

Relationship Between Anisotropic Orientation and Curing of Liquid Crystalline Epoxy Resin

Jun Yeob Lee

Department of Polymer Science and Engineering, Dankook University, Hannam-dong, Yongsan-gu, Seoul 140-714, Korea

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ABSTRACT: The effect of macroscopic orientation of liquid crystalline epoxy (LCE) resin, 4,4'-di(2,3-epoxypropyloxy)phenyl benzoate, on the curing and liquid crystalline phase of LCE/diaminodiphenylester (DDE) mixture was investigated. Birefringence and curing rate of uniaxially aligned LCE/DDE on rubbed PI surface was compared with those of unaligned LCE/DDE. Anisotropic orientation accel-

erated the curing of LCE and facilitated the formation of liquid crystalline phase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1712–1716, 2006

Key words: anisotropic orientation; liquid crystalline epoxy resin; curing

INTRODUCTION

Epoxy resins have been applied in many industrial fields, such as electronic packaging material and advanced composite, because of their good mechanical and thermal properties. In recent years, new epoxy resins into which liquid crystalline properties were incorporated were developed.^{1–5} Their thermal and mechanical properties could be enhanced owing to rigid rod aromatic mesogenic unit, and anisotropic properties could be induced by aligning the molecules uniaxially.

Uniaxial orientation of liquid crystalline material can be achieved by many different routes. Magnetic field,^{1–3,6} electric field,⁷ mechanical stress,⁸ and rubbed substrate⁹ are the means to orient liquid crystalline materials. Liquid crystalline polymers are aligned mainly by mechanical stress⁸ and low molecular weight liquid crystals are ordered by magnetic field and rubbed substrate frequently.^{1–3,9} Uniaxially oriented liquid crystalline polymer shows high modulus and low coefficient of thermal expansion along aligned direction, but transverse properties are poor. These disadvantages of liquid crystalline polymer can be overcome by the introduction of covalent bond between oriented chains through crosslinking of liquid crystalline material. The crosslinks fix the orientation of ordered network and impart great dimensional stability.

There are several works reported for the orientation of liquid crystalline epoxy (LCE) resin cured with aromatic amine. Jahromi et al. prepared macroscopically oriented LCE network through curing reaction between LCE and aromatic amine in magnetic field.^{1–2} It displayed anisotropic mechanical properties and birefringence in fully cured state. Ober et al. investigated the orientation of stilbene LCE in magnetic field and obtained LCE network with order parameter of 0.6.³ In their experiment, the macroscopic order was maintained up to decomposition temperature though the order parameter of LCE network was decreased above glass transition temperature.

In this work, we investigated the effect of orientation on curing and liquid crystalline properties of cured LCE network. The amount of curing agent and curing temperature were adopted as curing parameters and their relationship with alignment and liquid crystalline phase of LCE network was established. *In situ* monitoring of birefringence was performed at various curing conditions and order parameter of cured LCE network was measured.

EXPERIMENTAL

Materials

Liquid crystalline epoxy resin (LCE) used in this experiment was 4,4'-di(2,3-epoxypropyloxy)phenyl benzoate. It was synthesized according to the method reported in previous paper.¹⁰ Melting temperature of LCE was 119°C and nematic liquid crystalline phase appeared on cooling from 91 to 79°C. Diaminodiphenylester (DDE) synthesized by reduction of 4-nitrophenyl-4'-nitrobenzoate was used as curing agent.

Correspondence to: J. Y. Lee (leej17@dankook.ac.kr).

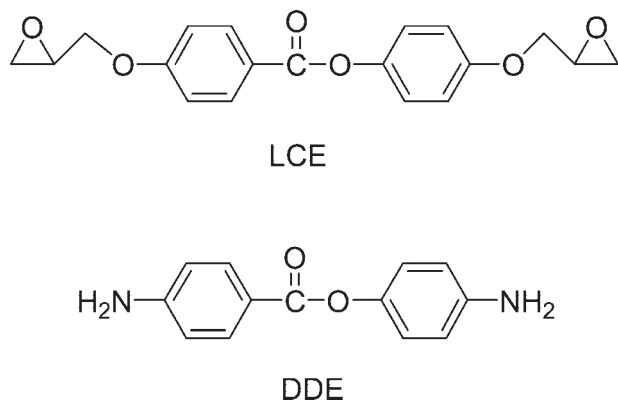


Figure 1 Chemical structures of LCE and DDE.

Amine to epoxy ratio was varied as 0.6, 0.7, 0.8, and 0.9. The samples are abbreviated as LCE6, LCE7, LCE8, and LCE9, respectively. LCE and DDE were mixed in dichloromethane/acetone cosolvent and the solvent was evaporated at room temperature in vacuum oven. The mixture was stored in refrigerator before use. Figure 1 shows the chemical structures of LCE and DDE.

Physical measurements

A differential scanning calorimeter (DSC, Du Pont 2910) was used to investigate the curing behavior of LCE/DDE mixture. Isothermal curing of the mixture was performed at 140, 150, 160, 170, 180, 190, and 200°C for 1 h. Two kinds of DSC samples were prepared to study the effect of orientation on the curing of LCE/DDE. LCE/DDE mixture was inserted between PI-coated glass plates and uniaxially rubbed PI-coated glass plates. It was cut into small pieces and was put in DSC pan. FTIR (Bomem MB 100) measurements were carried out in transmission mode at a resolution of 4 cm^{-1} with a scan number of 8. Birefringence was measured with FTIR and liquid crystalline phase of the mixture were observed with Nikon polarizing optical microscope provided with a Mettler FP82 hot stage and FP80 central processor. Optical retardation of oriented LCE/DDE on uniaxially rubbed PI-coated glass plates was measured using rotary compensator equipped with calcite compensator plate. The change of birefringence was monitored according to curing time at the isothermal temperature where macroscopic orientation is present. The thickness of sample was maintained with $2\ \mu\text{m}$.

RESULTS AND DISCUSSION

Curing of LCE/DDE on unidirectionally rubbed and unrubbed polyimide (PI) surface was carried out to investigate the influence of alignment on the curing behavior of LCE/DDE. The LCE and DDE did not

show any liquid crystalline phase within the curing temperature range investigated, while the LCE/DDE showed liquid crystalline phase (Fig. 2) during and after curing. The isotropic phase of the LCE/DDE mixture was transformed into liquid crystalline phase and the liquid crystalline phase of the LCE/DDE was maintained during curing.

The effect of alignment on curing was analyzed with isothermal DSC experiment. Prior to isothermal curing experiment, birefringence of LCE/DDE on rubbed PI surface was analyzed at various curing temperatures to confirm the alignment of LCE/DDE. Birefringence of LCE/DDE at 180°C is represented in Figure 3 according to curing time. It was recorded after development of nematic LC phase. The increase of birefringence was significant in LCE 6 and it was reciprocally proportional to DDE content. There are several factors influencing the birefringence of LCE networks. The rate of curing, aspect ratio of molecule, and temperature are the main factors determining the alignment of LCE. The rate of curing is important as sufficient time is required for orientation of LCE molecule. Aspect ratio related with anisotropic polarizability contributes to the stability of LC phase. The higher the anisotropy of LCE is, the higher the birefringence of cured LCE network is. Temperature affects the orientation of LCE network as the birefringence of LC material is reduced at high temperature. Decrease of mesophase stability and degree of order of LC material at high temperature mainly contribute to this tendency. In case of LCE/DDE, the rate of curing may play a major role in determining the birefringence considering the large increase of birefringence in LCE 6. Aspect ratio of prepolymer should be larger in LCE 9; how-

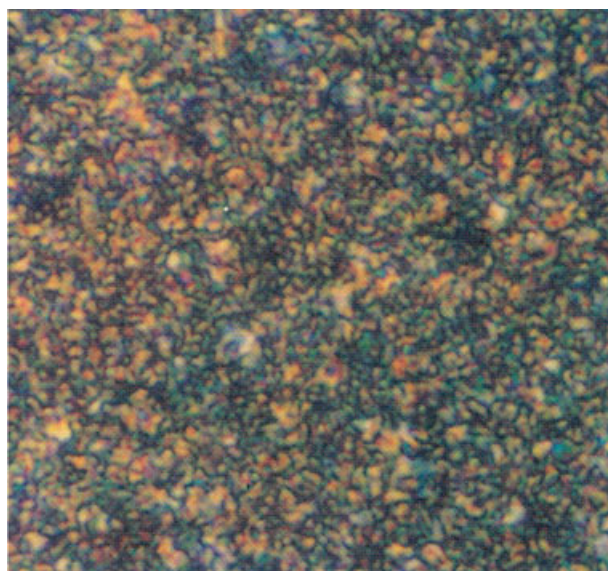


Figure 2 Polarized optical micrographs of LCE/DDE networks. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

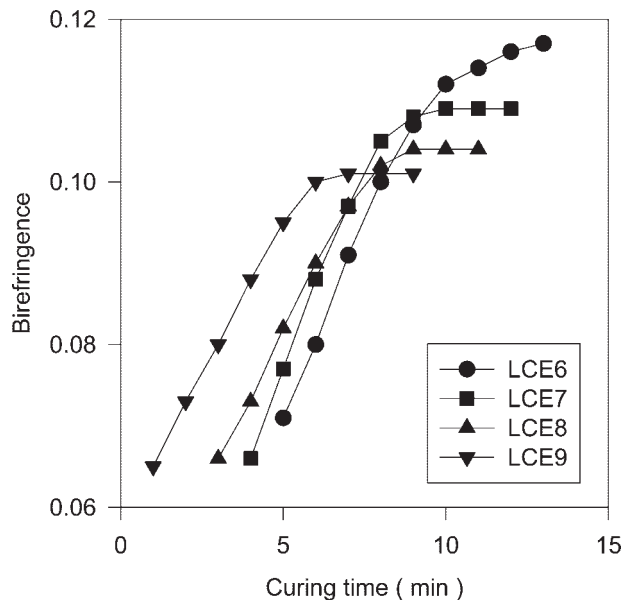


Figure 3 Birefringence of LCE/DDE at 180°C.

ever, the birefringence is small in LCE 9. Therefore, curing rate rather than aspect ratio of mesogen mainly determines the birefringence of LCE/DDE network.

Birefringence of LCE/DDE network cured at various temperatures for 60 min was measured (Fig. 4). There was little change of birefringence up to 160°C and sharp decrease above 160°C. This tendency implies that there is no barrier for rearrangement of LCE prepolymer along rubbed direction up to 160°C. Above 160°C fast curing and branch formation hinder the formation of ordered networks. The branch forma-

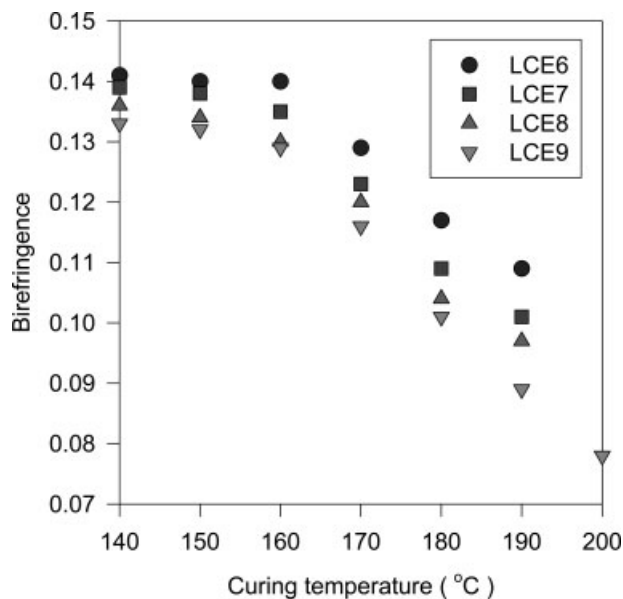


Figure 4 Birefringence of LCE/DDE networks cured at various temperatures.

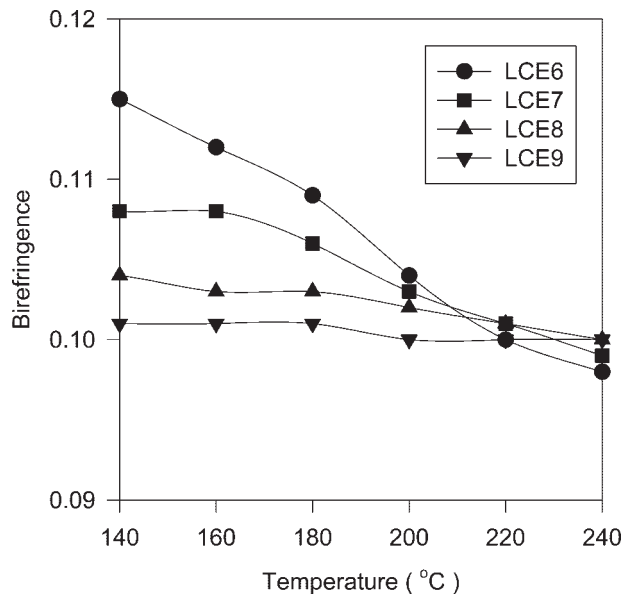


Figure 5 Birefringence of LCE/DDE networks cured at 180°C.

tion destabilizes the LC phase and disturbs the ordering of LCE prepolymer, leading to low birefringence in LCE 9. The birefringence of aligned LCE/DDE network could not be measured above 190°C due to the disappearance of LC phase.

Figure 5 is the birefringence of LCE/DDE network cured at 180°C for 60 min. It decreased gradually with increasing temperature and then reached a value of 0.098 at 240°C in case of LCE 7. The disruption of the ordering by thermal motion leads to the decrease of birefringence according to temperature. The extent of reduction of birefringence was prominent in LCE 6 as interchain interaction was weak and degree of cure was low in LCE/DDE network with low DDE content.

Order parameter of LCE/DDE network cured on uniaxially rubbed PI surface was measured. The order parameter of LCE/DDE is given in Figure 6. The order parameter of LCE was obtained from IR dichroism experiment. In IR dichroism, the internal vibration along the molecular long axis can be used for measurement of order parameter. It was calculated by the following equation

$$\langle P_2 \rangle = (3\cos^2\theta - 1)/2 = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$$

where A_{\parallel} is the absorbance parallel to orientation direction and A_{\perp} is the absorbance perpendicular to orientation direction.

There is a similarity between the change of birefringence and that of order parameter. LCE 9 cured at 140°C showed maximum order parameter of 0.42. As explained in birefringence data, this results from slow curing of LCE 9 at low curing temperature and high aspect ratio of LCE 9 prepolymer. However, the order

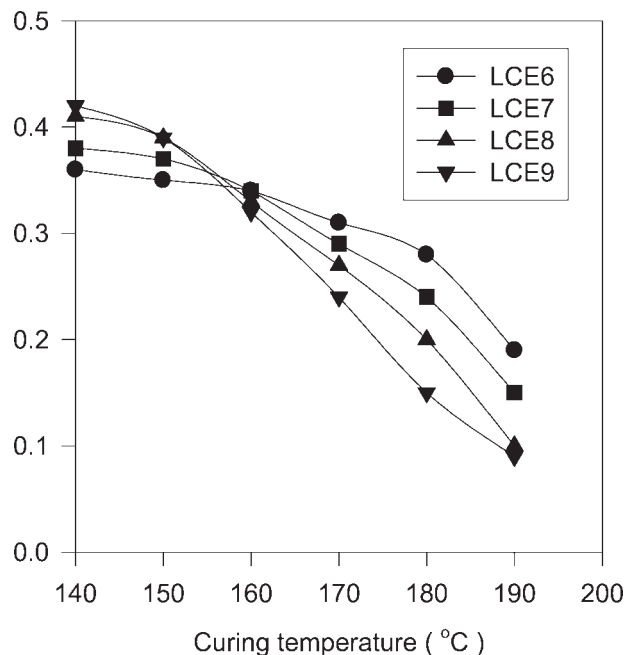


Figure 6 Order parameter of LCE/DDE networks cured at various temperatures.

parameter of LCE 9 was diminished catastrophically according to curing temperature as the curing rate of LCE 9 was sensitive to curing temperature. On the other hand, the decrease of birefringence in other LCE/DDE mixtures was slow because curing rate was not affected greatly by curing temperature. Extensive branch formation and uncontrollable curing reaction leading to reduction of aspect ratio are the main reasons for the decrease of order parameter at high curing temperature

Representative isothermal DSC thermograms of LCE 9 at 160°C are shown in Figure 7. Surface rubbing increased maximum curing rate of LCE 9, which implied the acceleration of curing by unidirectional surface rubbing effect. The reason for this is that reactive functional group of epoxy is closer to neighboring DDE in ordered state than in disordered state. Close packing of LCE and DDE reduces the distance between nearby chains and enhances the probability of curing reaction of HQEP2 with DDE.

Isothermal curing of other LCE/DDE mixtures was also carried out at the same temperature. Figure 8 shows the ratio of maximum curing rate of LCE/DDE on rubbed PI surface to that on unrubbed PI surface calculated from isothermal DSC thermograms. This experiment gives the information about the effect of orientation on the curing behavior of LCE/DDE. There was no significant difference between maximum curing rate on rubbed PI surface and that on unrubbed PI surface though surface rubbing increased maximum curing rate of LCE/DDE a little. Curing of LCE/DDE with amine to epoxy ratio below 0.9 pro-

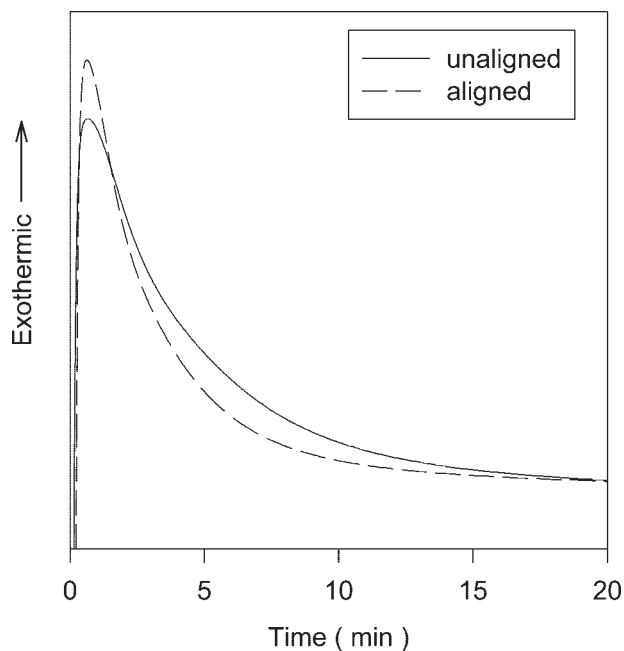


Figure 7 Isothermal DSC thermograms of LCE 9 at 160°C

ceeds in isotropic phase initially and then isotropic phase is transformed into nematic phase during curing. The conversion of LCE/DDE mixture at the onset time of LC phase is higher than the conversion at exothermic peak time in this thermogram, which means that the curing at exothermic peak time proceeds in isotropic phase. As orientation of LCE molecule was not induced in isotropic phase extensively, surface rubbing did not affect the maximum curing

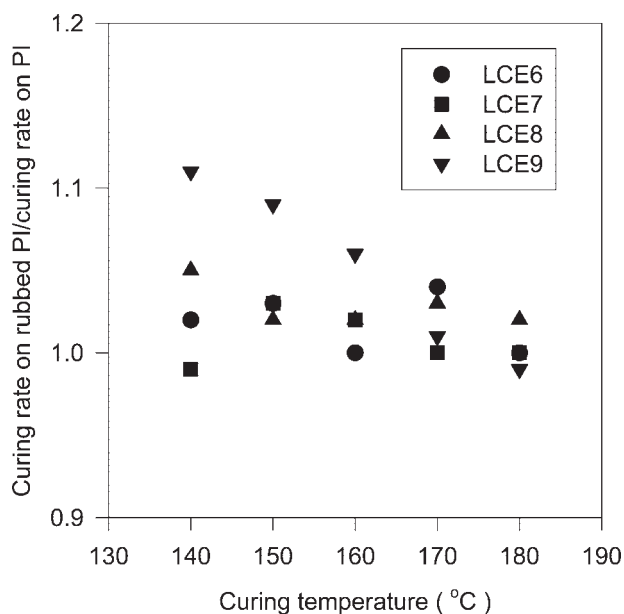


Figure 8 Relative ratio of curing rate on rubbed PI surface to curing rate on PI surface for LCE/DDE.

rate of LCE/DDE. This tendency was observed at all curing temperatures. Only in LCE 9, which displayed LC phase during curing, acceleration of curing was clearly observed.

CONCLUSIONS

The anisotropic orientation of LCE resins on rubbed PI surface was correlated with the order parameter and curing behavior. The anisotropic alignment of LCE on PI surface accelerated the curing of LCE and anisotropically aligned LCE network was induced by the curing on rubbed PI surface. High order parameter was obtained for the LCE network with high DDE content and cured at low temperature.

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