

The effect of substituent on the anisotropic orientation of liquid crystalline epoxy compounds

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Summary

The relationship between the chemical structure of liquid crystalline epoxy (LCE) compounds and anisotropic orientation of the crosslinked network was investigated. Three LCE compounds based on aromatic ester mesogenic group were cured with diaminodiphenylester (DDE) under strong magnetic field. Methyl substituent interrupted the orientation of LCE network, while chlorine had little influence on the anisotropic alignment of LCE network. Low coefficient of thermal expansion was observed in the direction of alignment in highly oriented LCE network.

Introduction

In recent years, anisotropic liquid crystalline networks have attracted much attention due to its peculiar properties such as anisotropic mechanical properties, low coefficient of thermal expansion (CTE). In particular, anisotropic orientation of liquid crystalline network is of great importance as it significantly improves the mechanical and thermal properties of cured networks.

Several results have been reported on the anisotropic alignment of liquid crystalline epoxy (LCE) networks[1-5]. Jahromi et al. crosslinked LCE monomer based on aromatic ester group under strong magnetic field and obtained macroscopically oriented networks[1]. The aligned network showed anisotropic CTE values and the CTE value of LCE network parallel to aligned direction was much lower than the CTE value perpendicular to oriented direction. In addition, high rubbery modulus along aligned direction was also observed in ordered network due to the rigidity of LCE main chain and anisotropic ordering in network. Ober et al. described macroscopic orientation of α -methylstilbene LCE under the influence of magnetic field[2]. Order parameter of 0.5 was obtained and the orientation of the crosslinked LCE network was stable at high temperature. Rozenberg et al. studied self-polymerization of LCE under magnetic field[3]. High rubbery modulus and low CTE values were observed in crosslinked LCE network. The macroscopic ordering of the cured network was stable up to decomposition temperature. Jahromi et al.[4] and Broer et al.[5] prepared anisotropically ordered LCE networks via photoinitiated polymerization of ester type

LCE on rubbed polyimide (PI) surface. Anisotropic ordering accelerated the polymerization of LCE in mesophase and birefringence was observed after photopolymerization. However, there have been no systematic investigations about the effect of chemical structure on the anisotropic orientation of LCE materials.

In this paper, anisotropic ordering of substituted LCE materials crosslinked under strong magnetic field was described to investigate the effect of substituent on the alignment of LCE compounds. Three LCE compounds with hydrogen, methyl and chlorine as substituents in the central phenyl ring were prepared and the relationship between chemical structure of LCE materials and anisotropic alignment of LCE was studied. In addition, thermomechanical properties of LCE networks were correlated with chemical structures of LCE compounds.

Experimental

Three LCE compounds, p-phenylene-di[4-(2, 3-epoxypropyloxy)benzoate](HQEP), p-(chlorophenyl)-di[4-(2, 3-epoxypropyloxy)benzoate](HQCIEP) and p-(methylphenyl)-di[4-(2, 3-epoxypropyloxy)benzoate](HQMeEP), used in this experiment were synthesized according to the procedure reported in previous paper[6]. Nematic transition (T_{KN}) of HQEP was observed at 181 °C and isotropic transition (T_{NI}) at 229 °C. HQCIEP and HQMeEP showed T_{KN} at 158 °C and 131 °C, and T_{NI} at 222 °C and 216 °C respectively. Diaminodiphenylester (DDE) was used as a crosslinking agent and it was prepared from reduction of 4-nitrophenyl-4'-nitrobenzoate. Chemical structures of LCE materials and DDE are shown in Fig. 1. Amine to epoxy mole ratio was fixed at 0.7. LCE compounds and DDE were mixed in dichloromethane/acetone(50/50 vol%) mixed solvent and the solvent was evaporated at room temperature in vacuum oven. The mixture was stored at -10 °C in refrigerator before use. Curing of LCE/DDE mixtures was carried out in MPMS superconducting magnet (Quantum Design, U.S.A). LCE mixtures were inserted into magnet system at curing temperature and magnetic field strength was 7 T. Curing and postcuring were conducted under strong magnetic field. Fully cured LCE/DDE networks were prepared after curing at 180 °C for 2 hr and postcuring at 230 °C for 2 hr.

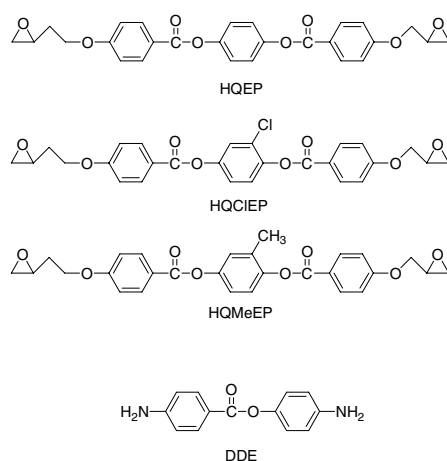


Figure 1. Chemical structures of liquid crystalline epoxy compounds and curing agent

Order parameter of LCE networks aligned under magnetic field was measured by using infrared dichroism. Dichroic ratio was determined using FT-IR fitted with a wire grid polarizer. Dynamic mechanical thermal analyzer (DMA, Rheometrics. Co, MK III) was used to observe thermomechanical properties of crosslinked LCE networks. Data were recorded in compression mode at a frequency 1 Hz and heating rate of 5 °C/min.

Results and discussion

HQEP/DDE formed a nematic liquid crystalline phase when it was cured between 172 °C and 275 °C. Nematic mesophase was developed immediately after melting and the crosslinking of LCE and DDE proceeded in mesophase during the whole curing process. The curing of HQCIEP/DDE and HQMeEP/DDE was also carried out in mesophase because the mixtures showed liquid crystalline phase at any temperature above T_{KN} of the LCE compounds. Therefore, it can be expected that the anisotropic orientation of LCE/DDE mixtures would be effectively induced via crosslinking under strong magnetic field (7 T). There are many experimental parameters affecting the anisotropic ordering of LCE compounds[1-5]. Curing temperature, magnetic field strength, curing agent contents and chemical structures of LCE compounds are the main factors determining the degree of order of liquid crystalline network. Among these parameters, curing temperature and chemical structures of LCE were chosen as variables influencing the orientation of LCE networks in this work. Methyl group was introduced as a bulky substituent and chlorine was selected as a polar substituent with little steric hindrance.

To confirm the formation of liquid crystalline network after crosslinking, the liquid crystalline phase of the cured network was investigated. Fig.2 shows optical micrographs of LCE compounds cured with DDE at 180 °C. Nematic textures were observed for all LCE networks after curing and the liquid crystalline phase of the cured network was stable up to decomposition temperature.

To compare the orientation of LCE networks with different substituents, order parameter of cured networks was measured with IR dichroism. Fig. 3 shows the order parameter of three LCE networks cured at different temperatures for 2 hr. Oriented HQEP networks could not be produced below 180 °C because of incomplete melting of HQEP and DDE, while aligned HQCIEP and HQMeEP networks were obtained above 150 °C. Ordering of cured LCE networks was reduced as the curing temperature was raised in all LCE networks. In particular, the decrease of degree of order was clearly observed above 180 °C and it can be explained by the curing behavior of LCE compounds. Curing of LCE/DDE mixtures is accelerated above 180 °C and the accelerated curing at high temperature hinders the orientation of LCE compound as LCE molecules cannot have enough time for orientation because of the increase of viscosity by crosslinking reaction. As anisotropic ordering of LCE network is difficult after gelation due to the immobilization of the network structure and difficulty in diffusional motion, the gel time is of crucial importance for the alignment of LCE network. Gel time of LCE/DDE was within 10 min in all LCE/DDE mixtures above 180 °C. Extensive branch formation in early stage of curing is another important reason for the low order parameter in LCE network cured at high temperature. It is well known that branched structure is readily formed at high curing temperature in epoxy curing reaction[7]. Branched structures induced during curing reaction of LCE

destabilize the liquid crystalline phase of LCE due to severe decrease of anisotropy in LCE prepolymer and disturb the ordering of LCE/DDE system. Comparing the degree of orientation of three LCE networks, HQEP and HQCIEP network displayed similar order parameters, while HQMeEP network showed relatively low order parameter. The reason for this can be found in the large van der Waals radius of methyl substituent. Bulky methyl group prevents the ordering of LCE due to steric hindrance of methyl group, resulting in lower degree of alignment in the densely crosslinked network. Unlike methyl substituent, chlorine substituent had no appreciable influence on the alignment of the cured network due to small van der Waals radius. This result implies that polarity of the substituent has little effect on the anisotropic orientation of LCE network and steric hindrance is the major factor determining the ordering of LCE network.

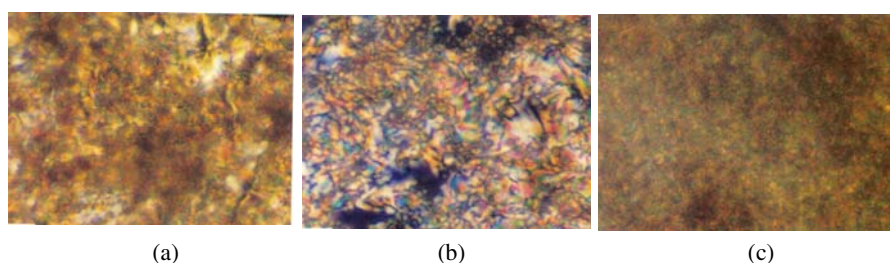


Figure 2. Optical micrographs of cured LCE networks
(a) HQEP/DDE (b) HQCIEP/DDE (c) HQMeEP/DDE

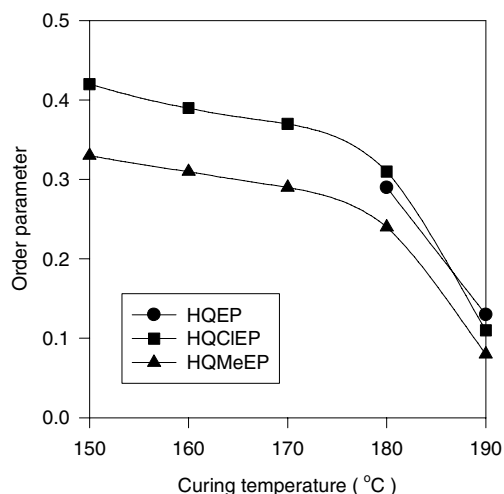


Figure 3. Order parameter of crosslinked liquid crystalline epoxy compounds

Dynamic mechanical measurements of the aligned LCE networks were carried out to correlate the order parameter of LCE compounds with the modulus of LCE networks. Elastic modulus of aligned HQEP and HQMeEP networks were calculated from DMA data and plotted against order parameter of cured network (Fig. 4). Linear relationship between modulus and order parameter was found and HQMeEP showed higher slope

than HQEP. High slope implies that the modulus of LCE networks are sensitive to the change of order parameter and elastic modulus of HQMeEP are greatly dependent on the order parameter. This result can be explained by the chemical structures of LCE molecules. HQMeEP has bulky methyl substituents in the central phenyl ring and deformation of oriented network of HQMeEP/DDE is hindered by macroscopic orientation due to strong interlocking of methyl group along molecular long axis. The interlocking effect of substituents was weakly observed in HQClEP/DDE and HQClEP network showed intermediate value between the modulus of HQEP3E and HQMeEPE network.

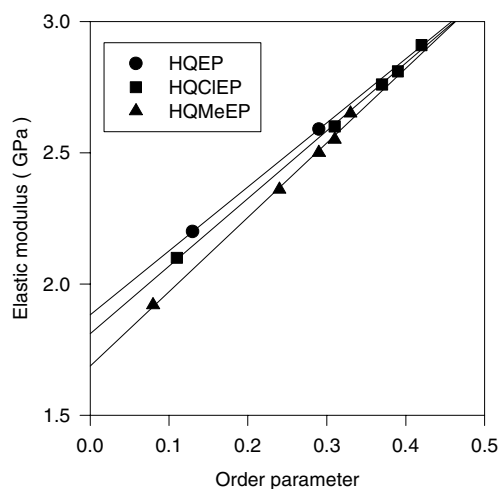


Figure 4. Plot of elastic modulus against order parameter of liquid crystalline epoxy compounds

CTE values of three networks parallel to oriented direction are presented in table 1. Thermal expansion of densely crosslinked network depends on degree of order, free volume and intermolecular forces between neighboring chains[2, 8-10]. The increase of CTE values in networks cured at high temperature is due to low degree of order because less chains are aligned along molecular long axis. High CTE of HQMeEP network compared with HQEP network cured at the same curing condition is caused by large free volume as well as low degree of order. Low CTE of HQClEP network comparable to that of HQEP can be understood in terms of strong intermolecular interaction offsetting expanded free volume.

Conclusions

In conclusion, the effect of substituents on the anisotropic orientation of LCE compounds was investigated. Hydrogen, methyl group and chlorine were introduced as substituents for the central ring of LCE compounds and all LCE compounds showed nematic liquid crystalline phase after curing. Methyl substituent had negative effect on the alignment of LCE, while chlorine had little influence on the alignment of LCE compounds. The anisotropically aligned LCE network showed low thermal expansion in the direction of alignment and the lowest CTE value of $12 \times 10^{-6} / ^\circ\text{C}$ were obtained for the HQClEP networks cured at low temperature.

Table 1. Coefficient of thermal expansion of aligned HQEP, HQCIEP and HQMeEP networks cured at different curing temperatures

	Curing temperature (°C)	CTE ($\mu\text{m}/\text{m } ^\circ\text{C}$)	
		Glassy region	Rubbery region
HQEP	180	14	18
	190	21	27
	160	12	15
HQCIEP	180	17	21
	190	25	34
	160	18	26
HQMeEP	180	31	37
	190	36	51

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