Synthesis, Characterization, and Thermomechanical Properties of Liquid Crystalline Epoxy Resin Containing Ketone Mesogen

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This study focuses on the synthesis of a novel liquid crystalline epoxy resin (LCER) based on ketone mesogenic group. The chemical structure, melting range, and liquid-crystalline phase transition behavior of the LCER were characterized using Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, mass spectroscopy, differential scanning calorimetry (DSC), and polarized optical microscopy (POM). The curing reaction of the LCER was monitored by DSC using diaminodipheylmethane (DDM) and diaminodiphenylsulphone (DDS) as curing agents, respectively. The results showed that the curing reaction of LCER/DDM proceeded faster than that of LCER/DDS in the initial stage. Birefringence was observed with POM during the curing processes. The results of thermomechanical properties showed that the glass transition temperatures of the cured LCERs were higher than 230°C, and that the LCER crosslinked networks were thermally stable up to 360°C. The LCER crosslinked networks showed much higher glass transition temperature, storage modulus, and thermal conductivity, and a lower coefficient of thermal expansion both in the glassy region and the rubbery region compared to those of a common epoxy resin (diglycidyl ether of bisphenol A).

INTRODUCTION

Epoxy resins are widely applied in the polymer industry as coatings, structural adhesives, insulating materials, and polymeric composites. They are used as engineering thermosets because of their excellent properties, such as strong bonding strength, chemical resistance, thermal stability, and good electrical properties [1–3]. The properties of epoxides can be greatly enhanced if rigid rod structures are introduced into their backbone during synthesis. Most rigid rod epoxies exhibit liquid crystalline (LC) behavior; such epoxies are referred to as LC epoxy resins (LCERs) [4].

LCERs show excellent properties for versatile applications due to the combination of a thermoset and the advantages of the anisotropy of the LC formation. Networks with an orderly arrangement of molecules and a highly crosslinked structure have been obtained [5–8]. LCERs have better properties compared to those of traditional epoxy resins, such as high thermal and orientation stability, high modulus and fracture toughness, low shrinkage during curing, low coefficients of thermal expansion (CTE), and anisotropic optical properties [9, 10]. LCERs can be used as high-performance materials for applications such as self-reinforcing composite materials, microelectronics, and optical devices [11].

Many researchers have reported the synthesis, phase behavior, curing behavior, and thermal properties of various LCERs that include several basic rigid rod mesogenic group types, such as biphenyl [12–17], ester [18–24], azine [31–33], and naphthalene [34, 35]. The biphenol-based LCER synthesized by Su [12] showed a high glass transition temperature (Tg) and a low CTE. Jang et al. [15] synthesized two types of LCER based on biphenol, and examined the liquid crystalline phase of LCERs cured with two aromatic amines. They found that the increase in crosslink density resulted in the nematic phase. The cured LCERs have exhibited high Tg, low CTE, and good mesophase stability. In order to obtain LCERs with high thermal properties, Liu et al. [24] synthesized a rigid rod epoxy monomer containing the long mesogenic unit of biphenyl and the aromatic ester group. The nematic phase was observed. The cured LCER showed a higher decomposition temperature than that of flexible epoxies and higher thermal resistance than that of other rigid rod epoxies. Cho et al. [30] synthesized a methylstilbene-based LCER (DOMS). Upon heating, DOMS melted from a crystalline state into an isotropic state, and upon cooling from the isotropic state, it showed a nematic liquid crystalline state and then a crystalline state. An LCER with glycidyl-terminated benaldehyde was synthesized and subsequently cured with an aromatic diamine by Carfagna et al. [31]. The influence of the curing temperature on the nematic textures was investigated. Harada et al. [33] synthesized an LCER containing the azine group and cured it at two different temperatures. The phases of the cured systems clearly showed isotropic and nematic textures, which depended on the curing temperature. The nematic polydomain structure system showed considerably higher fracture toughness than that of the isotropic structure. Carfagna et al. [34] synthesized an LCER containing the binaphthyl group, and Lee and Jang [35] synthesized an LCER based on naphthalene. Both LCERs showed a nematic phase with a wide temperature range, and the LCERs network cured with aromatic amine displayed a nematic phase in the curing temperature range. The cured LCERs showed high thermal resistance.
In this study, a LCER based on the ketone mesogenic group was synthesized and the mesogenic group type was different from previous literatures. The chemical structure, melting range, and liquid crystalline phase transition behavior of the LCER were studied. The LCER was cured with two aromatic amines, namely diaminodiphenylmethane and diaminodiphenylsulfone, to produce a high-heat-resistant LCER network. The influence of the curing agent on the curing behavior of the LCER was examined and the liquid crystalline phase of the LCER network was monitored according to curing temperature. The thermal and mechanical properties of the cured LCER network were also investigated.

**EXPERIMENTAL**

**Materials**

\( \rho \)-Hydroxybenzaldehyde (\( \rho \)-HBA) was purchased from Acros. Acetone was purchased from J.T. Baker. Epichlorohydrin (ECH) was purchased from TEDIA. 4,4\(^0\)Diaminodiphenylsulfone (DDS) was purchased from TCI. 4,4\(^0\)Diaminodiphenylmethane (DDM) was purchased from Fluka. They were used in analytical grade without further purification. All solvents were used directly as received.

**Synthesis of LCER**

The synthesis of the LCER was carried out in two steps.

**Step 1. Synthesis of 1,5-Bis(4-hydroxyphenyl)-1,4-pentadiene-3-one.** The synthesis pathway for 1,5-bis(4-hydroxyphenyl)-1,4-pentadiene-3-one (BHPPDO) is shown in Scheme 1. In a 500-mL three-neck flask equipped with a mechanical stirrer, \( \rho \)-HBA (24.42 g, 0.2 mol) and acetone (5.81 g, 0.1 mol) were dissolved absolute in ethanol (80 mL), and the mixture was vigorously stirred at room temperature for a few minutes. An aqueous solution of sodium hydroxide solution (20 wt%, 0.3 mol) was then added dropwise in 10 min. The reaction was stirred at room temperature for 48 h, after which 400 mL of distilled water was added. The resulting solution was neutralized by gently bubbling CO\(_2\) gas through it. The yellow precipitate produced was filtered off, washed with distilled water several times, and dried at 50°C in a vacuum oven for 24 h. Furthermore, the product was purified by recrystallization from an appropriate solvent, typically a MeOH–water mixture.

\[
\begin{align*}
\text{IR (KBr):} & \quad \nu_{\text{max}} 1,508, 1,564, 1,598, 1,658, \text{and } 3,313 \text{ cm}^{-1}; \\
\text{\( ^1\)H NMR (500 MHz, acetone-\( d_6 \))} & \quad \delta \text{ in ppm: } 6.91 \text{ (4H, d, aromatic), } 7.12 \text{ (2H, d, Ph–CH=), } 7.70 \text{ (4H, d, aromatic), } 7.73 \text{ (2H, d, } \\
\text{=CH–), } 9.04 \text{ (2H, s, –OH); MS: } m/z : 267 \text{ [M+1].}
\end{align*}
\]

**Step 2. Synthesis of 1,5-Bis(\( \rho \)-Glycidyloxy-Phenyl)-1,4-Pentadiene-3-One.** To a 500-L four-neck round-bottomed flask equipped with a mechanical stirrer, heating mantle, thermocouple, temperature controller, and a Dean-Stark trap with a reflux condenser, was added a mixture of the above-synthesized BHPPDO (5.32 g, 0.02 mol), ECH (57.5 g, 0.6 mol), and diethylene glycol dimethylether (3.38 g). After purging with nitrogen for 10 min and stirring at room temperature and atmospheric pressure to thoroughly mix the contents, the temperature was raised to 65°C and the pressure was reduced to 200 mm Hg (absolute). To the resultant solution was continuously added 1.64 g of 40 wt% sodium hydroxide solution at a constant rate via a metering pump over a period of 1 h while maintaining the reaction temperature at 65°C under a reduced pressure. In the meantime, the water of the reaction was removed from the system by codistillation with ECH; the distilled ECH was returned to the system. The organic phase was rotavaporated at 195°C under full vacuum over 3 h to remove the excess ECH. The residue was extracted with methyl isobutyl ketone (MIBK). The extract was washed four times with deionized water, and the MIBK was distilled off at 195°C under vacuum. After cooling, the residue was recrystallized several times with ethanol to produce a yellow powder. The synthesis scheme of LCER is shown in Scheme 2. The structure of the product was confirmed with Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry (MS). The epoxy equivalent weight (EEW) of LCER is 196.2 g eq\(^{-1}\).

\[
\begin{align*}
\text{FTIR (KBr):} & \quad \nu_{\text{max}} 913, 1,027, 1,510, 1,563, 1,599, \text{and } 1,645 \text{ cm}^{-1}; \\
\text{\( ^1\)H NMR (500 MHz, acetone-\( d_6 \))} & \quad \delta \text{ in ppm: } 2.75 \text{ (2H, dd, CH2 of epoxy), } 2.90 \text{ (2H, dd, CH2 of epoxy), } 3.34 \text{ (2H, m, CH of epoxy), } 3.93 \text{ (2H, dd, CH2 of glycidyl unit), } 4.27 \text{ (2H, dd, CH2 of glycidyl unit), } 6.92 \text{ (4H, d, aromatic), } 7.09 \text{ (2H, d, Ph–CH=), } 7.53 \text{ (4H, d, aromatic), } 7.69 \text{ (2H, d, =CH–); MS: } m/z : 379 \text{ [M+1]; EEW = 196.2 g eq}^{-1}.
\end{align*}
\]

**SCHEME 1. Synthesis of BHPPDO.**

**SCHEME 2. Synthesis of LCER.**
Two LCER networks synthesized in this experiment were cured using DDS and DDM as curing agents, respectively. The chemical structures of DDS and DDM are shown in Fig. 1. First, the LCER and both curing agents were pestled in an agate mortar, and then were mixed together in a stoichiometric ratio, respectively. LCER/DDM was prepared after curing at 180°C for 2 h and postcured at 220°C for 3 h and LCER/DDS was cured at 200°C for 2 h and postcured at 240°C for 3 h.

Characterization Methods

FTIR spectra were obtained (Perkin-Elmer GX50003). The spectra of BHPPDO and the LCER were taken by dispersing them in KBr followed by pelletization. ¹H NMR spectra were recorded on a high-field liquid NMR instrument (Varian Unity Inova-500) with acetone-D6 as the solvent and tetramethylsilane as the internal standard. The molecular weight of the LCER was obtained from the MALDI-TOF/TOF MS spectrum recorded with a Bruker Daltonics Autoflex III mass spectrometer. The EEWs of the epoxy resins were determined using the HClO₄/potentiometric titration method. [36]

Liquid crystalline phase transition behavior of the LCER was examined using differential scanning calorimetry (DSC; DSC Q200, TA Instruments). A heating rate of 10°C min⁻¹ and a nitrogen flow of 60 mL min⁻¹ as the purge gas were maintained during measurements. The liquid crystalline properties of the LCER and the texture formation during the curing of the LCER and curing agents were examined using polarized optical microscopy (POM, Olympus BS51) with a heating stage. Dynamic and isothermal curing were performed with DSC to observe the curing behavior of LCER/DDS and LCER/DDM.

Dynamic mechanical analysis (DMA) was carried out for the cured epoxy with a dynamic mechanical thermal analyzer (DMA Q800, TA Instruments). Samples with dimensions of 10 mm × 12 mm × 2 mm were tested in three-point bending mode from room temperature to 270°C at a heating rate of 3°C min⁻¹ and an oscillation frequency of 1 Hz. The coefficient of thermal expansion was obtained with a thermomechanical analyzer (TMA Q400, TA Instruments). The sample was heated from room temperature to 220°C at 20°C min⁻¹ in the first run to release the internal stress, followed by a second scan from 0 to 270°C at 5°C min⁻¹. Thermogravimetric analysis (TGA) was conducted with a TA Q500 thermogravimetric system. In a typical experiment, about 10 mg of the sample was heated to 800°C at 10°C min⁻¹ under nitrogen gas. The thermal conductivities of the cured epoxy were measured using a hot disk thermal conductivity analyzer (TPS-2500, Sweden) at room temperature.

RESULTS AND DISCUSSION

Structural Characterization

The structure of the synthesized LCER was confirmed by FTIR, ¹H NMR, and mass spectra. Figure 2 shows the FTIR
The IR spectra of \( \rho \)-HBA and BHPPDO show the O–H stretching peak at 3,164 and 3,313 cm\(^{-1}\), respectively. When \( \rho \)-HBA reacted with acetone, the peak at 1,668 cm\(^{-1}\) disappeared, which corresponded to the C=O stretching of aldehyde, and new peaks appeared at 1,658 and 1,598 cm\(^{-1}\), which correspond to the C=O stretching of ketone and the vibration of C–C stretching, respectively. After BHPPDO reacted with EPC, the peak at 3,313 cm\(^{-1}\) disappeared, which corresponded to the O–H stretching of aldehyde, and new peaks appeared at 1,027 and 913 cm\(^{-1}\), which correspond to the C–O–C stretching of ketone and the oxirane ring of epoxide groups, respectively.

Figures 3 and 4 show the \( ^1 \)H NMR spectra of BHPPDO and the LCER, respectively. The chemical shifts of all protons corresponding to the structure could be clearly assigned. Figure 3 shows the presence of a peak at 9.04 ppm (A), which confirmed the existence of the hydroxyl group. The multiplet at 6.91–7.70 ppm is attributed to the protons in the aromatic ring (B–E). Another multiplet at 7.12 and 7.73 ppm is attributed to the protons of the methenyl group (F and G). After BHPPDO reacted with EPC, the hydroxyl proton peak in Fig. 4 completely disappeared, and the protons of aliphatic groups appeared at 2.75–4.27 ppm (A–E). The protons in the aromatic ring appeared at 6.92–7.53 ppm (F–I). The protons of the methenyl group appeared at 7.09 and 7.69 ppm (J and K).

The chemical structure of LCER was also confirmed by mass spectra. Figure 5 shows the MS spectrum of the synthesized LCER (calcd mass 378). One strong single was observed at \( m/z \) [M+H]+ = 379. The structural characterization confirmed the successful synthesis of the LCER.

**Mesomorphic Phase Transition of LCER**

To investigate the LC behavior of the epoxy monomer, DSC and POM studies were carried out. Figure 6 shows the DSC diagram of the LCER obtained at a heating rate of 10°C min\(^{-1}\) and a cooling rate of 10°C min\(^{-1}\). The results show that there were two phase transitions in the heating scan but only one phase transition during the cooling process. During the heating course, the first endothermic peak at 111°C was associated with the transition from crystallization to the liquid crystalline phase, which revealed the schlieren texture of the smectic phase. When the temperature was increased to above 121°C, there was an isotropic transition for the LCER from the liquid crystalline phase. During the cooling course, when the temperature was decreased...
to below 82°C, a clear crystal phase pattern of the LCER was obtained.

The type of LC phase was confirmed by POM observations. A sample pressed between two glass slides was heated at a rate of 10°C min⁻¹. A smectic phase birefringent pattern appeared during the heating process. Figure 7 shows the smectic and isotropic phases of the LCER. The phase transition was consistent with the DSC curve. However, the specific smectic textures could not be confirmed because of the complexity of the smectic LC phase definition.

**Curing Behavior of LCER with Amine**

The curing behavior of LCER mixed with two diamines as curing agents in an equivalence ratio of 1:1 were investigated using DSC. The LC phase transition behavior of the LCER compounds during the curing process was observed. Dynamic DSC thermograms of LCER/DDM and LCER/DDS are shown in Fig. 8. The dynamic scans were performed at a heating rate of 10°C min⁻¹. An exothermic peak and two endothermic peaks appeared in the dynamic DSC thermogram of LCER/DDS. The endothermic peaks at 83 and 110°C were caused by the melting of DDS and the LCER, respectively. The melting peak of the LCER was weak because the curing reaction and melting of the LCER occurred at this temperature. The exothermic peak at around 212°C was attributed to the curing reaction of the LCER and DDS. For LCER/DDM, the melting peak of LCER/DDM appeared at 67°C, but that of DDM was not observed. This indicates that the curing reaction between the LCER and DDM occurred prior to the complete melting of the LCER and DDM. The exothermic peak at 150°C corresponds to the curing reaction of the LCER and DDM. LCER/DDM showed a much steeper initial slope of curing than did LCER/DDS, which means that the curing reaction of LCER/DDM proceeded faster.

![Figure 8. Dynamic DSC thermograms of LCER/DDM and LCER/DDS.](wileyonlinelibrary.com)

![Figure 9. Optical microphotographs of LCER/DDM and LCER/DDS.](wileyonlinelibrary.com)
than that of LCER/DDS in the initial stage. It is known by considering the chemical reactivity of the aromatic amine group of DDS and DDM. The curing reaction between the oxirane ring and amine is known to be a nucleophilic substitution reaction, whose rate is determined by the electron density at the reaction site. The sulfone group in DDS is more electron-withdrawing than the methylene group in DDM. Therefore, DDM is more reactive toward the oxirane ring than DDS. Similar curing behavior was reported for a phenyl-based LCER [15].

The liquid crystalline phase of LCER/DDM and LCER/DDS was investigated at various curing temperatures with POM. The LCER and curing agent mixtures were inserted into a heating stage at the isothermal temperature. The typical smectic schlieren texture was observed for the LCER and curing agent mixtures when they were cured for a few minutes starting from the crystal state. The POM images of LCER/DDM and LCER/DDS are shown in Fig. 9.

Isothermal curing experiments were also carried out to confirm the dynamic DSC data. Figure 10 shows isothermal DSC thermograms of LCER/DDM and LCER/DDS obtained at 180°C. The maximum curing rate of LCER/DDM is higher than that of LCER/DDS. This result is due to the difference of chemical reactivity between DDS and DDM. It is well known that the reactivity of the amine curing agent depends on the basicity of the amine unit. The basicity of the amine group of DDM is higher than that of DDS as DDS is more electron-withdrawing than DDM [35].

**Thermomechanical Properties of LCER Network**

The dynamic mechanical properties and the glass transition temperature of the resins were investigated using DMA. The storage modulus ($E'$) and loss modulus ($E''$) were determined from the in-phase and out-of-phase responses of the resins to an applied strain, representing the elastic and viscous portions, respectively. Moreover, the glass transition temperature was measured from the peak of the mechanical damping curve ($\tan \delta$), which was the ratio of $E''$ to $E'$. LCER/DDM was cured at 180°C for 2 h and postcured at 220°C for 3 h and LCER/DDS was cured at 200°C for 2 h and postcured at 240°C for 3 h. The degrees of curing of the two mixtures were similar, as determined from FTIR and DSC measurements. The epoxide deformation peak almost disappeared and showed no exothermic peak in the postcured LCER network, indicating that the curing of the LCER was nearly complete in this curing condition. Figures 11 and 12 show the thermal mechanical properties of LCERs and diglycidyl ether of bisphenol A (DGEBA) cured at...
a heating rate of 3°C min\(^{-1}\). The coefficient of thermal expansion (CTE) of cured LCERs was also measured. TMA thermograms of the LCER and DGEBA cured at a heating rate of 5°C min\(^{-1}\) are shown in Fig. 13. The glass transition temperatures of LCER/DDM and LCER/DDS were higher than 230°C. LCER/DDM and LCER/DDS showed similar CTE values in both the glassy and rubbery regions. They showed much lower CTE and higher glass transition temperature and storage modulus than commonly used epoxy resin DGEBA (see Table 1). This is due to the motion of the LCER network being difficult due to a rigid structure and the strong hydrogen bonding between LCER main chains.

The thermal conductivities of the two cured epoxy resins were measured using a hot disk thermal conductivity analyzer. The thermal conductivities of the LCER and DGEBA were 0.34 and 0.19 W m\(^{-1}\) K\(^{-1}\), respectively, as summarized in Table 2. The difference in the thermal conductivities is due to the partial ordered network structure containing a mesogenic group [37].

TGA thermograms of LCER/DDM and LCER/DDS networks obtained at a heating rate of 10°C min\(^{-1}\) in N\(_2\) are shown in Fig. 14. The initial decomposition begins at 310°C. The maximum decomposition of LCER/DDM and LCER/DDS occurs at around 363 and 388°C, respectively. The char yields of the two LCER networks were above 40 wt%. They were thermally stable since they are composed of rigid rod mesogenic units, which are resistant to thermal attack.

**CONCLUSIONS**

An LCER based on the ketone mesogen was successfully synthesized and its structure was confirmed by FTIR, \(^{1}H\) NMR, and MS. Two endothermal peaks and one exothermal peak appeared in the DSC curves and the liquid crystalline phase was observed by POM during heating and cooling. The curing reaction of LCER/DDM proceeded faster than that of LCER/DDS in the initial stage and the liquid crystalline phase appeared during the curing processes. The glass transition temperatures of the cured LCERs were higher than 230°C. The LCER crosslinked networks were thermally stable up to 360°C. The LCER crosslinked networks have excellent thermomechanical properties compared to those of the commonly used epoxy resin DGEBA, which showed much higher glass transition temperature, storage modulus, and thermal conductivity, and lower CTE in the glassy and rubbery regions.

**REFERENCES**
