

Curing Behavior of Liquid Crystalline Epoxy/DGEBA Blend

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Received 2 December 2005; accepted 24 July 2006

DOI 10.1002/app.25117

Published online 25 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of liquid crystalline epoxy (LCE) resin on the curing behavior and thermomechanical properties of diglycidylether of bisphenol A (DGEBA) was investigated. LCE was blended with DGEBA and curing behavior of the blend was studied according to LCE content in the blend. Curing of DGEBA was accelerated and thermome-

chanical properties of DGEBA were considerably improved by the addition of LCE, which acted as a molecular reinforcement. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2198–2203, 2007

Key words: thermosets; blends; liquid-crystalline polymers

INTRODUCTION

A liquid crystalline thermoset (LCT) is a kind of polymer material, which has unique properties such as low thermal expansion coefficient, low dielectric constant, high mechanical and thermal properties, and orientation induced by magnetic field or surface treatment. Because of these properties, it can be applied in many industrial fields such as advanced composites, electronic encapsulating materials, adhesives, and optical materials.

Basically, a LCT consisted of a rigid mesogenic unit and reactive functional units. Many LCTs with different mesogenic units and reactive functional units have been studied by many research groups.^{1–29} Among these LCTs, liquid crystalline epoxy (LCE) resins have been intensively investigated because of their excellent properties.^{30–51} LCEs with aromatic stilbene^{30–36} or aromatic ester,^{37–44} as a mesogenic unit, have been investigated and binaphthyl,⁴⁵ biphenol,^{46–48} aromatic azo,⁴⁷ azine,⁴⁹ azomethine,⁵⁰ and chalcone-based LCEs⁵¹ have also been studied. LCE resins can be classified into two groups according to chemical structure of LCE. One is a LCE with no flexible spacer and the other is a LCE with a flexible spacer. The former has superior mechanical and thermal properties and synthetic method is very simple; but it needs high curing temperature and degree of curing is low due to its restricted chain motion. In addition, curing rate depends on chemical structure of mesogenic units. Advantages of LCEs with flexible spacer are good mesophase stability, high degree of curing, and low curing

temperature. However, mechanical and thermal properties are degraded by aliphatic flexible spacer. Therefore, LCEs with no flexible spacer can be candidates as a matrix for advanced composites. Our group already reported a new LCE resin with aromatic ester mesogenic group and no flexible spacer.⁴⁴ It showed high glass transition temperature of 230°C and mechanical properties of the thermosets were maintained up to 200°C.

In this article, LCE was blended with DGEBA and then cured with an aromatic diamine to improve the heat resistance and mechanical properties of common DGEBA resins. The influence of LCE on curing behavior of DGEBA was studied according to LCE content and thermomechanical properties of LCE/DGEBA blends were studied.

EXPERIMENTAL

Materials

LCE resin used in this experiment was synthesized in our laboratory. The synthetic method of LCE is described in a previous work.⁴⁴ Crystalline-nematic transition temperature of LCE was 181°C and nematic-isotropic transition temperature was 229°C. Diglycidylether of bisphenol A (DGEBA) was supplied from Kukdo Chem. and epoxy equivalent weight of DGEBA was 184 g/eqiv. Diaminodiphenylsulfone (DDS) was supplied from Aldrich Chem. and it was used without further purification. Chemical structures of epoxy resins and curing agent are shown in Figure 1.

Physical measurements

A differential scanning calorimetry (Du Pont 2910 DSC) was used for the study of dynamic and isother-

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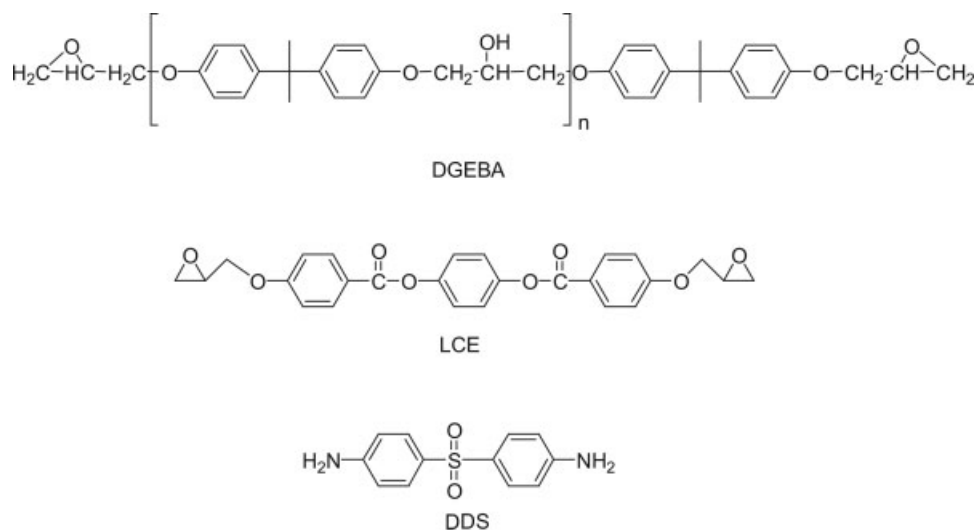


Figure 1 Chemical structures of epoxy resins and curing agent.

mal curing behavior of LCE/DGEBA blends. Isothermal curing temperature was changed from 180 to 240°C and curing time was 2 h. Heating rate of dynamic experiment was 5, 10, 15, and 20°C/min. Morphology of LCE/DGEBA blends and cured thermosets was observed with Leitz optical microscope equipped with a Mettler FP82 hot stage and FT80 central processor. Fourier transform infrared analyzer (FTIR) was used to calculate the degree of cure of epoxy blends. IR spectra were obtained in absorption mode at a resolution of 4 cm⁻¹ and eight coaddition. The degree of cure of was calculated by dividing the peak area of epoxy ring deformation at 915 cm⁻¹ with that of aromatic ring stretching at 1640 cm⁻¹. A dynamic mechanical thermal analyzer (Rheometris MK III) was used to measure glass transition temperature (T_g) and modulus of cured thermosets. Data were collected in bending mode at a frequency of 1 Hz and heating rate was 5°C/min.

Curing of epoxy resins

LCE/DGEBA blends were cured using DDS as a curing agent. DDS was used to produce high heat resistant networks and to slow down the curing reaction of LCE/DGEBA blends. The mole ratio of DDS to epoxy resins was fixed at 0.45. LCE content was 0, 10, 25, 50, 75, 90, and 100 mol % and each blend was abbreviated as LC 0, LC 10, LC 25, LC 50, LC 75, LC 90, and LC 100 according to LCE mol %. Curing mixtures were prepared by dissolving LCE, DGEBA, and DDS in chloroform/acetone mixed solvent and removing the solvent under reduced pressure at room temperature. LC 0 was cured at 180°C for 6 h and then postcured at 200°C for 4 h. LC 10, LC 25, and LC 50 were cured at 200°C for 6 h and postcured at 220°C for 4 h. Curing of

LC 75, LC 90, and LC 100 was performed at 200°C for 6 h and 240°C for 4 h.

RESULTS AND DISCUSSION

Figure 2 represents dynamic DSC thermograms of LCE/DGEBA blends at a heating rate of 20°C/min. All blends showed exothermic peaks corresponding to curing reaction of epoxy and DDS. Endothermic peak around 170°C is due to melting transition of LCE. As DGEBA content increased, the endothermic peak was shifted to lower temperature by solvation effect of DGEBA and it was not observed in blends with low LCE content (≤ 25 mol %). After the melting

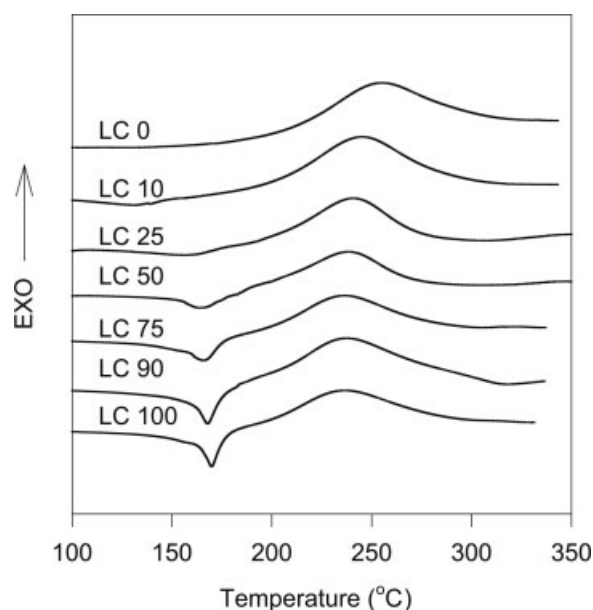


Figure 2 Dynamic DSC thermograms of liquid crystalline epoxy/DGEBA blends.

TABLE I
Heat of Reaction and Activation Energy for Dynamic Curing of LCE/DGEBA Blends

	Heat of reaction (KJ/epoxy)	Activation energy (KJ/mol)
LC 0	63.1	61.2
LC 10	63.3	55.3
LC 25	63.3	52.1
LC 50	62.1	46.1
LC 75	61.7	41.7
LC 90	62.2	40.0
LC 100	61.8	39.4

of LCE resins, an exothermic peak appeared and initial slope of curing was steep for the blends with high LCE content (≥ 50 mol %). This indicates that the curing reaction of LCE/DGEBA blends with high LCE content is fast in the initial stage of curing reaction. DGEBA rich blends showed symmetrical exothermic peaks, but LC 90 and LC 100 showed unsymmetrical exothermic curves because of additional postcuring reaction above 280°C. The exothermic peak above 280°C was not observed in LCE/DGEBA blends with LCE content below 75 mol %.

Results of dynamic experiment are summarized in Table I. Exothermic peak temperature was decreased with increasing LCE content and it was almost constant for LCE rich blends. The constant peak temperature of LCE rich blends is due to the fact that curing reaction of LCE with DDS is very fast and liquid crystalline character of LCE. Therefore, peak temperature of curing was lowered even for the blend with 10 mol % of LCE. Total heat of reaction of LCE/DGEBA blends calculated from dynamic experiments was almost the same irrespective of blend composition, indicating that the degree of cure achieved after dynamic curing is nearly constant for all blends even though curing behavior is different depending on blend composition. This also means that high curing temperature is required to reach high degree of curing for blends with high LCE content. Activation energy of curing was calculated from peak temperature of exothermic curves at different heating rate according to Ozawa method.⁵² The activation energy of curing was decreased by the addition of LCE and it was 55.3 KJ/mol for LC 10 when compared with 61.2 KJ/mol for pure DGEBA observed in LC 10. In a previous work,⁴⁴ we reported that the activation energy of curing was very low for LCE resins composed of a rigid rod ester mesogenic unit because of liquid crystalline character of LCE. Therefore, the curing of DGEBA was facilitated by the addition of LCE.

Figure 3 represents isothermal DSC thermograms of LCE/DGEBA blends at 180°C. LCE formed a nematic liquid crystalline phase at this temperature but liquid

crystalline phase disappeared during curing and changed into an isotropic phase. Initial curing of LCE rich blends preceded in nematic phase for less than 1 min, but the nematic phase was changed into isotropic phase during curing. Curing rate of LCE/DGEBA blend increased according to LCE content in DGEBA rich blends and it was kept constant in LCE rich blends. This result is due to the fast curing reaction of LCE and the similar curing rate in LCE rich blends is attributed to the fact that LCE curing reaction dominates initial curing rate of LCE/DGEBA blends in LCE rich blends. Therefore, initial curing rate was almost the same irrespective of composition in LCE rich blends. However, the initial curing rate of LCE/DGEBA blends was not affected greatly by blend composition in the temperature range ($>220^\circ\text{C}$) at which LCE formed a isotropic phase irrespective of LCE content (which is not presented in this figure), even though it was a little faster for LCE rich blends. This proves that the curing of LCE is fast in nematic liquid crystalline phase. In addition, the curing rate of LCE/DGEBA blend at 220 and 240°C showed little difference for LCE rich blends. This also supports the accelerating effect of LCE in liquid crystalline phase for the curing reaction of LCE/DGEBA blends.

Isothermal peak time of LCE/DGEBA blends at various isothermal curing temperatures is presented in Figure 4. Isothermal peak time decreased with increasing curing temperature, but isothermal peak time of LCE/DGEBA blend was little affected by temperature in LCE rich blends. We reported in the previous work⁴⁴ that curing temperature had little effect on curing rate LCE resins and the same trend was found in LCE rich blends. This behavior is due to the fact that

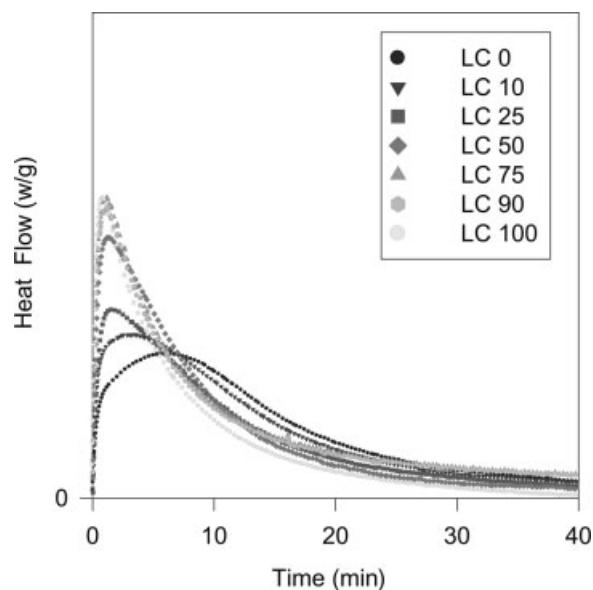


Figure 3 Isothermal DSC thermograms of liquid crystalline epoxy/DGEBA blends at 180°C.

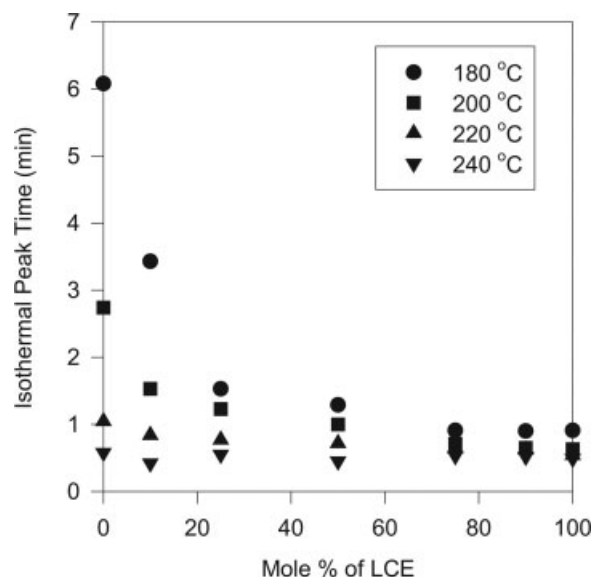


Figure 4 Isothermal peak time of liquid crystalline epoxy/DGEBA blends at various curing temperatures.

LCE is a continuous phase and curing behavior is dominated by LCE phase in the initial stage of curing. On the contrary, isothermal peak time decreased considerably in DGEBA rich blends according to LCE content because initial curing behavior was dependent on the amount of LCE. The effect of LCE content on initial curing reaction can be clearly seen in this figure. In the temperature range at which LCE has liquid crystalline phase (180–220°C), isothermal peak time decreased considerably by the addition of LCE in DGEBA rich blends, indicating that LCE acts as an accelerator in the curing of LCE/DGEBA blends.

Figure 5 shows isothermal heat of reaction of LCE/DGEBA blends. Isothermal heat of reaction of LCE/DGEBA blends was decreased by the addition of LCE and the heat of reaction of LCE was only 80% of that of DGEBA. The low heat of reaction of LCE is due to the rigid rod character of LCE molecule as it consisted of rigid aromatic ester mesogenic units. The diffusion of ester mesogenic unit is limited by restricted chain motion and strong hydrogen bonding with hydroxyl and amine group during network formation. In DGEBA rich blends, LCE had little effect on the degree of curing since flexible DGEBA formed a continuous phase. However, in LCE rich blends, DGEBA plays a role of a flexible linkage between rigid LCE units and helps the diffusion of chain molecules produced by curing reaction. Therefore, the heat of reaction of LCE/DGEBA blends was increased by the addition of small amount of DGEBA.

DMTA thermograms of LCE/DGEBA blends are shown in Figure 6. Storage modulus curves of LCE/DGEBA blends were plotted against temperature and LCE rich blends showed higher modulus than DGEBA rich blends. As LCE has very stiff and rigid

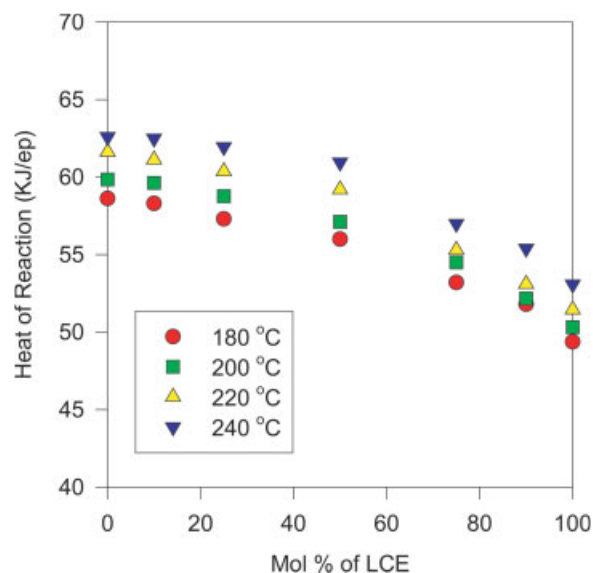


Figure 5 Isothermal heat of reaction of liquid crystalline epoxy/DGEBA blends at various curing temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mesogenic units resistant to the mechanical deformation, LCE rich blends showed high storage modulus. The rather high storage modulus of LC 90 and LC 75 compared to LC 100 is due to high degree of cure of LCE/DGEBA blends. Degree of cure of LC 75, LC 90, and LC 100 calculated from epoxide ring deformation peak at 915 cm^{-1} of FTIR was 97, 96, and 92%.

T_g measured from peak maximum of $\tan \delta$ curves of DMTA experiments is shown in Figure 7. T_g of LCE/DGEBA blends was increased with increasing LCE

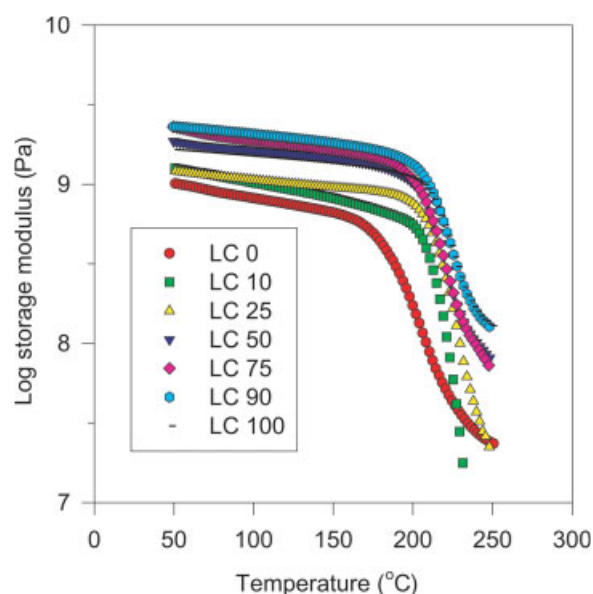


Figure 6 DMTA thermograms of cured liquid crystalline epoxy/DGEBA blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

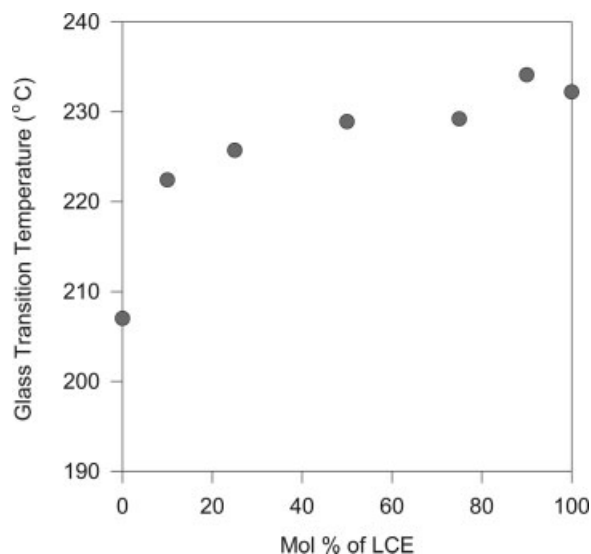


Figure 7 Glass transition temperature of liquid crystalline epoxy/DGEBA blends.

content, which is in agreement with previous results reported by D'Souza et al.^{42,43} In their results, T_g of common epoxy networks was increased as the concentration of LCE increased. This result proves that LCE is very effective in increasing the T_g of DGEBA. LCE unit acts as a reinforcing unit and it raises the T_g of LCE/DGEBA blends. A mesogenic unit in LCE has a high aspect ratio and prohibits chain motion of cured thermosets. High T_g of LC 90 when compared with LC 100 is attributed to high degree of cure of LC 90.

CONCLUSIONS

Curing behavior and thermomechanical properties of LCE/DGEBA blends were investigated according to LCE content in blends. LCE accelerated the curing of LCE/DGEBA blends and DGEBA acted as a flexible unit and enhanced the degree of cure of LCE/DGEBA blend. Curing behavior of LCE rich blends was very similar to that of LCE and even small amount of LCE was very effective in increasing the curing rate of LCE/DGEBA blends. The curing rate of LCE/DGEBA blends increased with increasing LCE content in nematic phase but it was almost constant in isotropic phase. LCE had a long rigid rod mesogenic unit and this was very effective in improving thermomechanical properties of DGEBA by acting as a reinforcement. T_g of LCE/DGEBA blends was increased by LCE as LCE prohibited chain motion of cured thermosets.

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