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1,3,4-Oxadiazole epoxy resin-based liquid crystalline thermosets and their cure kinetics

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Abstract Liquid crystalline thermosets were synthesized based on a difunctional liquid–crystal (LC) epoxy resin monomer, namely 2,5-*bis*(4-glycidyloxyphenyl)-1,3,4-oxadiazole with various tetrafunctional crosslinkers such as diaminodiphenyl methane, diaminodiphenyl sulfone, and diaminodiphenyl ether. The epoxy monomer was characterized by infrared and nuclear magnetic resonance spectroscopy. Cure kinetics of a stoichiometric mixture of epoxy monomer and diaminodiphenyl methane was investigated by differential scanning calorimetry (DSC) for specimens cured under various cure conditions. The nematic LC texture for the cured specimen was identified by polarized microscopy and confirmed by X-ray diffractometry. Phase diagram of cure time versus transition temperature was constructed based on the DSC data for epoxy/DDM system. The diagram displayed the changes of melting transition, isotropic transition, and glass transition temperatures as curing proceeds.

Introduction

Epoxy resin is one of the most versatile classes of thermosetting polymer and widely used in diversified industrial applications owing to toughness, low shrinkage, and good alkali resistance properties [1–4]. In recent years, growing interest has been focused on liquid crystalline thermosets, due to ordered, anisotropic network structures, and their uses as wave-guides, electronic packaging, and matrix materials for advanced composites. Because of easy handling and processability, epoxy resins are identified as matrix resins for structural composites and focused on formation of liquid–crystal (LC) texture in these resins [5]. The literature revealed that LC epoxy resins prepared so far from binaphthyl [6], azine [7], methylstilbene [8], or biphenyl [9, 10] units as rigid structure in the diepoxy compounds.

Curing of mesogenic diepoxide has been contemplated by various researchers [11]. Amine curing of aromatic diglycidyl ethers was investigated by Kirchmeyer for thermosets from 4-(2,3-epoxypropoxy)phenyl 4-(2,3-epoxypropoxy)benzoate and isomeric diaminophenyl benzoates [12]. Carfagna et al. [9] reported the reaction of 4,4′-*bis*(2,3-epoxypropoxy)biphenyl with 2,4-diaminotoluene. Ober and co-authors [13] used 4,4′-*bis*(2,3-epoxypropoxy)-α-methylstilbene as mesogenic diepoxide which was cured with different diamines.

Curing property of LC epoxy resin using diglycidyl ether of 2,5-diphenyl-1,3,4-oxadiazole as rigid rod segment is focused in this study. Heterocyclic unit in this rigid block has high potential to form thermotropic LC phases as well as high thermally stable materials [14]. Introduction of oxadiazole ring can provide hexagonal columnar phases when oxadiazole rings are used as central core unit [15]. Here in, we present synthesis and characterization of a nonlinear-shaped liquid crystalline epoxy resin containing oxadiazole ring. Thermal and mesomorphic properties of epoxy monomer with various diamine curing agents were investigated. To understand the phase changes, a time–temperature phase diagram during isothermal curing of epoxy/amine system was constructed and discussed.

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Experimental details

Materials

Polyphosphoric acid (Spectrochem, Mumbai, India), hydrazine hydrate (Spectrochem), *p*-hydroxybenzoic acid (SRL, Mumbai, India), epichlorohydrin (SRL), 4,4′-diaminodiphenyl methane (DDM), 4,4′-diaminodiphenyl sulfone (DDS), and 4,4′-diaminodiphenyl ether (DDE) were used as received. Acetone and methanol were purified and dried before use as reported elsewhere [16].

Synthesis of precursor and monomer

2,5-Bis(4-hydroxyphenyl)-1,3,4-oxadiazole

Polyphosphoric acid (150 g) was heated to 50 °C. To this, *p*-hydroxybenzoic acid (24 g) followed by hydrazine hydrate (80%; 5 mL) was added drop wise with continuous stirring. Temperature of the reaction mixture was slowly elevated to 125 °C for 30 min and refluxed for 8 h. At the end of the reaction, mixture was stirred with water (500 mL) to precipitate the product. A white precipitate thus obtained was filtered and washed with plenty of water and dried in vacuo (Yield 51%; m.p: 335 °C) [17].

IR: 3186 cm^{-1} (H-bonded OH), 1074 cm^{-1} (C–O–C stretching of oxadiazole ring), 1560 cm^{-1} o(C=N). ^{1}H-NMR (DMSO-d6) δ: 7.01 (2-ArH, d), 7.93 (2-ArH, d), 10.40 (s, OH). ^{13}C-NMR (DMSO-d6) δ: 165 (oxadiazole-C), 115–162 (Ar–C).

2,5-Bis(4-glycidyloxyphenyl)-1,3,4-oxadiazole

2,5-*Bis*(4-hydroxyphenyl)-1,3,4-oxadiazole (9 g) was refluxed with epichlorohydrin (80 mL) at 60 °C for 1 h. A solution of NaOH (3 g in 10 mL water) was added drop wise to the reaction mixture and heated at 90 °C for 12 h. Then, excess epichlorohydrin was removed under reduced pressure. Residue was extracted with methanol to remove the precipitated sodium chloride, followed by removal of methanol to yield the title compound (yield 61%; m.p: 184 °C) [18].

IR (KBr): 1560 cm^{-1} (C=N), 2923 cm^{-1} (C–H stretching of methylene group), and 910 cm^{-1} (epoxy). ^{1}H-NMR (DMSO-d6) δ: 7.01 (d, 2-ArH), 8.02 (d, 2-ArH), 3.8–4.9 (2H, m, CH_2 glycidyl), 3.5 (1H, m, CH epoxy), 2.1–2.5 (2H, CH_2 epoxy). ^{13}C-NMR (DMSO-d_6) δ: 163 (oxadiazole-C), 114–160 (aromatic-C), 72 (Ar–O–CH_2), 63 (–CH– of epoxy), 47 (CH_2 in epoxy ring).

Characterization

Infrared spectra were obtained by using Bruker IFS 66V Fourier transform spectrometer using KBr pellet. High-resolution ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker spectrometer of 300 and 75.4 MHz, respectively. DMSO-d_6 and TMS were used as solvent and internal standard, respectively. Thermogravimetric analysis was performed on a Mettler TA3000 thermal analyzer in nitrogen atmosphere at a heating rate of 20 °C min^{-1} with a sample weight of 3–5 mg. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo STAR^{e} system for the polymers in sealed aluminum pans in a dry nitrogen atmosphere with an empty aluminum pan as reference. Scans were carried out at a heating rate of 10 °C min^{-1}. Liquid crystalline textures were observed by polarized optical microscope (POM) using Euromex polarizing microscope equipped with a Linkem HFS91 heating stage and a TP-93 temperature programmer. 1:1 equivalents of finely powdered epoxy resin [2,5-*bis*(4-glycidyloxyphenyl)-1,3,4-oxadiazole (BGPOD)] and curing agent were mixed homogeneously and placed between two thin microscopic slides. Textures were observed during heating at a rate of 5 °C min^{-1}. Photographs were taken by a Nikon FM 10 camera and exposed on a Konica film.

Results and discussion

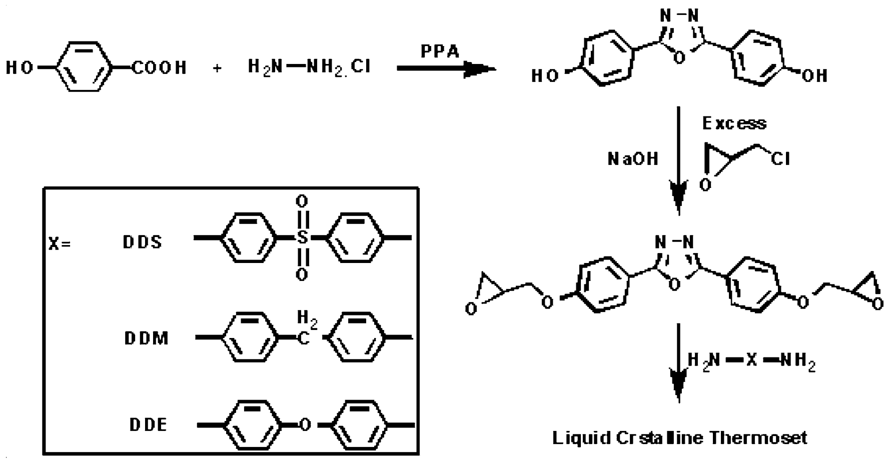
Synthesis, thermal, and mesomorphic properties of LC epoxy monomer

Synthesis of epoxy resin monomer is shown in Scheme 1 and characterized by FT-IR and NMR techniques. Thermal and mesomorphic properties of epoxy monomer were examined using DSC as well as a POM. DSC thermogram of the epoxy monomer is shown in Fig. 1. It evidences two endothermic peaks; one at lower temperature due to melting ($T_m = 187$ °C) and other at higher temperature attributed to isotropization ($T_i = 195$ °C). Above 200 °C, the monomer starts decomposed evidenced by an exothermic peak on the DSC thermogram. The monomer BGPOD exhibited nematic mesophase (Fig. 2) in the melt between T_m and T_i. The data reveal that temperature interval between T_m and T_i (ΔT) stands for extends of LC phase region.

Reaction between LC epoxy monomer (BGPOD) and curing agents

Curing studies of epoxy monomer was investigated with three different diamines namely, DDM, DDS, and DDE. Cure reaction of LCT's can have an influence on the liquid crystalline phase of final cured material. Depending on the monomer and type of reactive group, the curing reactions may decrease or increase orientation of liquid crystalline

Scheme 1 Synthesis of monomer and preparation of LCT



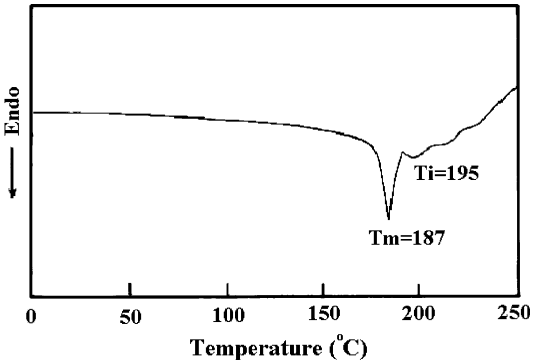


Fig. 1 DSC thermogram of 2,5-*bis*(4-diglycidyloxyphenyl)-1,3,4-oxadiazole

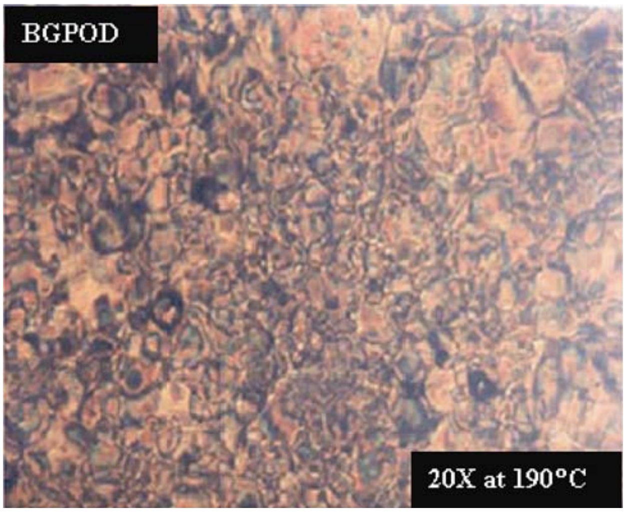


Fig. 2 Optical texture of LC epoxy monomer (BGPOD)

phase [19]. To access thermal stability of cured specimens, homogeneous mixture was obtained by dissolving stoichiometric amounts of epoxy monomer and curing agent in common solvent (ethanol), and solvent was removed under reduced pressure at room temperature. The curing reaction of BGPOD with aromatic diamines was examined under nitrogen atmosphere in DSC at a rate of 10 °C min^{-1} and results are presented in Table 1. Thermogram revealed maximum exothermic temperature of curing was in the order of DDS > DDE > DDM. The DDM and DDS displayed high and low reactivity toward diepoxide, respectively. This is attributed to electron-donating nature of methylene group in DDM would enrich electron density of amine toward oxirane ring; however, DDS contains a strong electron-withdrawing group to exhibit low reactivity [20].

Thermal property of cured epoxy resin was evaluated by thermogravimetric analysis (TGA) (Fig. 3) under nitrogen atmosphere and data are summarized in Table 1. The results suggested that the thermal stability of BGPOD/DDS system is higher than other systems. Cured BGPOD sample was analyzed by FT-IR spectroscopy. The N–H characteristic absorbance at 3300–3400 cm^{-1} was decreased and O–H stretching band around 3500 cm^{-1} increased. The results witnessed crosslinking of BGPOD proceeded almost quantitatively by thermal curing process.

Curing kinetics of LC epoxy monomer with DDM

A stoichiometric mixture of epoxy monomer and DDM was cured under various isothermal cure conditions. The cure conditions are listed in Table 2 and their transition temperatures (T_g, T_m, or T_i) observed by DSC after completion of curing reaction are in accordance with POM observations. Table 2 displayed cure conditions include two different methods of curing namely, single-step at an isothermal cure temperature and dual-step at two successive cure temperatures for various cure times. Based on the transition temperatures of epoxy monomer, three different cure temperatures were used in this experiment; 185 °C (below T_m), 190 °C (between the T_m and T_i), and 198 °C (just above T_i) for each single-step. For the dual-step,

Table 1 Thermal properties of epoxy resin (BGPOD) and aromatic diamines

Sl. no.	Curing agents	m. p. of curing agents (°C)	BGPOD/curing agent	Endo (°C)	Exo (°C)	TGA (weight loss) (%)		Char yield at 700 °C (%)
						10	50	
1	DDM	89–91	2:1	82; 174	220	345	470	15.07
2	DDE	189–192	2:1	162	222	321	448	14.56
3	DDS	175–177	2:1	83; 176	228	404	514	17.63

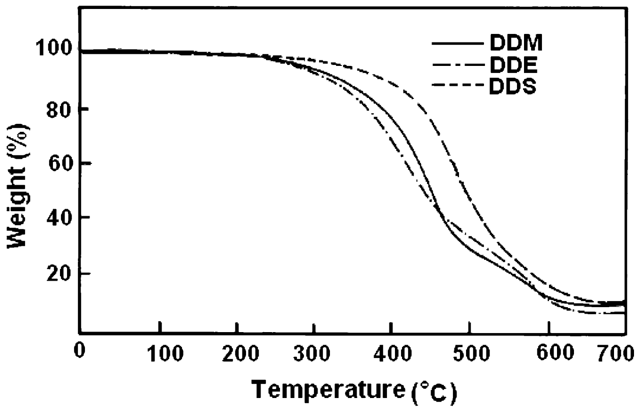


Fig. 3 TGA traces of the cured BGPOD with different diamines

Table 2 Dependence of transition temperatures of BGPOD/DDM mixture on various curing conditions

Curing condition Temperature (°C)/time (min)	T_g (°C)	T_m (°C)	T_i (°C)	ΔT ($T_i - T_m$)
Before curing	–	176	–	–
185/10	–	161	174	13
185/20	–	134	169	35
185/30	–	133	167	34
185/40	–	132	165	33
185/50	108	–	–	–
185/60	119	–	–	–
185/80	121	–	–	–
190/5	–	137	166	29
190/10	–	134	145	11
190/20	106	–	–	–
198/5	–	–	–	–
198/10	109	–	–	–
198/20	113	–	–	–
198/30	117	–	–	–
198/50	126	–	–	–
185/30 → 140/10	–	134	169	35
185/30 → 140/30	–	132	171	36
185/30 → 140/60	106	–	174	–
185/30 → 140/120	108	–	179	–
185/30 → 140/300	116	–	181	
185/30 → 140/600	128	–	195	–

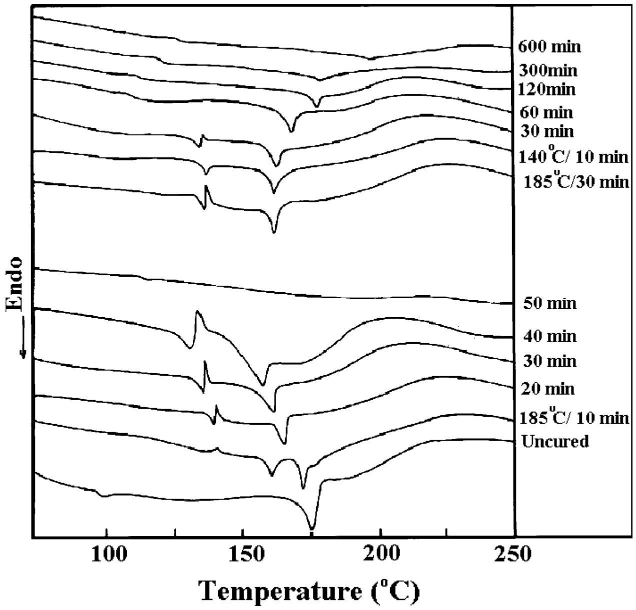


Fig. 4 DSC thermograms of BGPOD/DDM mixture of uncured and cured at various time intervals

uncured mixture was cured at 185 °C for 30 min first and then cooled down to 140 °C for various times up to 600 min. Here, the second temperature is lower than the first in dual-step (Fig. 4). The cure temperature and time for dual-step were determined from the results obtained in single-step as follows.

During curing at 185 °C in single-step, T_m and T_i appeared for 10–40 min and T_g emerged after 50 min instead of T_m and T_i as shown in Table 2. The values of T_m and T_i decreased from 161 to 132 °C and from 174 to 165 °C between 10 and 40 min, respectively, whereas T_g increased from 108 to 121 °C between 50 and 80 min of cure. At 185 °C cure temperature, ΔT was 13 °C at 10 min and then rapidly enlarged to 33–35 °C at 20 min. The enlarged LC region maintained up to 40 min at 185 °C and decreased thereafter. However, enlarged LC region appeared from beginning of cure and maintained up to 5 min cure at 190 °C. Thus, DSC analysis and microscopic observation for single-step cure were mainly made at 185 °C because LC phase existed for longer period of cure time in wide temperature range. Although no mesomorphic evidence existed in the uncured mixture, nematic organization was observed between 10 and 40 min of cure. However, nematic texture disappeared and no LC phase was observed beyond 50 min.

The results revealed that the LC phase was unable to retain when curing continued in isotropic state for longer period than 50 min at 185 °C. In addition, nematic LC region between T_m and T_i shifts to lower temperature as the reaction proceeds, thus, to obtain LC thermoset, it is necessary to catch up with LC region. In this study, specimen was cured at 185 °C for 30 min within wide LC phase region, and cure temperature was then lowered to 140 °C to maintain LC phase. The second cure temperature (140 °C) chosen is in LC region between T_m (133 °C) and T_i (167 °C) of specimen pre-cured at 185 °C/30 min as shown in Table 2. From dual-step curing method, T_m was observed at 134 °C for 10 min and 132 °C for 30 min, whereas T_g appeared at 106 °C from 60 min and increased to 128 °C for 600 min. The nematic texture was observed for all specimens cured at different time intervals in dual-step curing method and representative photographs are shown in Fig. 5. This evidenced that LC phase formed in single-step can be persisted by post-curing at a low temperature in the LC region.

The DSC thermogram showing transition for specimens uncured and cured by single-step (185 °C up to 40 min) and dual-step (185 °C/30 min → 140 °C/various times) are shown in Fig. 4. The DSC scan of uncured mixture displayed a sharp melting transition at a temperature of 176 °C with no indication of LC phase. As cure proceeds, non-LC mixture begins to show melting and isotropization transition on the thermograms, indicating the formation of LC phase. During second stage at 140 °C in dual-step, peak area for melting decreased rapidly and disappeared at 60 min, whereas peak areas for isotropization were retained up to 300 min cure. After 600 min isotropization, endotherm was hardly seen on the thermogram. Polarized microscopic observations revealed that the specimen after 600 min prevailed highly birefringent and exhibited no change in optical texture until decomposition. This is attributed to molecular organization of LC phase almost retained in the cured system assumed as during curing reaction of epoxy/amine system, oligomers formed at initial stages and attain sufficient high-molecular-weight species. Consequently, the sample was pre-cured until obtaining maximum LC phase duration and then post-cured within this region for a longer period, thus the mesophase will be retained by both chain extension and crosslinking. This may be attributed to the fact that continuation of post-cure in nematic state results in development of permanent linkages. Time–temperature phase diagram for the BGPOD/DDM system was constructed based on the results obtained from DSC and shown in Fig. 6a, b. Figure 6a represents phase changes during the initial stage of isothermal cure at 185 °C for 30 min. This depicts T_m and T_i shifted to lower temperature and temperature range of LC nematic phase is rapidly expanding up to 30 min and continued almost

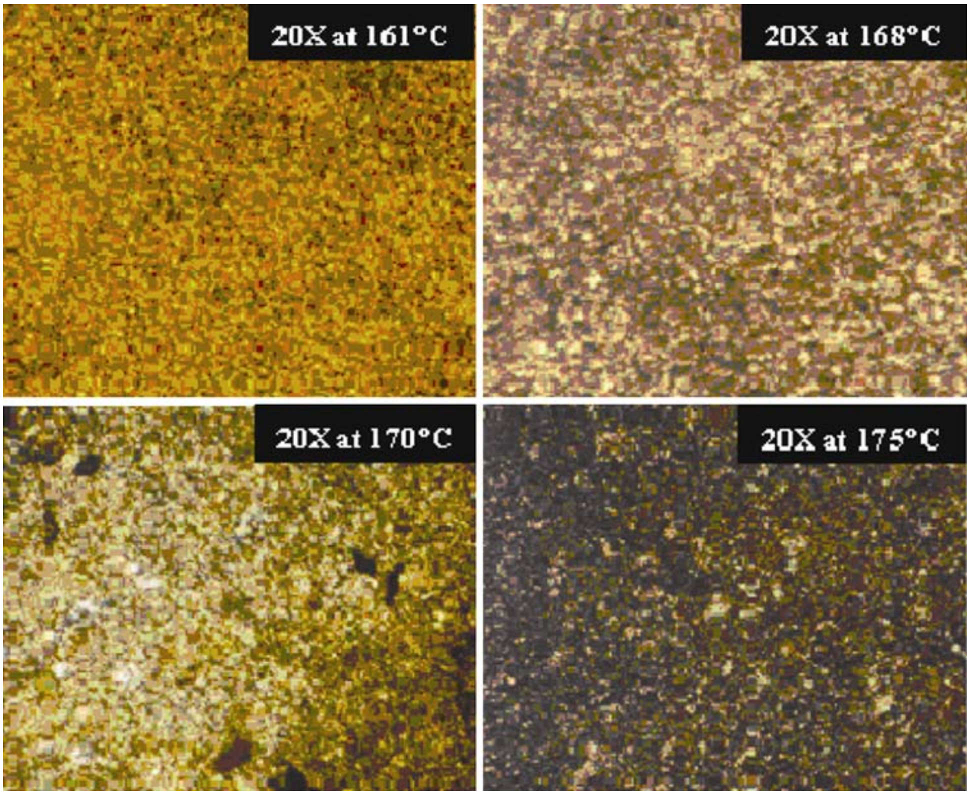


Fig. 5 Optical textures of BGPOD/DDM mixture cured at various temperatures

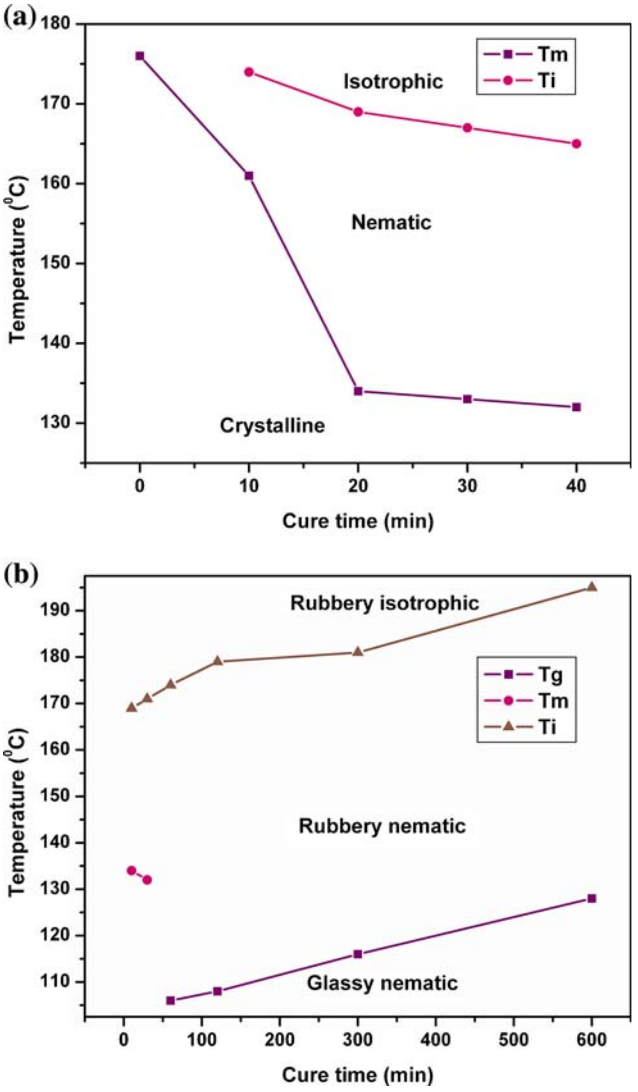


Fig. 6 Time–temperature phase diagram of BGPOD/DDM mixture system: **a** cured at 185 °C for different time intervals; **b** post-cured at 140 °C for different time intervals after cured at 185 °C/30 min

constant thereafter. This exhibits the LC phase, which was not observed for uncured mixture, started to develop within 20 min of curing. In Fig. 6b, both values of T_g and T_i are continuously grew with cure time, wherein rubbery nematic phase maintained almost constant during curing. The increase in T_g and T_i may be ascribed to restriction of molecular weight and formation of network.

Shiota and Ober [21] have carried out similar studies for LC epoxy monomer/sulfanilamide (SAA) system during isothermal cure at 120 °C for specimen pre-cured at 160 °C for 30 min and they noticed that there was a gradual development of LC phase (30–45 min cure time) and increased network stability with maximum cure temperature obtaining a LC network at approximately 190 °C [22]. But in this study, a reverse trend was observed. This may be ascribed that DDM possibly enhances the development of LC phase through an increased reaction rate, more extended chain conformations. As shown in Table 2, melting transition was gradually decreased up to 30 min of cure and was disappeared after 60 min with appearance of glass transition temperature.

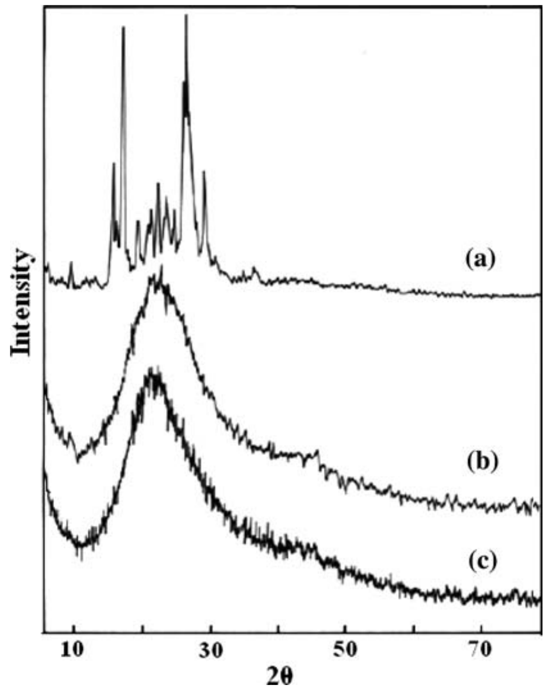


Fig. 7 XRD pattern for the BGPOD/DDM system: (*a*) Uncured; (*b*) post-cured at 140 °C/30 min after curing at 185 °C/30 min; and (*c*) cured at 198 °C/20 min

X-ray diffraction studies

Figure 7 shows diffractograms of a wide angle X-ray diffractometer for specimens: (a) uncured; (b) cured in dual-step (185 °C/30 min → 140 °C/30 min.); and (c) cured in a single-step (198 °C/20 min). Uncured specimen (Fig. 7a) exhibited sharp diffracted peaks, revealing that mixture of BGPOD and curing agent is crystallized. Specimen cured in dual-step has no specific peaks due to nematic LC phase on a diffused halo from amorphous region in epoxy network as ascertained in the literature [23, 24]. Curing at 198 °C produced only amorphous phase. The X-ray results are in accordance with DSC and POM data.

Conclusion

Liquid crystalline epoxy monomer based on 1,3,4-oxadiazole mesogen was synthesized and curing kinetics of the epoxy monomer with amine curing agents were investigated. The molecular structure of the epoxy monomer was identified by FT-IR and NMR spectroscopic analysis. The thermal behavior of epoxy/amine mixture was investigated by DSC and TGA analysis. The BGPOD/DDM system was eventually selected as the most suitable combination to examine the cure kinetics of BGPOD behavior studied. In the DSC study of epoxy/DDM system, T_m and T_i decreased and temperature range forming nematic phase expands rapidly in the beginning of cure. Remarkable change in DSC scan is attributed to the formation of network with low crosslinking density that may be considered to behave as highly viscous liquid in the mesophase. Since the region showing nematic LC phase shifts to lower temperature, uncured specimen was reacted by dual-step at two successive temperatures (high → low). During curing at second lower temperature, values of T_g and T_i increased with cure time. Region between T_g and T_i corresponds to rubbery nematic phase. Increase in T_g and T_i is attributed to the increase in molecular weight with high crosslinking density. Finally, highly crosslinked LC elastomer with highest T_g of 128 °C could be obtained by curing at 185 °C/30 min → 140 °C/600 min. LC thermoset could be prepared successfully through dual-step curing method. A time–temperature phase diagram is constructed based on the DSC results provided the proper cure conditions for processing of LC thermosets.

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