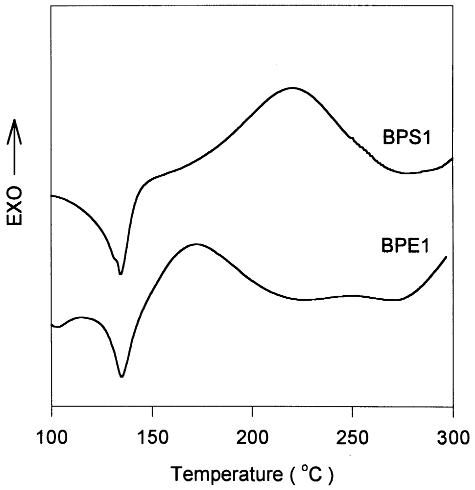


Figure 3 Dynamic DSC thermograms of BPS1 and BPE1

Curing of LCE with amine

The curing behaviour of two LCE resins mixed with two diamines in a mole ratio of 1:0.45 was examined using DSC. Dynamic scans were performed at a heating rate of 10°C/min. Dynamic DSC thermograms of BPS1 and BPE1 are represented in *Figure 3*. BPS1 shows two melting peaks below 150°C, which correspond to the melting of BP1 and DDS. The exothermic peak around 220°C is attributed to the curing reaction of BP1. In the case of BPE1, melting peak of BP1 appears below 150°C, but that of DDE is not observed, which indicates that the curing reaction between BP1 and DDE occurs prior to complete melting of DDE. The exothermic peak centred at 172°C corresponds to the curing reaction of BP1 with DDE, and the broad peak near 252°C is the postcuring peak of LCE. The postcuring peak comes from the rigid nature of the DDE structure. The end to end distance of DDE is 11.2 Å, while that of DDS is 9.9 Å. This explains the postcuring peak which exists in the BPE1 DSC thermogram. The total heat of reaction was 127.0 kJ mol^{-1} and 126.6 kJ/mol^{-1} for BPS1 and BPE1, respectively. However, BPE1 showed much a steeper initial slope of curing than BPS1, which implied that the curing reaction of BPE1 proceeded faster than that of BPS1 in the initial stage of the curing reaction. This is known by considering the chemical reactivity of the aromatic amine group of DDS and DDE. The curing reaction between the oxirane ring and amine is known as a nucleophilic substitution reaction. The reaction rate of the nucleophilic substitution reaction is determined by the electron density in the reaction site. The sulfone unit in DDS has more electron-withdrawing character in comparison with the ester group in DDE. Therefore, DDE is more reactive toward the oxirane ring than DDS.

Figure 4 displays the dynamic DSC thermograms of BPS2 and BPE2. Both BPS2 and BPE2 show two exothermic peaks. The peak at the lower temperature results from the curing reaction of BP2 with curing agent and that at around 300°C comes from the postcuring reaction which accompanies thermal decomposition of the cured LCE network. This phenomenon is due to the structural difference between BP1 and BP2. The mesogenic length of BP1 is 9.9 Å, while that of BP2 is 22.6 Å. The long rigid

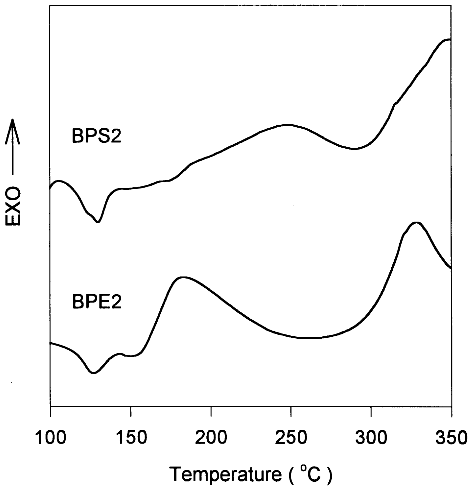


Figure 4 Dynamic DSC thermograms of BPS2 and BPE2

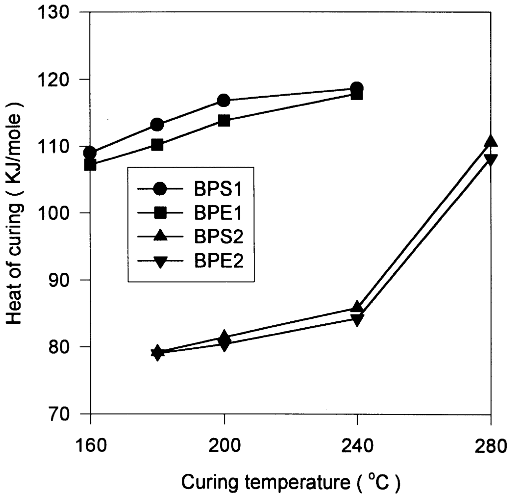


Figure 6 Isothermal heat of curing of liquid crystalline epoxy resins at various temperatures

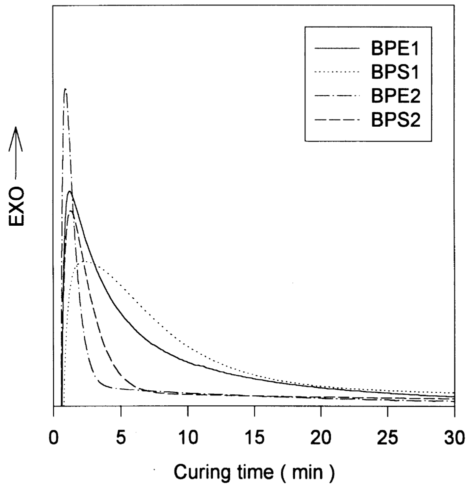


Figure 5 Isothermal DSC thermograms of liquid crystalline epoxy resins at 180°C

rod mesogenic group of BP2 restricts the motion of the cross-linked prepolymer of BP2. The difference in the peak temperature and initial slope of curing between BPS2 and BPE2 is caused by the structural difference between DDS and DDE, as explained in *Figure 3*. Isothermal experiments were performed to investigate the isothermal curing behaviour of BP1 and BP2. Isothermal DSC thermograms of four LCE mixtures at 180°C are shown in *Figure 5*. Two peculiar characteristics are observed in this figure. First, the maximum curing rate is highest for BPE2 and lowest for BPS1. The isothermal peak time has the same tendency as the maximum curing rate. The chemical reactivity of LCE and curing agent is the main factor for this behaviour. BP2 has an aromatic ester mesogenic group which has electron-withdrawing character. It reduces the electron density of the oxirane ring, which leads to higher chemical reactivity of BP2 compared with BP1. The reason for higher chemical reactivity of DDE compared to DDS was explained in *Figure 3*. The presence of the liquid crystalline phase is another reason in the case of BP2. BP2 exhibits a nematic liquid crystalline phase at this temperature, which helps the ordering and flow of the LCE monomer. According to the result reported by Carfagna *et al.* [11], the curing reaction of the liquid crystalline monomer is facilitated in the nematic liquid crystalline phase because LCE monomers are close to each other and flow is much easier in the nematic phase than in the isotropic phase. A similar result was also reported by Broer *et al.* [2]. Secondly, the peak shape of isothermal curing of BP1 mixtures differs from that of BP2 mixtures. Curing of BP1 mixtures proceeds gradually with curing time up to 30 min, while that of BP2 mixures completes within 10 min. This is due to the fact that BP2 is more reactive than BP1 and diffusion of the cross-linked prepolymer of BP2 is very difficult at this isothermal temperature.

The isothermal heat of curing of four LCE mixtures measured from an isothermal DSC experiment is presented in *Figure 6* as a function of isothermal curing temperature. The heat of curing was higher for BP1 mixtures than for BP2 mixtures at the same curing temperature. This is attributed to the rigid rod character of BP2 and the strong hydrogen bonding of the ester unit with hydroxyl group or amine group. The hydrogen bonding of the BP2 network persists above 200°C and hinders the motion of cross-linked prepolymers. The heat of curing of BP1 mixtures increased as the curing temperature increased. However, the effect of curing temperature on the heat of curing of BP2 was not so prominent, especially above 200°C. This implies that the curing of BP2 be performed above 240°C to attain a high degree of cure.

Thermomechanical properties

Dynamic mechanical observations were performed to analyze the dynamic elastic modulus and T_g of four LCE mixtures. BPS1 and BPE1 were cured at 180°C for 6 h, and postcured at 220°C for 4 h. The cured BPS2 and BPE2 networks were prepared after curing at 200°C for 6 h and postcuring at 240°C for 4 h. DMA thermograms of four LCE mixtures are presented in *Figure 7*. BPS2 and BPE2 showed much higher T_g than BPS1 and BPE1. The T_gs of BPS2 and BPE2 were 278 and 280°C, respectively, while those of BPS1 and BPE1 were 221 and 225°C. In general, the T_g of the thermoset depends greatly on the chemical structure and degree of cure of the thermoset. The degree of cure was large for BPS1 and BPE1 compared to BPS2 and BPE2, and LCE cured with DDS showed a higher degree of cure than that cured with DDE. Comparison of T_g and heat of reaction in four cured LCE networks revealed that the chemical structure of LCE rather than the degree of cure played a

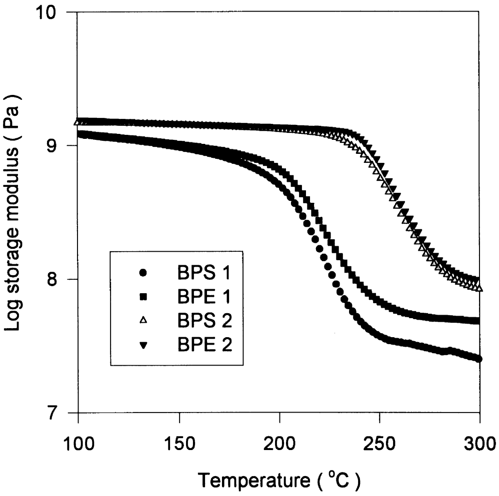


Figure 7 DMA thermograms of liquid crystalline epoxy resins

Table 1 Coefficient of thermal expansion of biphenol-based LCE networks

	CTE (μm/m°C) Glassy region	Rubbery region
BPS1	64	75
BPE1	61	74
BPS2	39	40
BPE2	37	39

major role in determining the T_g of the LCE network. In addition, the T_g of BP2 was much higher than any other epoxy or LCE resin reported in the literature up to now [12].

A common bifunctional epoxy resin has a T_g around 200°C and a tetrafunctional epoxy resin has a T_g of about 250°C. It was even close to the T_g of polyimide (300°C), widely used as a heat-resistant material. This suggests that the T_g of the LCE networks can be elevated drastically by controlling the chemical stucture of mesogen. The dynamic elastic modulus of BP1 and BP2 mixtures showed the same tendency as T_g. The elastic modulus of BPS2 and BPE2 was higher than that of BPS1 and BPE1 both in the glassy and rubbery region. This is connected with the long rigid rod mesogenic group of BP2 and the strong intermolecular interaction of BP2 with a neighbouring chain, e.g. intermolecular hydrogen bonding of carbonyl with hydroxyl group. Another reason is the liquid crystalline phase of the LCE network. BPS2 and BPE2 form a liquid crystalline phase on curing and have a densely packed structure in comparison with isotropic BPS1 or BPE1. Densely packed BPS2 and BPE2 interact with the neighbouring chain strongly even above T_g, and the deformation of BPS2 and BPE2 in the rubbery region is extensively suppressed. The glassy modulus of the BP2 network was kept up to 250°C though it decreased slightly. This implies that the use temperature of the BP2 network can be greater than 200°C. It can be concluded from these DMA results that a rigid liquid crystalline network is more resistant to the mechanical and thermal deformation than an isotropic one, and can be used at elevated temperature.

The CTE of the cured LCE network was also determined in the glassy and rubbery region (*Table 1*). BPS2 and BPE2 showed a much lower CTE than BPS1 and BPE1 at all temperatures. The CTE of BPS1 and BPE1 were similar and increased in glass transition region, as is usually observed in common thermoset material. Unlike BPS1 and BPE1, BPE2 and BPS2 had similar CTE values both in the glassy and rubbery region. This is related to the rigidity of the mesogenic group of BP2 and strong intermolecular hydrogen bonding between neighbouring chains, which restricts the thermal chain motion of the cured LCE network, as explained in the DMA data. Considering the thermomechanical analysis results, a highly cross-linked BP2 network is suitable for highly heat-resistant structural materials with dimensional stability at elevated temperature.

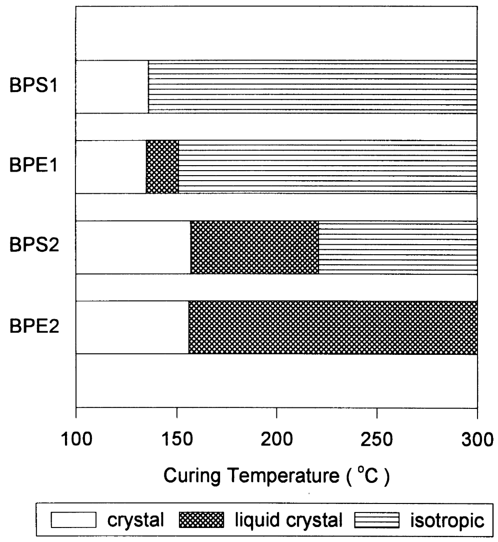


Figure 8 Phase diagrams of liquid crystalline epoxy resins

Liquid crystalline phase of the LCE network

Polarized optical measurements were carried out to observe the liquid crystalline phase of BP1 and BP2 on curing with DDS and DDE. The liquid crystalline phase of BP1 and BP2 was recorded according to the curing time at various temperatures. The phase diagram of four LCE mixtures is presented in *Figure 8* according to isothermal curing temperature. BPS1 did not show any liquid crystalline phase on curing and other mixtures displayed liquid crystalline phase. BPE1 exhibited a nematic liquid crystalline phase when it was cured between 140 and 150°C. The liquid crystalline phase of BPE1 was stable up to decomposition after 2 h curing in this temperature range. BPE1 displayed a biphasic liquid crystalline phase when it was cured at around 150°C and formed an isotropic phase above 150°C. In the case of BPS2, a nematic liquid crystalline phase appeared when it was cured below 230°C after melting of BP2.

This reveals that BPS2 must be cured in the liquid crystalline temperature range of BP2 to produce a cured thermoset with liquid crystalline phase. BPE2 showed a nematic liquid crystalline phase when it was cured at any temperature up to 300°C, though a biphasic liquid crystalline phase appeared at a curing temperature above 280°C. In other words, BPE2 formed a liquid crystalline phase even in an isotropic temperature range of BP2. This is attributed to the potential mesogenic character of DDE which has an end-to-end distance of 11.2 Å. These results prove that the mesogenic length of LCE and curing agent is the most important factor in determining the mesophase range of LCE network, and the phase of the cured LCE network is largely dependent on the curing temperature. The liquid crystalline phase of cured LCE was maintained up to the decomposition temperature, as the cross-link locks the chain covalently together.

CONCLUSIONS

Synthesis, curing and thermomechanical properties of biphenol-based liquid crystalline epoxy resin were investigated to produce a thermally stable liquid crystalline network. The liquid crystalline epoxy resin with biphenol and aromatic ester unit in the mesogenic group (BP2) showed a higher curing rate compared to biphenol epoxy resin (BP1). The postcuring peak was observed in the curing of BPE1, BPS2 and BPE2. The heat of curing was much larger in the case of BP1 than BP2 due to the restriction of the motion of the mesogenic group in BP2. BP2 showed a higher T_g and dynamic elastic modulus in comparison with BP1 both in the glassy and rubbery region.

Especially, the T_g of a densely cross-linked BP2 network was much higher than that of other epoxy resins reported in the literature. The glassy modulus of the BP2 network remained almost constant up to 250°C, and dimensional stability was excellent in both the glassy and rubbery region. A liquid crystalline phase was detected in the case of BPE1, BPS2 and BPE2. BPE2 formed a liquid crystalline network at any curing temperature, and BPS2 showed a liquid crystalline phase when it was cured in the liquid crystalline temperature range of BP2. BPE1 exhibited a liquid crystalline phase only in a narrow temperature range (140–150°C).

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