Polymer Bulletin 59, 261–268 (2007)
DOI 10.1007/s00289-007-0761-1

Polymer Bulletin

Anisotropically ordered liquid crystalline epoxy network on carbon fiber surface

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Received: 27 November 2006 / Revised version: 6 March 2007 / Accepted: 16 March 2007

Summary

Anisotropic orientation of liquid crystalline epoxy(LCE) resin on carbon fiber(CF) surface was investigated and it was correlated with curing behavior and thermomechanical properties of LCE. Anisotropic orientation of a LCE resin was spontaneously induced on CF surface along a long molecular axis of CF during curing and the anisotropic orientation was maintained after curing. Curing of LCE was accelerated by alignment of LCE on CF and anisotropic orientation of LCE enhanced dynamic modulus of CF reinforced LCE composites.

Introduction

Liquid crystalline epoxy (LCE) resins have been studied by many research groups because they have many advantages such as anisotropic orientation, high heat resistance, high mechanical properties, low coefficient of thermal expansion, low dielectric constant, and good dimensional stability. Therefore, they can be used in various applications such as matrix for advanced composites, microelectronic packaging, structural adhesives, and optical materials.

In particular, anisotropic orientation of LCE molecules is an unique property of LCE. Therefore, many studies have been focused on the unidirectional alignment of LCE molecules during curing[1-5]. Several methods have been attempted to induce anisotropic alignment of LCE molecules. Magnetic field[1-3], electric field[4], and rubbed polyimide coated glass plate[5] have been widely used to get uniformly oriented LCE networks. Carbon fiber was also used to get uniaxially aligned low molecular weight liquid crystal[6,7]. However, no report has been published concerning anisotropic orientation of LCE on a carbon fiber surface even though Carfagna et al. reported the application of LCE resins as matrix materials for advanced composites[8-10]. It was reported by Mallon et al. that liquid crystal could be aligned along long molecular axis of carbon fiber through microgroove on carbon fiber surface[6,7]. Therefore, it is expected that LCE can also be oriented along carbon fiber surface and can form an anisotropically aligned network. This can be very useful in composite application because the alignment of LCE can occur spontaneously without any other additional treatment. This can make advanced thermoset composites more excellent in mechanical properties.

The aim of this work is to investigate the uniaxial alignment of an aromatic ester based LCE resin on a carbon fiber surface and preparation of uniaxially oriented carbon fiber reinforced composites with excellent mechanical properties. A polarized optical microscope and wide angle X-ray measurements were performed to characterize the alignment of the LCE on carbon fiber surface. The relationship between anisotropic orientation and dynamic mechanical properties of carbon fiber reinforced LCE composites was also discussed.

Experimental

Carbon fiber (CF) under the trade name of T-300 was purchased from Torayca co. and was used after cleaning CF in dichloromethane for 5 days and in distilled water for 2 days. The CF was dried in a vacuum oven at 100°C for 2 days. Liquid crystalline epoxy resin (LCE) was synthesized according to the method proposed by our group in previous paper[11]. Nematic transition temperature of LCE was 158°C and isotropic transition temperature was 222°C. Diaminodiphenylsulfone (DDS) and diaminodiphenylester (DDE) were used as curing agents for the curing of LCE. DDS was supplied from Aldrich Chem. Co. and DDE was synthesized by reduction of 4-nitrophenyl-4-nitrobenzoate. LCE was denoted by HQClEP and LCE/DDE and LCE/DDS mixtures were abbreviated as HQClEPE and HQClEPS, respectively. Fig. 1 shows chemical structures of LCE resin and curing agents. Unidirectional CF/LCE composites were manufactured by a resin infusion process[12]. They were cured at various curing temperatures for 2 h and postcured at 230°C for 2 h.

A differential scanning calorimeter (DSC, Du Pont 2910) was used to investigate the curing behavior of CF/LCE mixtures. A dynamic curing of CF/LCE was carried out at a heating rate of 20°C/min in nitrogen atmosphere. A liquid crystalline phase of CF/LCE was observed with a Nikon Optiphot 2-POL optical microscope equipped with a Mettler FP 82 hot stage and FP80 central processor with a magnification of 200. Samples were introduced into a heating cell at isothermal temperature. Wide angle X-ray diffraction (WAXD) patterns of the composites were obtained with MAC science M18XHF. X-rays were produced by a generator operated at 45 kV and 20 mA and nickel filtered copper Kα radiation was used. A dynamic mechanical thermal analyzer (DMA, Rheometris co. MK III) was used to measure the damping properties and dynamic modulus of cured LCE networks. Data were collected in a bending mode at a frequency of 1 Hz and a heating rate was 5°C/min. Coefficients of thermal expansion (CTE) of cured CF/LCE composites were determined with the DMA in tensile mode. Heating rate was fixed at 5°C/min and applied load was 100 mN.

Results and discussion

An usual way to align LC material homogeneously is to rub the substrate, whereby surface effects like microgrooves and re-orientation of substrate molecule are induced, which can induce an anisotropic alignment of rod-like LC materials. CF has a microgrooved structure due to micro-fibrils having a width of about ten nm and preferred orientation along a longitudinal direction. In addition, a turbostratic graphite structure and perfectly aligned graphite are known to be present on CF surface and be aligned along the axial direction of CF. These structural features of CF can make LCE molecules spontaneously oriented on CF surface. Based on this idea, the alignment of LCE resin and LCE/DDE systems around CF was investigated.

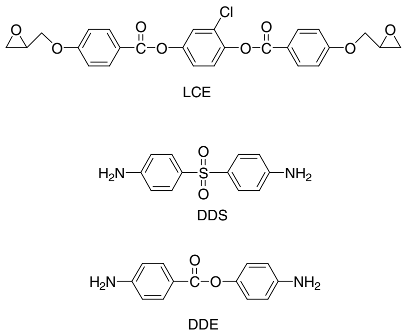
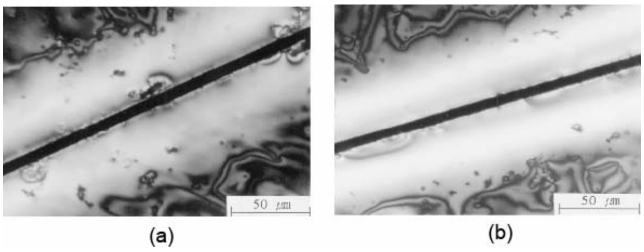


Figure 1. Chemical structures of liquid crystalline epoxy resin and curing agents.



(a) (b)

Figure 2. Polarized optical microscopic pictures of CF/HQClEP(a) and CF/HQClEPE(b).

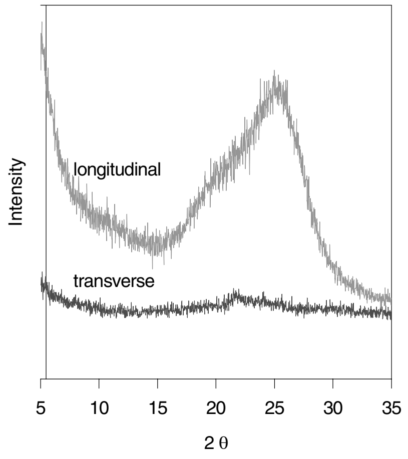


Figure 3. Wide angle X-ray diffraction patterns of CF/HQClEPE composite parallel and perpendicular to fiber direction.

The alignment of HQClEP resin and HQClEPE on CF surface was confirmed with a POM. Fig. 2(a) and Fig. 2(b) are POM pictures of CF/HQClEP and CF/HQClEPE network cured at 180°C. Similar POM pictures were obtained in both cases, indicating that the liquid crystalline phase of HQClEP monomer is maintained after crosslinking. The liquid crystalline phase of LCE was modified near CF, which implied that CF affected the liquid crystalline phase of LCE. A continuous change of homogeneous colors in the transverse direction of CF indirectly indicates the alignment of LCE along CF long axis. The orientation of LCE on CF is thought to be due to a grooved and oriented surface structure of PAN based CF as CF can induce the alignment of rigid rod LCE molecules along uniaxially oriented CF surface. Similar results were reported by Mallon et al. for the orientation of low molecular weight LC molecules on a grooved CF surface[6-7]. They proposed that the existence of the grooved structure on CF surface induced the orientation of LC. However, considering the results reported for the alignment of LC on rubbed PI surface, the main factor responsible for the orientation of HQClEP on CF may be the oriented surface structure of CF rather than the microgroove[13,14]. The microgrooved structure only determines the direction of alignment of LCE on CF surface. The POM picture of CF/HQClEPE cured at 180°C indicates that the anisotropic orientation of HQClEP is maintained after curing with DDE. The anisotropic region was kept up to a distance of 30 μm from the fiber surface. The anisotropic alignment of HQClEP was confirmed with a wide angle X-ray diffraction experiment. X-ray diffraction pattern of CF/HQClEPE composite in the direction of fiber alignment and in the vertical direction of fiber axis is given in Fig. 3. A strong shoulder peak at 18.6 ° in the direction of fiber alignment and disappearance of it in the transverse direction prove the alignment of HQClEPE network along fiber long axis.

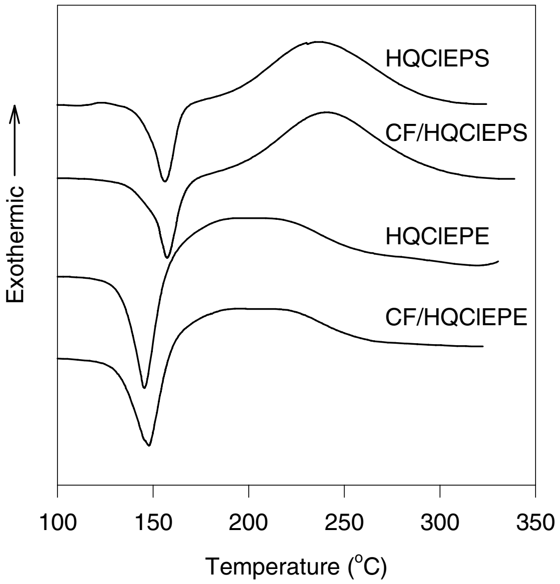


Figure 4. Dynamic DSC thermograms of HQClEPS, HQClEPE, CF/HQClEPS and CF/HQClEPE.

To investigate the effect of anisotropic ordering on the curing of LCE resin, curing behavior of HQClEP resin was studied for CF/HQClEPE and CF/HQClEPS. HQClEPE showed a liquid crystalline phase during curing, while HQClEPS exhibited an isotropic phase during curing. Fig. 4 represents dynamic DSC thermograms of CF/HQClEPS and CF/HQClEPE. DSC thermograms of curing mixtures without CF were added in this figure for comparison. Exothermic peak temperatures corresponding to the curing reaction between HQClEP and curing agent were raised in HQClEPS and slightly lowered in HQClEPE by addition of CF. These results indicate that CF accelerates the curing of LCE molecule in liquid crystalline phase, while it retards the curing of LCE in isotropic phase. Curing retardation in CF/HQClEPS can be explained by the fact that CF acts as a heat sink and diffusion barrier in the curing of epoxy resin. Heat absorption of CF and other inorganic fillers was observed in other reports[15,16]. Contrary to these results, accelerating effect of polar CF on the curing of epoxy resin was reported by several research groups[17-19]. However, a surface cleaned CF retarded the curing reaction of epoxy as it had few polar groups to catalyze the curing reaction of epoxy. Accelerating effect of CF on the curing of HQClEPE contrary to HQClEPS mixture implies that CF acts as a curing aid in CF/HQClEPE. It is speculated that CF accelerates the curing of HQClEPE not through polar interaction or specific interaction but through anisotropic orientation. A spontaneous orientation of LCE molecule along the long molecular axis of CF may facilitate the curing of LCE near CF. As described in POM and wide X-ray diffraction results, HQClEPE aligns itself on CF surface in the direction of fiber axis spontaneously. Anisotropic alignment of LCE molecule leads to a close packed network structure and shortens the distance between neighboring chains. As a result, curing of HQClEPE is accelerated in ordered state.

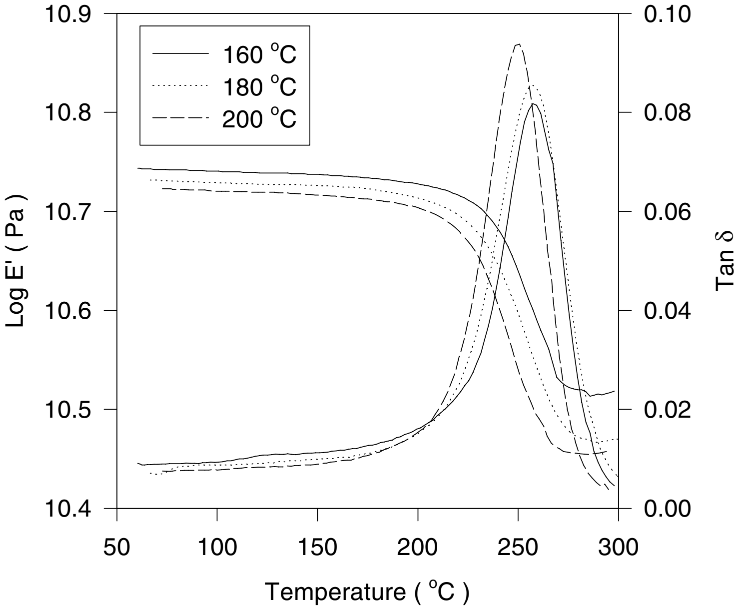


Figure 5. DMA thermograms of CF/HQClEPE composites cured at various temperatures.

Dynamic mechanical properties of CF/HQClEPE composites cured at various temperatures were investigated. DMA thermograms of CF/HQClEPE composite parallel to aligned direction are presented in Fig. 5. They were cured at 160°C, 180°C and 200°C respectively and postcured at 230°C for 2 h. An increase of rubbery modulus in networks cured at low curing temperature is clearly seen in this figure, while glassy modulus was almost constant irrespective of curing temperature. This result can be explained by anisotropic ordering of LCE networks. In other reports, storage modulus of unaligned HQClEPE network was not altered substantially by curing temperature up to 180°C[11], while an anisotropic ordering greatly enhanced the storage modulus of HQClEPE network at the same curing temperature. In other words, anisotropically aligned HQClEPE network cured at low curing temperature showed much higher rubbery modulus than HQClEPE network cured at high temperature. Similar results were also obtained in CF/HQClEPE networks. Anisotropic ordering of LCE on CF increased rubbery modulus of CF/HQClEPE composites cured at low curing temperature. Considering the fact that birefringence of CF/HQClEPE network cured at 160°C and 200°C was 0.11 and 0.04, the high rubbery modulus of CF/HQClEPE composites is due to extensive anisotropic orientation of LCE molecules along fiber axis. Tan δ curves of CF/HQClEPE composites are also shown in Fig. 5. An increase of glass transition temperature was observed in the composites cured at low temperature. The high Tg of the composite cured at low temperature is due to the fact that thermal motion of LCE networks is restrained by molecular packing of LCE molecule on CF surface. LCE molecules were regularly ordered on CF at low curing temperature, resulting in high barrier for chain motion of LCE in the network structure.

Conclusions

Spontaneous anisotropic alignment of LCE resin on CF surface was identified and correlated with a curing rate and dynamic mechanical properties. HQClEP resin was aligned along long molecular axis of CF and its orientation was effectively induced at low curing temperatures. The uniaxial orientation of HQClEP was maintained after crosslinking with DDE and it was frozen in after curing. Dynamic modulus of CF/HQClEPE composites was enhanced by anisotropic orientation of HQClEP. In particular, rubbery modulus of the composite cured at low temperature increased considerably due to extensive orientation of LCE networks.

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