Synthesis and characterization of liquid crystalline epoxy with cholesteric structure for modification of epoxy resin

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ABSTRACT
A novel liquid crystalline epoxy resin, 4-(4-oxiranyl-methoxyl)-benzoicacid cholesterol ester (OAC), is synthesized and characterized by spectroscopic techniques. The mesogenic behavior of the monomer is measured by polarized optical microscopy (POM); OAC presents various textures in the range of 130–215 °C. The curing behavior of OAC with 1,4-phenylenediamine is investigated by means of differential scanning calorimetry(DSC), POM, and wide-angle X-ray diffraction (WAXD). Information about distribution of OAC in blend system results from FT-IR Imaging System, indicating molecules of OAC can agglomerate to form anisotropic domains. The improvement of mechanical properties of Diglycidyl Ether of Biphenol A (DGEBA) modified with OAC has been achieved. Scanning electronic microscopy shows that extremely rough and highly deformed fracture surface can be obtained. Moreover, the influence of the concentration on the glass transition temperature has been characterized by dynamic mechanical analysis (DMA).

1. Introduction
Epoxy resins are widely employed to engineering materials because of their outstanding mechanical and thermal properties.[1–3] However, their brittleness and poor resistance to crack propagation have limited their industrial applications.[4] Hence, modification of epoxy resins has been the subject of forceful research interest.

In comparison with ordinary epoxies, liquid crystalline epoxy resins (LCERs), which combine the thermosets and liquid crystal formation capability, have become attractive for enhanced properties such as anisotropic orientation, high modulus and tensile strength, and low coefficient of thermal expansion.[5] Much attention in the past few years has been paid to the synthesis, curing behavior, phase behavior, and thermal properties of various LCERs.[6–13] Most of these reports focused on the preparation and characterization of LCERs with different mesogenic groups, such as aromatic stilbene,[14] biphenol,[15] azine,[16] aromatic ester,[17] binaphthyl,[18] and so forth. Unfortunately, to the best of our knowledge, there are only a few references about LCERs with cholesteric structures. Furthermore, chiral liquid crystal with cholesteric structure, which imparts unique optical and electrical properties to liquid crystal, has attracted considerable interest.[19]

In addition, the common epoxy resin is modified by copolymerizing with LCERs to improve mechanical properties.[20] In this way, liquid crystalline epoxy resins extend the technological applications for its high economic costs. As is known to us, LCERs must have appropriate melting and clearing temperatures to fit the curing procedure of the common epoxy resins for modifying a given ordinary epoxy resin. Cholesteric possesses flexible long-chain and substituents not only make the monomer more flexible, but also depress the monomer’s melting point and transition temperature.

This article explored the synthesis and characterization of liquid-crystal epoxy resins on the basis of the cholesteric structure. The locked mesophase of the LCT (liquid crystal templating) achieved with 1,4-phenylenediamine (PDA) as the curing agent was characterized via POM and WRXD. So far, there have been very few reports on distribution of LCERs in the final blend system, which has major influence on the properties of materials. Therefore, spectrum spotlight FT-IR imaging system was used to investigate the distribution of LCER during co-cure reaction of DGEBA with OAC. The fracture surface morphology of cured blend systems was discussed by SEM, and the effects of OAC content on mechanical properties were surveyed. Moreover, the thermal properties of cured epoxy systems were also researched with DMA.
2. Experimental section

2.1. Materials

DGEBA was supplied by Resin Factory of Bluestar New Chemical Materials Co., Ltd. (Wuxi, China). Cholesterol was purchased from Henan Xinyi Medical (China). p-hydroxybenzonic acid, allyl bromide, ethanol, potassium hydroxide, potassium iodide, ethyl acetate, hexane, thionyl chloride, pyridine, dichloromethane, 1,4-phenylenediamine (PDA), metachloroperbenzoic acid (MCPBA), and toluene were analytical grade commercial products (Shenyang Chemical of China) and were applied without further purification. The solvents were pretreated according to general process before use.

2.2. Instruments

FT-IR was measured on a Nicolet 510 FT-IR spectrometer (Nicolet Instruments, Madison) using samples in KBr pellets; ¹H-NMR was tested by Varian WH-90PFT NMR Spectrometer (Varian Associates, Palo Alto, CA) with CDCl₃ and dimethyl sulfoxide (DMSO) as a solvent, and tetramethylsilane (TMS) as an internal standard. Calorimetric studies were carried out with a NETZSCH instruments DSC 204 (Netzsch, Wittelbachstrasse, Germany) at a scanning rate of 10 °C/min under a flow of dry nitrogen. The texture of OAC was observed with a polarized optical microscopy (Leica DMRX Germany) equipped with a Linkam THMSE-600 (Linkam, Surrey, England) hot stage connected to a TP-92 temperature control unit at a heating and cooling rate of 3 °C/min. WAXD measurements were performed with a nickel-filtered Cu–Ka radiation with a DMAX-3ARigaku powder diffractometer. The recorded diffraction patterns ranged from 2° to 40°. Sample was placed on the reflectivity stage. X-ray experiments on cross-linked samples were performed at room temperature. Distribution of OAC in composites was characterized by using FT-IR imaging (Spotlight 300 infrared imaging system, PerkinElmer). The film sample was located in the measure stage during isothermal curing at 140°C; infrared ray scanned the same position at a different time. The fracture surface morphology of the samples which was fractured in impact strength experiments was observed using a scanning electron microscope (SEM; Hitachi S-4700, Japan). All sample surfaces were coated with a thin gold layer by plasma sputtering to avoid a charging effect due to non-conductivity of the polymer. The tensile strength, elongation at break, and bending strength tests of the samples were recorded with Universal Testing Machine (CMT4204, MTS) at speed of 5 mm/min according to China State Standard GB/T 1040–92 and GB/T 9341–2000. Impact tests were performed using the impact testing instrument (GT-7045-MD, GOTECH) according to China State Standard GB/T 1843–1996. At least five specimens of each composition were tested and the average values were recorded. Thermal properties were measured with a DMA (NETZSCH DMA 200) and a three-point bending configuration at a heating rate of 3 °C/min.

2.3. Synthesis

2.3.1. Synthesis of 4-(2-allyloxy)benzoic acid

Potassium hydroxide (8.0 g, 0.14 mol) and potassium iodide (0.35 g, 0.002 mol) was added to a solution of p-hydroxybenzonic acid (8.3 g, 0.06 mol) in 200 mL of ethanol. After the reaction mixture was stirred at room temperature for 1 h, allyl bromide (9 g, 0.08 mol) was added dropwise to the mixture. The resulting mixture was heated under reflux overnight. After this had cooled to room temperature, 1 mol/L HCl solution was added to neutralize the reaction mixture. The white precipitate was filtered and recrystallized twice from ethanol to obtain white piece crystals in 88% yield and with melting point (Tm) at 165 °C.

IR (KBr cm⁻¹): 3056 (=CH), 2973–2857 (–CH₃, –CH₂), 1680 (C=O), 1580, 1500 (Ar), 1250 (C–O–C). ¹H-NMR (600 MHz, DMSO, δ): 12.6 (d, H, COOH), 7.87 (d, J = 8.4 Hz, 2H, Ar–H), 6.99 (d, J = 8.4 Hz, 2H, Ar–H), 6.05–5.99 (m, 1H, CH=CH₂), 5.39 (d, 2H, CH=CH₂), 4.61 (d, 2H, OCH₂CH₃).

2.3.2. Synthesis of 4-(2-allyloxy)benzoicacyl chloride

8.9 g of 4-(2-allyloxy)benzoic acid, 15 mL of thionyl chloride were added to a round-bottomed flask equipped with an absorption instrument of hydrogen chloride. The mixture was stirred at room temperature for 4 h, and then heated to 60 °C for 6 h; the excess thionyl chloride was distilled under reduced pressure to give the corresponding acid chloride. Yield: 97%.

2.3.3. Synthesis of 4-(2-allyloxy)benzoic acid cholesterol ester (AC)

7.84 g (0.04 mol) of 4-(2-allyloxy)benzoic acid chloride was added dropwise to a cold solution of 15.44 g (0.04 mol) of cholesterol in 40 mL of chloroform and 2 mL of pyridine. After the reaction mixture was stirred at room temperature for 1 h, allyl bromide (9 g, 0.08 mol) was added dropwise to the mixture. The mixture was heated under reflux overnight. After this had cooled to room temperature, 1 mol/L HCl solution was added to neutralize the reaction mixture. The white precipitate was filtered and recrystallized twice from ethanol to give white piece crystals in 88% yield and with melting point (Tm) at 165 °C.

IR (KBr cm⁻¹): 3056 (=CH), 2973–2857 (–CH₃, –CH₂), 1680 (C=O), 1580, 1500 (Ar), 1250 (C–O–C). ¹H-NMR (600 MHz, DMSO, δ): 12.6 (d, H, COOH), 7.87 (d, J = 8.4 Hz, 2H, Ar–H), 6.99 (d, J = 8.4 Hz, 2H, Ar–H), 6.05–5.99 (m, 1H, CH=CH₂), 5.39 (d, 2H, CH=CH₂), 4.61 (d, 2H, OCH₂CH₃).
2.3.4. Synthesis of 4-(4-oxiranyl-methoxyl)-benzoic acid cholesterol ester (OAC)

5.46 g of AC was dissolved in 50 mL of dry CH₂Cl₂ and was added dropwise to a solution of meta-chloroperbenzoic acid (mCPBA, 4.3 g, 0.025 mol) in 300 mL of dry CH₂Cl₂ under continuous stirring. The reaction mixture was stirred and refluxed for 48 h. After cooling and subsequent filtration, the solvent was evaporated to dryness in rotary evaporator. The crude product obtained was washed with ethanol and then filtered three times. The yield of OAC is 80% with Tm at 129 °C.

IR (KBr cm⁻¹): 2973–2857 (–CH₃, –CH₂–), 1704 (C=O), 1610, 1494 (Ar–), 1278, 1172 (C–O–C), 915 (epoxy). ¹H nMR (600 MHz, CDCl₃, δ): 7.97–7.95 (d, J = 9 Hz, 2H, Ar–H), 6.92 (d, J = 9 Hz, 2H, Ar–H), 4.30 (m, 1H), 3.99 (m, 1H), 3.36 (s, 1H), 3.26 (s, 1H), 3.11 (s, 1H), 2.91 (m, 1H), 2.76 (m, 1H), 2.30–0.61 (m, 44H, cholesteryl–H).

2.4. Curing process of blending of OAC and DGEBA

In order to evaluate mechanical properties of the blends, the pre-weighed amount of OAC and DGEBA was mixed uniformly in dichloromethane, and then a solution of stoichiometric PDA in CH₂Cl₂ was also added to the above system under continuous stirring. Later then, the solvent was evaporated by rotary evaporator at 40 °C. Afterward, the mixture was degassed under vacuum oven at 60 °C for 20 min. After that, it was poured into a polished polytetrafluoroethylene mold, and then the mixture was cured for 2 h at 140 °C and postcured for 3 h at 160 °C.

3. Results and discussion

3.1. Synthesis and characterization of monomers

Crosslinkable liquid crystalline monomers have generally been synthesized from a rigid mesogenic core with an attached reactive end-functional group. Our target in projecting the liquid crystalline epoxy monomer containing cholesteric structure was to achieve cholesteric liquid crystal for potential applications[21,22] on the other hand, alkyl group of cholesterol plays an instrumental role in reducing melting point and increasing its mesophase stability.

Figure 1 outlines the synthesis routes consisting of well-known simple reactions in this article. The first synthetic step involves the nucleophilic substitution of both bromine atoms of allyl bromide by p-hydroxybenzonic acid in the presence of potassium hydroxide and potassium iodide. The product was insoluble in the reaction media at room temperature and was separated by simple filtration. The crude product obtained was washed with ethanol and then filtered three times. The yield of OAC is 80% with Tm at 129 °C.

IR (KBr cm⁻¹): 2973–2857 (–CH₃, –CH₂–), 1704 (C=O), 1610, 1494 (Ar–), 1278, 1172 (C–O–C), 915 (epoxy). ¹H NMR (600 MHz, CDCl₃, δ): 7.97–7.95 (d, J = 9 Hz, 2H, Ar–H), 6.92 (d, J = 9 Hz, 2H, Ar–H), 4.30 (m, 1H), 3.99 (m, 1H), 3.36 (s, 1H), 3.26 (s, 1H), 3.11 (s, 1H), 2.91 (m, 1H), 2.76 (m, 1H), 2.30–0.61 (m, 44H, cholesteryl–H).

3.2. Mesomorphic phase transition of OAC

Liquid crystalline phase behavior of OAC was examined by differential scanning calorimetry (DSC) and POM. Figure 3 illustrates the texture morphology of monomer
observed, and then cholesteric droplets appear between 195 and 215 °C. At temperatures greater than 215 °C, OAC reveals the isotropic structure because drastic thermal molecular motions interfere with the π–π stacking interaction of the mesogenic groups.

3.3. Curing behavior of the OAC/PDA mixtures

The cross-linking process can be carried out in the mesophase range so as to obtain LCTs, therefore, curing agent...
epoxy monomer and curing agent was heated at 140 °C for 50 min, the focal-conic fan texture was observed. It was reasonable to assume that the system acquired smectic structure. Subsequently, based on the curing reaction condition mentioned previously, the system was continuously postcured. The birefringence pattern was also preserved when the sample was cooled to room temperature and the texture of the LCT was simultaneously conserved at a higher temperature (220 °C). In terms of the above-obtained conclusion, we believe that a locked LC phase structure formed at the curing temperature.

The polydomain structure of this system was confirmed in further by WAXD. The X-ray diffraction patterns are shown in Figure 6. For the system cured at 140 °C for 2 h, there is a high intensity peak at 2θ = 5.17° corresponding to a distance of 18.9 Å and there is a broad diffraction at 2θ = 20.5° corresponding to a lateral distance between mesogens of 4.8 Å, which signifies a typical smectic LC phase.

3.4. Morphologies of the cured system of OAC and DGEBA/PDA

Liquid crystalline epoxy resins can provide a unique way to modify the properties of epoxy resins by creating additional
LC mesophases in the system. In order to evaluate the development of mesogens ordered in the resin matrix, the POM was used to trace texture of the mixed system at every stage of the curing reaction. According to above conclusion in this article, uniform mixed samples were cured at 140 °C for 2 h at hot stage under POM, as the reaction, we observed birefringence spot through POM. When the curing reaction was achieved, the texture was retained no matter how temperature changed. By means of the polarized optical micrographs, we concluded that the ordered organization was fixed in the blend system by the cure process. Figure 7 exhibits optical micrographs of cured blend systems with different OAC contents at room temperature. By contrast with neat epoxy, the bright domains were observed in the blending system, and then the bright spots increased gradually along with the content of OAC, which is similar with the result observed by J. Gao etc.[24] It would be natural to assume that structure oriented in microdomains, which was formed by self-oriented alignment of OAC molecules due to its rigidity of mesogen component, has much faster reaction rate and stronger tendency of self-conglomeration than DGEBA molecules. The consequence was further measured with spectrum spotlight FT-IR imaging System in the next section.

3.5. Distribution of OAC in cured system

As previously mentioned, compared with general epoxy, the OAC has a much faster reaction rate owing to the arrangement of molecules which caused liquid crystalline domain structure in blends. Therefore, the composite material consists of anisotropic domains and leads to a remarkable performance in all directions.[10,25,26]

Spectrum spotlight FT-IR imaging system is an effective way to obtain information about distribution of component in blends system; we can distinguish between the chemical composition of the visible image by using FT-IR imaging system, different color region directly reflects the chemical ingredient in the images. In order to investigate OAC distribution during curing process in mixed system, the sample was monitored using the FT-IR imaging system from initial state to the final end of curing reaction. C=O characteristic peak at 1704 cm⁻¹ distribution, not observed in DGEBA, was selected to represent liquid crystalline epoxy. As shown in Figure 8, the colors from red to blue derived from the intensity of IR absorption varied from strong to weak and planar axis represents the selected region of the blends film. All the pictures are taken from the same area of the same sample. Before the curing reaction, the blend system presents equivalent absorption intensity, in DGEBA, was selected to represent liquid crystalline epoxy. As shown in Figure 8(a), the colors from red to blue derived from the intensity of IR absorption varied from strong to weak and planar axis represents the selected region of the blends film. All the pictures are taken from the same area of the same sample. Before the curing reaction, the blend system presents equivalent absorption intensity. Therefore, OAC molecular was dispersed well in resin matrix; the microstructure of system was isotropic and homogeneous. As the reaction progresses, Figure 8(b, c) displays distribution of C=O characteristic peak which was inhomogenous and had tendency of self-conglomeration. The phenomenon illustrates self-oriented alignment of OAC molecules can agglomerate to form anisotropic

![Figure 7](image7.png)

**Figure 7.** POM photographs of the DGEBA/PDA systems at 25 °C (×200): (a) 0wt% OAC (b) 5wt% OAC (c) 10wt% OAC.

![Figure 8](image8.png)

**Figure 8.** Distribution images of OAC in 10wt% OAC/DGEBA/PDA system during the curing process with FT-IR Imaging System. (a) initial stage before curing; (b) 30 min for curing process at 140 °C; (c) 60 min for curing process at 140 °C.
domains. The conclusion affirmed that a similar structure of sea-island exited in composite materials obtained by POM analysis.

### 3.6. Mechanical properties

The influence of content of OAC on tensile, impact, and bend properties of the cured blends was characterized. The result shown in Figure 9 demonstrates that the samples exhibit a significant enhancement in their tensile, impact, and bend strength with the increment of OAC content. Tensile strength improved 30% compared with neat one and elongation at break from 2.3 to 3.7% in the system of the epoxy/15wt% OAC. Meanwhile, the impact strength of epoxy/15% OAC improved 72.7% compared with unmodified epoxy and the epoxy/10wt% OAC exhibits the highest bend strength. It was recognized that these results were attributed to the system constituted by anisotropic domains that were formed by the presence of orientational order, and then liquid crystalline phase conferred crack-stopper properties, which effectively dispersed stress and prevented crack propagation.

Another reason can be illustrated as flexible chain of incorporated OAC decreases density of network, which was further confirmed in DMA test. As Farren expected, although macroscopically isotropic, the degree of order at the microdomain level can be related to the network physical properties.[27]

### 3.7. Fracture morphology

In order to further support the mechanical results, the morphologies of the fracture surfaces after impact tests were investigated by SEM (Figure 10). From Figure 10(a), it can be seen that neat epoxy exhibits a smooth and featureless impact fracture surface, in accordance with its poor impact strength, which is typical of a brittle thermosetting polymer. Compared to unmodified epoxy, the fracture surface of the 10wt% OAC presents rough and highly deformed fracture, as shown in Figure 10(b), indicating that the bulk plastic deformation occurred. This can be attributed to the presence of liquid crystalline phase which could distort the path of the crack tip, comparatively higher amount of energy was required for the crack to propagate.

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**Figure 9.** Effect of OAC content on the mechanical properties of DGEBA/OAC blends.

**Figure 10.** SEM micrographs of the tensile fracture surface. (a) 0wt% OAC/DGEBA (b) 10wt% OAC/DGEBA.
4. Conclusions

A novel liquid crystalline monomer with cholesteric structure was synthesized and characterized in this study, expressed oily streaks and cholesteric droplets. The monomer was crosslinked in LC state by PDA and anisotropic thermoset with smectic phase was obtained. In the following, the texture was further confirmed by WAXD. The impact strength of conventional epoxy resin was enhanced by incorporating OAC without sacrificing tensile strength and bending strength. POM and FT-IR Imaging System studies indicated the presence of an LC phase in the blend system had an important effect on the properties. The improvement of the strength was matched with the results obtained from SEM. Moreover, the glass transition temperature increased 21 °C compared with the DGEBA/PDAsystem.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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