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The effect of mesogenic length on the curing behavior and properties of liquid crystalline epoxy resins

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Abstract

The effect of mesogenic structure on the properties of liquid crystalline epoxy (LCE) resins was investigated. The mesogenic lenght of the LCE was changed by changing the length of the rigid rod unit of LCE and it was correlated with the curing behavior and thermomechanical properties of LCE resins. The curing of LCE resins was accelerated in the LCE with LC phase during curing and storage modulus and glass transition temperature of LCE thermosets were high in the epoxy networks with long mesogenic group. In addition, the LC phase of LCE was stable for LCE with long mesogenic group and it was maintained until decomposition.

Keywords: Liquid crystalline epoxy resin; Mesogenic length; Mesophase

1. Introduction

In recent years, many studies have been focused on the subject of liquid crystalline thermosets [1–26]. Liquid crystalline thermosets were developed to enhance the mechanical and thermal properties of common thermosets and to overcome the disadvantages of thermoplastic liquid crystalline polymers. Liquid crystalline thermosets are very interesting because they have many peculiar properties such as excellent anisotropic mechanical and optical properties. Many research groups have studied the synthesis, curing behavior, mechanical properties and optical properties of liquid crystalline thermosets [1–26]. Various liquid crystalline thermosets with different mesogenic groups and reactive end functional groups have been prepared. Among these materials liquid crystalline epoxy (LCE) resins have gained considerable interest due to their advantages like controllable curing rate, high heat and chemical resistance and high mechanical properties. Epoxy resins with aromatic stilbene structure were investigated by many research groups [1–8]. Ober et al. reported the synthesis, curing behavior and anisotropic mechanical properties of stilbene epoxy resins [1–5]. Yee et al. investigated the morphology of stilbene epoxy resin and the effect of curing reaction on liquid crystallinity [6] Carfagna et al. observed the isothermal curing behavior and morphological change of stilbene epoxy resin [7]. Mallon et al. studied LCE resins with aromatic ester unit in the main chain [8]. Ober et al. synthesized symmetric twin LCE resins [9] and Jahromi et al. [10–13] and Broer et al. [14] reported the curing reaction of aromatic ester based LCE resins. In addition, biphenol epoxy resin [8,15–17], azo epoxy resin [16], chalcone epoxy resin [18], azine epoxy resin [19], azomethine [20] and binaphthyl epoxy resin [21] were studied by many research groups. These studies mainly reported the curing behavior, anisotropic orientation and morphology of cured liquid crystalline thermosets. However, little was known about the relationship between structure and properties of LCE resins. Our group reported several liquid crystalline epoxy resins with different chemical unit and studied the effect of chemical structure on the curing and thermomechanical properties of the crosslinked networks. Depending on the substituents on the mesogenic group [22], mesogenic structure [23,24] and bridging group between mesogenic group and epoxide functional group [25], the curing behavior and thermomechanical properties of the thermosets were greatly changed.

In this study, we synthesized a series of epoxy resins based on aromatic ester mesogenic units to investigate the effect of mesogenic length on the properties of LCE resins. Mesogenic length of epoxy resins was varied by changing the number of benzene rings in the rigid rod unit. The curing behavior,

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mechanical properties and thermal properties were observed and the morphology of the LCE resins was also analyzed.

2. Experimental

2.1. Synthesis of liquid crystalline epoxy resins

2.1.1. 1,4-Di(2,3-epoxypropenyloxy)benzene

2.1.1.1. 1,4-Di(2-propenyloxy)benzene (1a). Hydroquinone (44 g, 0.4 mol) and 3-bromopropene (121 g, 1.0 mol) were dissolved into 200 ml of ethanol and then the solution was put into the aqueous solution containing KOH. The mixture was boiled for 6 h and then cooled to room temperature. The cooled solution was poured into the mixture containing 500 ml of water and 200 g of ice. An oil layer was separated and then it was extracted with 200 ml of diethylether. After separation the diethylether solution was extracted with 10% KOH aqueous solution three times. The diethylether solution was washed with water three times and then was dried over $MgSO_4$ and then diethylether was evaporated. The resulting oil was not purified further. Yield: 75% (57 g).

2.1.1.2. 1,4-Di(2,3-epoxypropenyloxy)benzene (1b). Diallyl monomer 1a (19 g, 0.2 mol) was added to 300 ml CH_2Cl_2 solution containing 3-chloroperoxybenzoic acid (78 g 0.45 mol). The mixture was boiled for 48 h. After cooling and filtration, the filtrate was washed with 5% aqueous solution of Na_2SO_3 (200 ml), 5% aqueous solution of $NaHSO_3$ (200 ml) and saturated aqueous solution of NaCl (200 ml). The CH_2Cl_2 layer was dried over $MgSO_4$ and CH_2Cl_2 was evaporated. Yield: 68% (30 g) T_m: 113 °C.

^{1}H NMR ($CDCl_3$): δ(ppm) 2.75(2H, dd, CH_2 of epoxy), 2.89(2H, dd, CH_2 of epoxy), 3.33(2H, m, CH of epoxy), 3.90(2H, dd, CH_2 of glycidyl), 4.15(2H, dd, CH_2 of glycidyl), 6.85(4H, s, aromatic).

2.1.2. 4,4′-Di(2,3-epoxypropenyloxy)phenyl benzoate

2.1.2.1. 4,4′-Dihydroxy phenyl benzoate (2a). 4-Hydroxybenzoic acid (60 g, 0.43 mol) and NaOH (38 g, 0.96 mol) were added to 900 ml of water and then stirred for 10 min at 5 °C. Ethylchloroformate (54 g, 0.50 mol) was put into the solution and then reacted for 10 min. Five hundred millilitres of 2 N HCl solution was poured into the solution and then white precipitate was filtered and washed with water several times. The solid product was recrystallized in acetone and white need like crystal was obtained. The produced white crystal and a few drops of DMF were poured into the thionyl chloride and boiled for 1 h. The excess thionyl chloride was evaporated under vacuum and the last trace at 10^{-2} mmHg. The product was dissolved in 300 ml CH_2Cl_2 and the solution was added to the THF solution containing hydroquinone (55 g, 0.50 mol) and pyridine (40 ml, 0.50 mol). After reaction for 12 h at room temperature, the solution was precipitated in 2 N NaOH solution. After filtration, the precipitate was washed with excess water and then dissolved in ethanol. 2 N NaOH solution and CH_3CO_2H were added successively to ethanol solution. After stirring for 2 h, ethanol was evaporated and then the product was washed with water. It was recrystallized in methylcellusolve acetate. Yield: 68% (67 g) T_m: 247 °C.

2.1.2.2. 4,4′-Di(2-propenyloxy)phenyl benzoate (2b). A mixture of dihydroxy compound 2a (33 g, 0.2 mol), 3-bromopropene (26 ml, 0.30 mol), K_2CO_3 (70 g, 0.5 mol) was put into the 400 ml of acetone and then boiled for 24 h. The solid was filtered and acetone was evaporated. The remaining solid was washed successively with 5% Na_2CO_3 solution, excess water and 200 ml of cold ethanol. After drying, white powder was obtained. It was recrystallized in acetonitrile/isopropanol (1:1). Yield: 74% (46 g) T_m: 69 °C.

2.1.2.3. 4,4′-Di(2,3-epoxypropenyloxy)phenyl benzoate (2c). This compound was prepared in the same manner as described for the synthesis of 1b. Diallyl monomer 2b (31 g, 0.1 mol) was oxidized with 3-chloroperoxybenzoic acid and the product was recrystallized in acetonitrile/isopropanol (1:1). Yield: 75% (25 g) T_m: 116 °C.

^{1}H NMR ($CDCl_3$): δ(ppm) 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), 6.85(4H, s, aromatic), 6.97(2H, d, aromatic), 7.02(2H, d, aromatic), 7.12(2H, d, aromatic), 8.15(2H, d, aromatic).

2.1.3. p-Phenylene-di[4-(2,3-epoxypropenyloxy)benzoate]

2.1.3.1. 4-(2-Propenyloxy)benzoic acid (3a). A mixture of ethyl-4-hydroxybenzoate (99 g, 0.6 mol), 3-bromopropene (90 g, 0.75 mol), K_2CO_3 (126 g, 0.9 mol), 800 ml of acetone was refluxed for 24 h. The solid was filtered and the solvent was evaporated. Four hundred millilitres of diethylether and 200 ml of water were poured into the remaining solution. The diethylether layer was separated and it was washed with 200 ml of 10% NaOH solution three times. After evaporation of the diethylether the residue was boiled with 900 ml of ethanol/ water (1:2) solution containing 90 g of KOH until the solution was cleared. 2 N HCl solution was added until pH 2 and the solid was filtered and washed with excess water. It was recrystallized in ethanol and we obtained white plates. Yield: 50% (58 g) T_m: 170 °C.

2.1.3.2. p-Phenylene-di[4-(2-propenyloxy)benzoate] (3b). A mixture of 3a (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 was poured into the solution. After addition of hydroquinone (6.3 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 in ethyl acetate. Yield: 85% (22 g) T_{KN}: 104 °C T_{NI}: 163 °C.

2.1.3.3. p-Phenylene-di[4-(2,3-epoxypropenyloxy)benzoate] (3c). 3c was prepared according to the procedure for the synthesis of 1b. Diallyl monomer 3b (13 g, 0.030 mol) was oxidized and pure product was obtained after recrystallization from ethylacetate/isopropanol. Yield: 68% (8.9 g) T_{KN}: 181 °C T_{NI}: 229 °C.

^{1}H NMR ($CDCl_3$): δ(ppm) 2.82(2H, dd, CH_2 of epoxy) 2.94(2H, dd, CH_2 of epoxy) 3.43(2H, s, CH of epoxy) 4.12(2H, dd, CH_2 of glycidyl) 4.35(2H, dd, CH_2 of glycidyl) 7.03(4H, d, aromatic) 7.34(4H, s, aromatic) 8.12(4H, d, aromatic).

2.1.4. 4,4′-Di[4″-(2,3-epoxypropenyloxy)benzoyloxy]phenyl benzoate

2.1.4.1. 4,4′-Di[4″-(2-propenyloxy)benzoyloxy]phenyl benzoate (4a). A mixture of 3a (21 g, 0.11 mol) and $SOCl_2$ (29 ml, 0.4 mol) was refluxed for 2 h. Excess $SOCl_2$ was evaporated in vacuum and the last traces were evaporated at 10^{-2} mmHg. Excess pyridine was poured into the remaining solution. After addition of 2a (13 g, 0.055 mol) to the pyridine solution, 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 of 1 N HCl aqueous solution. The solid was filtered and washed with 500 ml of 5% Na_2CO_3 aqueous solution, 500 ml of water and ethanol. After drying in vacuum oven, a brownish powder was obtained. Yield: 82% (25 g) T_{KN}: 160 °C.

2.1.4.2. 4,4′-Di[4″-(2,3-epoxypropenyloxy)benzoyloxy]phenyl benzoate (4b). 4b was prepared by the method described for the synthesis of 1b. Diallyl monomer (11 g, 0.020 mol) was oxidized and pure product was obtained. Yield: 66% (7.7 g) T_{KN}: 191 °C T_{NI}: 271 °C.

^{1}H NMR ($CDCl_3$): δ(ppm) 2.80(2H, dd, CH_2 of epoxy), 2.95(2H, dd, CH_2 of epoxy), 3.41(2H, s, CH of epoxy), 4.00(2H, dd, CH_2 of glycidyl), 4.35(2H, dd, CH_2 of glycidyl), 7.04(4H, d, aromatic), 7.25(4H, s, aromatic), 7.35(2H, d, aromatic), 8.16(4H, d, aromatic) 8.28(2H, d, aromatic).

2.2. Physical measurements

A differential scanning calorimetry (Du Pont 910 DSC) was used for the study of dynamic and isothermal curing behavior of epoxy resins synthesized in this experiment. Isothermal curing temperature was varied from 180 to 220 °C and curing time was fixed with 2 h. Heating rate of dynamic experiment was 5, 10, 15 and 20 °C/min. Morphologies of epoxy monomer and cured thermosets were observed with Leitz optical microscope equipped with a Mettler FP82 hot stage and FT80 central processor. A dynamic mechanical thermal analyzer (Rheometris Co. MK III) was used to measure the glass transition temperature and modulus of cured thermosets. Data were collected in tensile mode at a frequency of 1 Hz and heating rate was 5 °C/min. Thermal stability of cured thermoset was analyzed with a thermogravimetric analyzer (Du Pont 900 TGA) at a heating rate of 10 °C/min.

2.3. Curing of epoxy resins

Four epoxy resins synthesized in this experiment were cured using diaminodiphenylsulfone (DDS) as a curing agent. DDS was used to produce high heat resistant material and to slow down the curing reaction of epoxy resins. The mole ratio of DDS to epoxy resins was fixed with 0.45. Curing mixtures were prepared by dissolving the epoxy resins and DDS in chloroform/acetone mixed solvent and removing the solvent under reduced pressure at room temperature. Each mixture will be named as LCE 1, LCE 2, LCE 3 and LCE 4 according to the number of benzene rings in mesogenic unit. LCE 1 and LCE 2 were cured at 180 °C for 6 h and then postcured at 220 °C for 4 h and curing of LCE 3 and LCE 4 was performed at 200 °C for 6 h and 240 °C for 4 h.

3. Results and discussion

Four different LCE resins were synthesized to investigate the effect of mesogenic structure on the curing behavior and properties of LCE networks. The chemical structures of each epoxy resin are presented in Fig. 1. The transition temperature, mesogenic length, aspect ratio of mesogen and epoxy equivalent weight (EEW) of LCE monomers are given in Table 1. Mesogenic length and aspect ratio were determined by MNDO method. Four epoxy resins can be classified into two groups, one having a liquid crystalline character in the curing temperature (LCE 3, LCE 4) and the other having no liquid crystalline character in the curing temperature (LCE 1, LCE 2). Four epoxy resins investigated in this experiment have same reactive functional group but differ only in mesogenic group. All compounds except LCE 1 had ester functional group in the mesogenic unit and the mesogenic length was varied by changing the number of benzene rings. As the mesogenic length of epoxy resin increases, the mesophase stability of the nematic phase was enhanced. LCE 1 did not show any liquid crystalline phase because its aspect ratio was only 1.3. LCE 2 exhibited monotropic liquid crystalline phase on cooling from 93 to 79 °C. LCE 3 had thermotropic liquid crystalline transition between 181 and 229 °C and LCE 4 showed liquid crystalline phase in the wide temperature range between 192 and 271 °C. Nematic mesophase was observed in LCE 2, LCE 3 and LCE 4. The same mesophase was observed for the respective diallyl precursors. The polar oxirane ring in LCE resins increased the transition temperature but decreased the mesophase stability compared with that of corresponding diallyl precursors.

Dynamic curing of LCE was performed in DSC to investigate the effect of mesogenic length on the curing behavior of LCE resins. Dynamic DSC thermograms are displayed in Fig. 2. All four epoxy resins showed exothermic peak in the temperature range between 180 and 280 °C. The exothermic peak temperature of LCE 3 and LCE 4 was lower than that of LCE 1 and LCE 2. This can be explained by the morphology and chemical reactivity of the LCE resins at curing conditions. It is well known that curing reaction of LCE resin proceeds faster in the nematic liquid crystalline phase. Broer et al. [14] reported that the curing reaction of diepoxide with flexible spacer group was fast in the nematic phase irrespective of temperature. Carfagna et al. [7] observed fast curing reaction of LCE resin in the nematic phase. In our work,

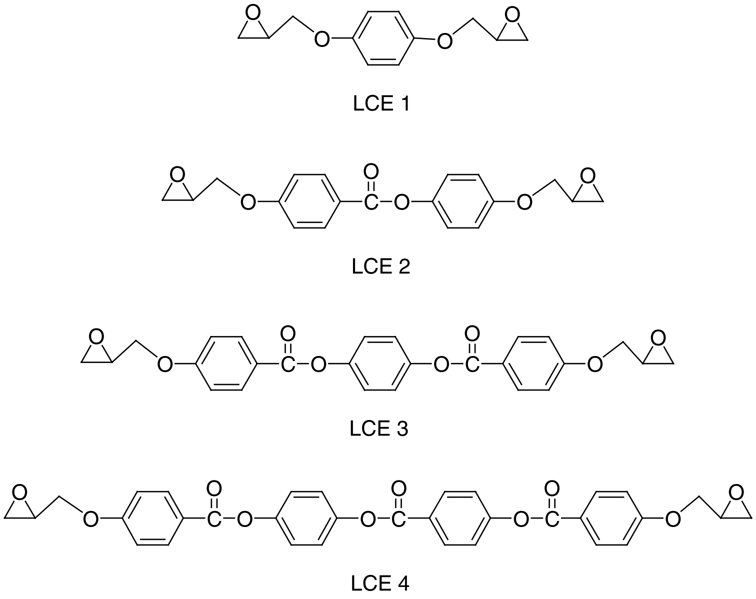

Fig. 1. Chemical structures of liquid crystalline epoxy resins.

LCE 3 and LCE 4 showed LC phase at the curing temperature, while LCE 1 and LCE 2 were cured at isotropic temperature range. Therefore, the curing of LCE 3 and LCE 4 was accelerated compared with the curing of LCE 1 and LCE 2. The steep initial slope of exothermic peak which is shown in LCE 3 and LCE 4 is also due to the fast curing reaction caused by the low viscosity of epoxy resin in the nematic phase. The other factor for the low exothermic peak temperature is the high chemical reactivity of the epoxide group in LCE 3 and LCE 4. In general, the reaction of oxirane ring with amine is known as nucleophilic substitution reaction, so electron withdrawing groups increase the curing rate of epoxy resins [26]. According to the result reported by Tanaka et al. [27] for the epoxy resins with different substituent group, the order of reactivity toward amine was 3-chloro-1,2-epoxypropane > 2,3-epoxy-1-propylphenylether > phenyloxirane > 1,2-epoxyoctane. General conclusions can be drawn from his result that electron withdrawing group increases the curing rate of epoxy resins. In the case of this experiment, LCE 3 and LCE 4 have carbonyl unit in both sides of oxirane ring. Because carbonyl unit has electron withdrawing character, it can increase the curing rate of epoxy resins and make the curing reaction of epoxy resin easy. In the case of LCE 3 and LCE 4, second exothermic peak appears at high temperature above 270 °C, which is not shown clearly in this figure. The long rigid rod ester mesogenic unit of LCE 3 and LCE 4 is the reason for this exothermic peak. As LCE 3 and LCE 4 have long rigid rod mesogenic unit, its motion is very restricted in the later stage of curing. Rigid rod mesogenic unit prevents the translational motion of LCE after gelation. In addition, hydrogen bonding between hydroxyl group produced by the curing reaction and carbonyl group present in LCE 4 can retard the curing reaction of epoxy resin. The retarding effect of ester unit in the curing of epoxy resin was reported by Gough et al. [28]. As the carbonyl unit acts as a hydrogen acceptor, retardation phenomenon is observed in the curing of epoxy resin with ester, ketone, ether, sulfone and nitro unit. This indicates that the diffusion of LCE 4 after gelation requires higher energy than that of other LCE resins.

Table 1
Physical properties of various liquid crystalline epoxy resins

	LC phase (°C)	Mesogenic length (Å)	Aspect ratio	EEW
LCE 1	–	5.6	1.3	111
LCE 2	93–79	9.7	2.6	171
LCE 3	181–229	18.3	3.3	231
LCE 4	192–271	24.5	4.3	291

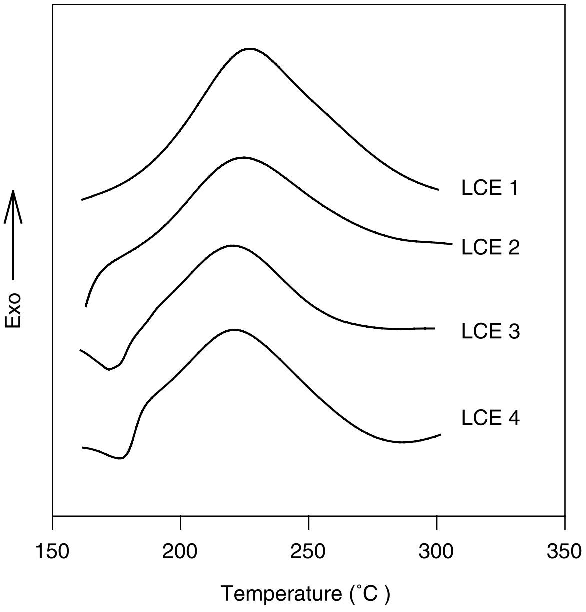

Fig. 2. Dynamic DSC thermograms of liquid crystalline epoxy/DDS.

Table 2
Heat of reaction and activation energy for liquid crystalline epoxy resins

	Heat of reaction (kJ/ep)	Activation energy (kJ/mol)
LCE 1	63.1	59.6
LCE 2	62.7	55.6
LCE 3	61.8	39.4
LCE 4	61.2	41.6

Results of dynamic DSC experiment are summarized in Table 2. The total heat of reaction of epoxy resins is almost constant irrespective of the mesogenic length. This reveals that mesogenic length does not affect the degree of cure in the dynamic curing experiment. However, activation energy of curing is much lower for LCE 3 and LCE 4 than for LCE 1 and LCE 2. The activation energy was calculated from peak temperature from peak temperature of exothermic peak at different heating rate according to Ozawa method [29]. This is thought to be due to the liquid crystalline character and high chemical reactivity of LCE 3 and LCE 4.

Isothermal curing experiment was performed in DSC to measure the curing rate and degree of curing of LCE resins. Curing temperatures were 180, 200 and 220 °C. Fig. 3 shows isothermal DSC thermograms of LCE resins at 200 °C. Initial slope of curing and maximum curing rate were much higher for LCE 3 and LCE 4 than for LCE 1 and LCE 2. At 200 °C LCE 3 and LCE 4 showed nematic liquid crystalline phase, while LCE 1 and LCE 2 exhibited isotropic phase. Since, curing reaction of LCE 3 and LCE 4 proceeds in the liquid crystalline phase in the initial stage of curing, the curing rate of LCE 3 and LCE 4 is much faster than that of LCE 1 and LCE 2. The high chemical reactivity of ester based epoxy resin is also another reason for this behavior. This result is consistent with the dynamic DSC results. The higher curing rate of LCE 2 than LCE 1 may also be due to high reactivity of oxirane ring in LCE 2. The carbonyl group accelerated the curing of LCE 2 compared with LCE 1.

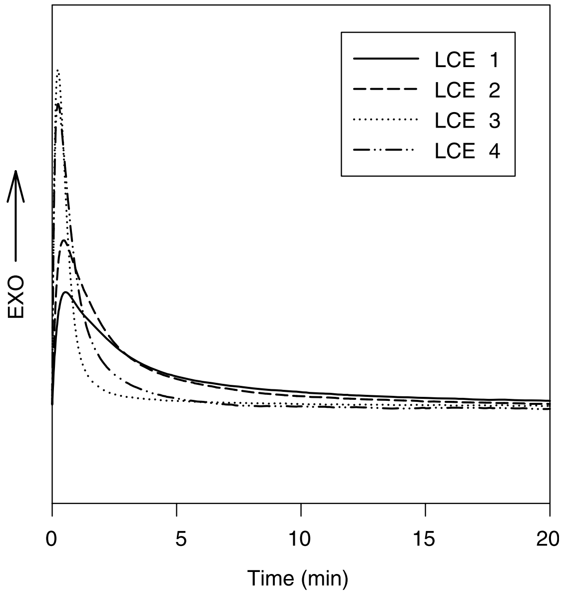

Fig. 3. Isothermal DSC thermograms of liquid crystalline epoxy/DDS.

The heat of reaction from isothermal DSC experiment is presented in Fig. 4. Heat of reaction of LCE 3 and LCE 4 is much smaller than that of LCE 1. From these data we can know that diffusional motion of LCE 3 and LCE 4 is very restricted because of its rigid rod ester mesogenic unit. In the case of LCE 3 and LCE 4, the diffusion of epoxy resin is very difficult due to structural and chemical factors. In detail, long rigid rod mesogenic unit prohibits the motion of whole chain because translation and rotation of rigid rod unit need high activation energy. Hydrogen bonding is another important factor since it reduces the reactive site in epoxy curing and limits the chain motion. Generally, it is known that many reactions occur in epoxy curing. The reaction between oxirane ring and primary or secondary amine is the major reaction occurring in epoxy curing. However, the reaction between hydroxyl group and oxirane ring can also happen in epoxy curing. Therefore, the hydrogen bonding between hydroxyl group and ester unit prevents the curing reaction by decreasing the reaction site and constrains the motion of neighboring chain by locking segments. Intramolecular hydrogen bonding mainly reduces the reaction site and intermolecular hydrogen bonding locks the chain motion as well as decreases the reaction site. The hydrogen bonding in LCE resins is well described in the paper published by our group [30]. According to the result, intramolecular and intermolecular hydrogen bonding exist until 240 °C. Therefore, hydrogen bonding affects the curing rate of LCE resins. The heat of reaction of LCE resins shows the same tendency as that of common epoxy resin according to the curing temperature, but little change was observed for LCE 3 and LCE 4. This indicates that high temperature is required to obtain high degree of curing for LCE 3 and LCE 4. In these data, LCE 3 and LCE 4 showed almost the same heat of reaction. According to the explanation suggested above it is predicted that LCE 4 has low heat of reaction. The rather high heat of reaction of LCE 4 is thought to be due to the presence

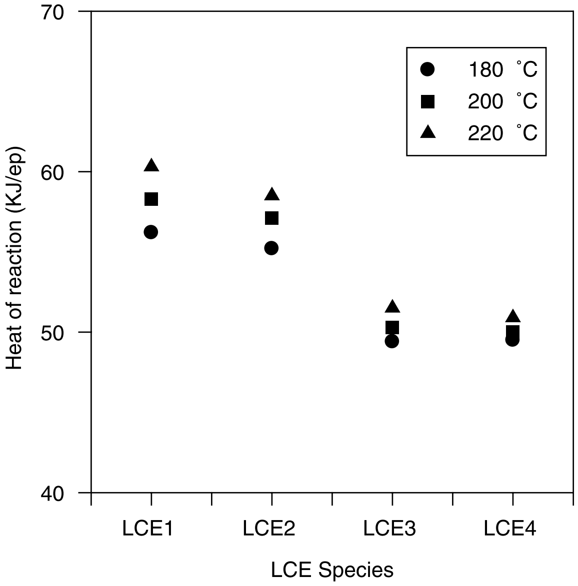

Fig. 4. Isothermal heat of reaction of liquid crystalline epoxy/DDS at various curing temperature.

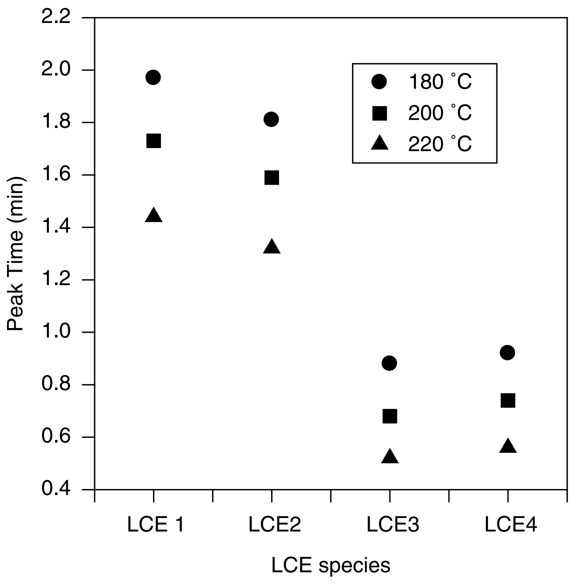

Fig. 5. Isothermal peak time of liquid crystalline epoxy/DDS at various curing temperature.

of nematic liquid crystalline phase on curing. Since, the formation of nematic mesophase causes a reduction of viscosity, the diffusion of epoxy resin in the nematic phase is easier than in the isotropic phase. Therefore, in spite of more rigid character of mesogenic group LCE 4 has almost the same heat of reaction as LCE 3.

Fig. 5 represents the isothermal peak time of each epoxy resin according to the curing temperature. The lower peak time of LCE 3 and LCE 4 is attributed to the liquid crystalline character and higher chemical reactivity of oxirane ring and the lower peak time of LCE 2 to LCE 1 is due to the higher chemical reactivity of oxirane ring. As isothermal curing temperature increases, isothermal peak time shows decreasing tendency. This tendency corresponds with the result observed for common epoxy resin. However, in the case of LCE 3 and LCE 4, the isothermal peak time was little affected by the curing temperature. From these data it can be known that temperature effect is not so prominent in the liquid crystalline phase as in the isotropic phase for the curing of LCE resin.

To investigate the thermal and mechanical properties of epoxy resins DMTA data were collected for the cured LCE resins. Fig. 6 represents the storage modulus of cured LCE resins. The modulus of LCE resins tends to increase with increasing the mesogenic length. In general, modulus of thermoset resins is known to be mainly affected by the chemical structure and crosslinking density. The more rigid the chemical structure is, the higher the modulus of thermoset resins and the modulus of thermoset resins also increases with increasing the crosslinking density. As already shown in isothermal DSC data, crosslinking density of LCE resins showed decreasing tendency with the mesogenic length. However, the modulus was high for the LCE resins with long mesogenic group. This result implies that rigid character of the mesogenic unit is the main reason for the increase of modulus. In other words, mesogenic length is more important than crosslinking density in determining the modulus of the LCE thermosets.

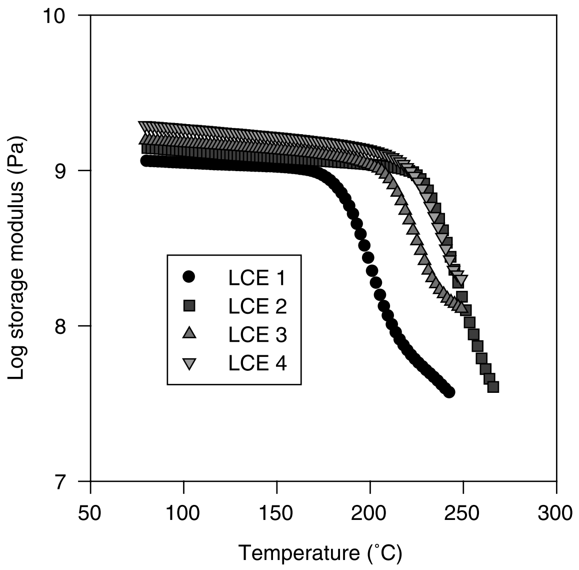

Fig. 6. DMTA thermograms of cured liquid crystalline epoxy/DDS.

To relate the modulus of liquid crystalline thermoset with the mesogenic length, modulus and glass transition temperature were plotted against the aspect ratio of mesogen (Fig. 7). The modulus was proportional to the aspect ratio of the mesogen within the aspect ratio range investigated. This result indicates that modulus of LCE resins is closely related with the aspect ratio of the mesogen. This also implies that activation energy for local motion of cured thermoset is higher for the LCE resins with long mesogen than for short mesogen. The relationship between modulus and aspect ratio was maintained up to 200 °C. Glass transition temperature of LCE resin showed the same tendency as storage modulus. In common, epoxy resins crosslinking density is the major factor in determining the glass transition temperature of cured thermoset resin. As already shown in isothermal DSC results, heat of reaction decreased with increasing the mesogenic length. The adverse tendency was observed for the glass transition temperature of LCE resins synthesized in this experiment. This

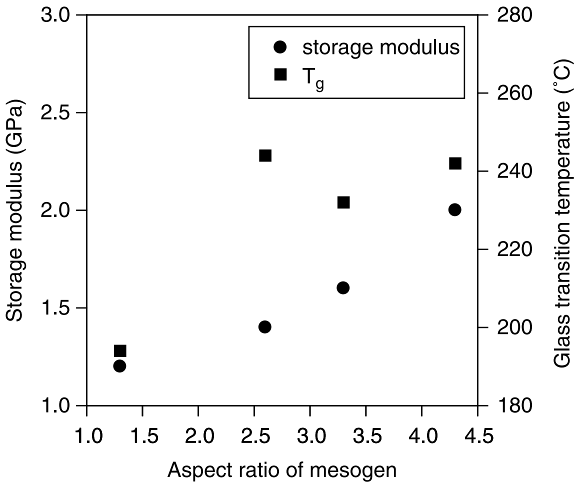

Fig. 7. Plot of storage modulus and T_g against mesogen aspect ratio.

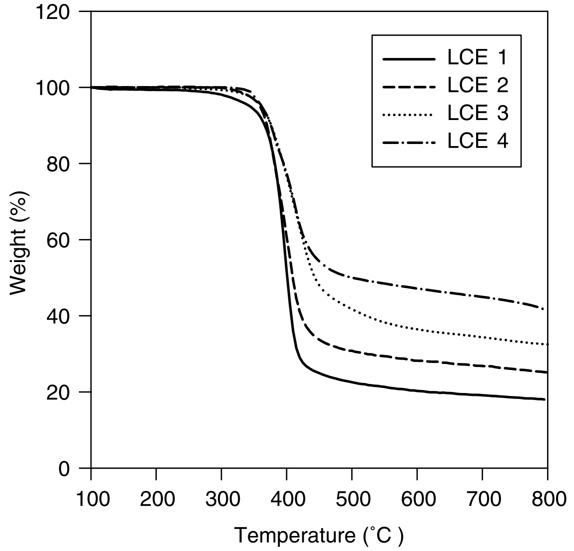

Fig. 8. TGA thermograms of cured liquid crystalline epoxy/DDS.

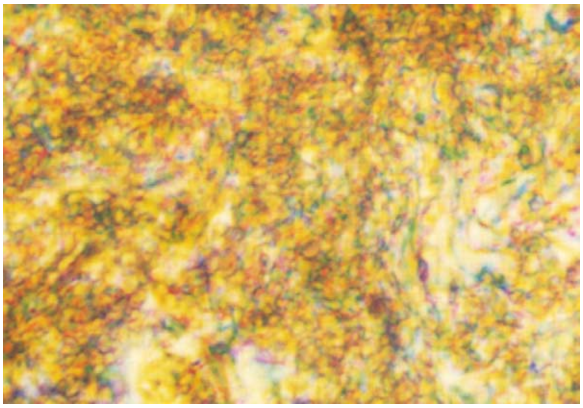

Fig. 9. Polarizing optical micrographs of LCE 4 cured at 180 °C for 20 min.

indicates that mesogenic length plays a major role in determining the glass transition temperature of LCE resin.

Thermal stability of LCE/DDS network was investigated with TGA. TGA thermograms of cured LCE resins are presented in Fig. 8. Maximum decomposition temperature and char yield were high for LCE networks with long mesogenic group. This is due to the fact that long rigid rod mesogen is resistant to the thermal decomposition. The initial decomposition temperature was above 350 °C for LCE 3 and LCE 4. Therefore, we can conclude that thermal stability of LCE resins is enhanced with increasing the mesogenic length. Judging from these thermal and mechanical analysis data, LCE 4 is better than other LCE resins to get high performance thermosets.

Fig. 9 represents the optical micrographs of LCE 4 cured at 180 °C for 20 min. LCE 1 and LCE 2 did not show any LC phase on curing, while LCE 3 and LCE 4 showed nematic LC phase during curing. However, the LC phase of LCE 3 changed from nematic to isotropic as curing goes on, while LCE 4 kept its thread like nematic phase during curing. The phase transformation in LCE 3 from LC phase to isotropic phase during curing is due to the fact that its LC domain formation was interrupted by the DDS with bent structure and by the three-dimensional network formation, which occurs after gelation. However, LCE 4 has long rigid rod mesogenic group, its LC phase was not affected by curing with DDS. The LC phase of LCE 4 was maintained up to decomposition temperature.

4. Conclusion

A series of LCE resins with different mesogenic structure were synthesized to investigate the effect of mesogenic length on the properties of cured LCE thermosets. The curing of LCE resins was accelerated in the LC phase, while the heat of reaction was low for LCE resins with long mesogenic group due to motional restriction of long mesogenic group. Activation energy of curing was low for LCE resins with nematic mesophase and chemical reactivity of epoxy ring was enhanced by introducing ester unit in the main chain. Storage modulus and glass transition temperature of LCE resins increased with increasing the mesogenic length in spite of low heat of reaction. The liquid crystalline phase of LCE 3 changed from nematic to isotropic phase, while LCE 4 kept its nematic liquid crystalline phase until decomposition.

References

[1] Barclay GG, Ober CK, Papathomas K, Wang D. J Polym Sci, Part A: Polym Chem 1992;30:1831.
[2] Ober CK, Barclay GG. Mat Res Soc Symp Proc 1991;227:281.
[3] Barclay GG, McNamee SG, Ober CK. Polym Mater Sci Eng 1990;63:387.
[4] Barclay GG, Ober CK, Papathomas K, Wang D. Polym Mater Sci Eng 1990;63:356.
[5] Barclay GG, McNamee SG, Ober CK, Papathomas K, Wang D. J Polym Sci, Part A: Polym Chem 1992;30:1845.
[6] Lin Q, Lee AF, Earls JD, Hefner RE, Sue H. Polymer 1994;35:2679.
[7] Carfagna C, Amendola E, Giamberini M. Liq Cryst 1993;13(4):571.
[8] Mallon JJ, Adams PM. J Polym Sci, Part A: Polym Chem 1993;31:2249.
[9] Shiota A, Ober CK. J Polym Sci, Part A: Polym Chem 1996;34:1291.
[10] Jahromi S, Lub J, Mol GN. Polymer 1994;35:622.
[11] Jahromi S, Kuipers WAG, Norder B, Mijs WJ. Macromolecules 1995;28:2201.
[12] Jahromi S. Macromolecules 1994;27:2804.
[13] Jahromi S, Mijs WJ. Mol Cryst Liq Cryst 1994;250:209.
[14] Broer DJ, Lub J, Mol GN. Macromolecules 1993;26:1244.
[15] Su WFA. J Polym Sci, Part A: Polym Chem 1993;31:3251.
[16] Koscielny B, Pfitzmann A, Fedtke M. Polym Bull 1994;32:529.
[17] Lin CL, Chien LC. Macromol Rapid Commun 1995;16:869.
[18] Sadafule DS, Raghuraman RN, Navale NG, Kumbhar CG, Panda SP. Macromol Sci Chem 1988;25:121.
[19] Carfagna C, Amendola E, Giamberini M. Macromol Chem Phys 1994;195:279.
[20] Mikroyannidis JA. Makromol Chem 1989;190:1867.
[21] Carfagna C, Amendola E, Giamberini M. Macromol Chem Phys 1994;195:2307.
[22] Lee JY, Jang J. J Polym Sci, Part A: Polym Chem 1998;36:911.
[23] Lee JY, Jang J, Hong SM, Hwang SS, Kim KU. Polymer 1998;39:6121.
[24] Lee JY, Jang J. J Polym Sci, Part A: Polym Chem 1999;37(4):419.
[25] Lee JY, Jang J, Hong SM, Hwang SS, Kim KU. Polymer 1999;40(11):3197.
[26] Chapman NB, Isaacs NS, Parker RE. J Chem Soc 1959;1925.
[27] Tanaka Y. J Macromol Sci Chem 1967;1:1059.
[28] Gough LJ, Smith IT. J Oil Colour Chem Assoc 1960;43:409.
[29] Ozawa T. Bull Chem Soc 1965;38:1881.
[30] Lee JY, Jang J. Polym Bull 1997;38:447.