## Liquid Crystalline Epoxy Resin Modified Cyanate Ester/Epoxy Resin Systems

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**ABSTRACT:** Liquid crystalline epoxy resin (LCE) modify cyanate ester/epoxy resin blend systems were studied by scanning electron microscope, polarizing optical microscope, thermogravimetric analyzer, differential scanning calorimetry, thermal mechanical analysis, and rheometers. With the addition of LCE resin, the blends showed both an enhanced curing rate and increased glass transition temperature of cured samples. The phase structures of the blends changed from homogenous to liquid crystalline phase when the con-

INTRODUCTION

Thermosetting polycyanurates prepared from polycyclotrimerization of aromatic cyanate ester resins have drawn increasing attention due to their important application in microelectronic and aerospace industries.<sup>1</sup> This crosslinked polycyanurates distinguished themselves from other thermosetting polymers by their excellent dielectric properties, thermal and dimensional stability, and low moisture absorption, which facilitated their applications in the electronic and composite areas.

Blending cyanate ester resins with epoxy resins provide cured resin products with cost and performance intermediate between the epoxies and the generally more expensive cyanate homopolymer. tent of LCE was increased. At the same time, the mechanical properties were also improved and thermal expansion coefficients were lowed down. The thermal degradation temperatures showed little differences, while the residue char yields were slightly increased with the addition of LCE. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2964–2972, 2008

**Key words:** liquid crystalline polymers; modification; thermosets; mechanical properties; thermal properties

Therefore, the cyanate ester/epoxy blends are also widely used in microelectronic industry.

Though cyanate resins and their blends with epoxy resins (CE/EP) are known to be relatively tough compared with other rigid thermosetting polymers, some applications required improved fracture toughness.<sup>2,3</sup> The toughening of polycyanurates was previously achieved by the incorporation of modifiers, such as thermoplastics like polysulfones,<sup>4,5</sup> poly (ether sulfone),<sup>6</sup> poly(ether-imide),<sup>7,8</sup> and so on. However, the thermoplastics are usually very difficult to be dispersed in precursors and always sharply increase the viscosity of the blends.

Recently, liquid crystalline (LC) thermosets have drawn attention as a new type of material, combining the advantages of liquid crystalline polymers and highly crosslinked thermosets.<sup>9,10</sup> Many research groups have studied the synthesis, curing behavior, and mechanical properties of liquid crystalline thermosets.11-15 Various liquid crystalline thermosets with different mesogenic units and reactive end functional groups have been prepared. Mallon et al. studied liquid crystalline epoxy (LCE) resins with aromatic ester unit in the main chain.<sup>16</sup> Serra et al. synthesized a series of liquid crystalline azomethynic epoxy resins with different spacers, and studied their curing behaviors with different aromatic diamines and other hardeners.<sup>17,18</sup> Among these materials LCE resins have gained considerable interest due to their advantages like controllable curing rate, high

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Scheme 1 Chemical structures of epoxy, cyanate ester resin and liquid crystal.

thermal and chemical resistance, and good mechanical properties.

The incorporation of mesogens into thermoset networks as well as the use of new crosslinking reagents results in network passing through a mesophase while curing, and retains a mesophase in the final structure. The retained mesophase structure would increase the fracture toughness of the network, and these materials are expected to have applications as structural and self-reinforced materials.

In our previous works,<sup>19–21</sup> we have synthesized a series of LCE resins with aromatic azomethine groups, which possessed very good properties including easy synthesis, high yields, broad meso-genic region, and excellent thermal mechanical properties. These LCE resins have shown very good performances for the modification of epoxy and bismaleimide resins. In this work, we studied the influences of mesogenic epoxy modifiers concentration on the curing process, morphology, processing properties, and thermal physical properties of CE/EP resin blends.

#### **EXPERIMENTAL**

#### Materials

Diglycidyl ether of Bisphenol A (DGEBA) was supplied by Dow Chemical (DER331, with epoxide equivalence weight in the range of 182–192 g/eq). A bisphenol A dicyanate ester resin (BADCy) 4,4'-Isopropylidenediphenyl cyanate, with cyanate equivalent weight 139, melting point  $81^{\circ}$ C, was supplied by Shanghai Huifeng Technical and Business (Shanghai, China). Copper acetoacetate (Cu(AcAc)<sub>2</sub>) and nonylphenol was purchased from the Aldrich Chemical. Other chemicals (Sinopharm Chemical Reagent, Shanghai, China) for synthesis of LCE resin were used as purchased. The solvents were pretreated according to general process before use.

*N*,*N*'-bis [4-(2,3-epoxy propoxy phenyleneininomethyl)]-2,2'-dimethyl biphenylene (LCE, Scheme 1) was synthesized according to our previous work.<sup>20</sup> The LCE have a mesogenic region of 150–215°C as we have characterized before.

The homogeneous mixture of liquid crystal modified cyanate ester/epoxy was prepared by dissolving LCE to the stirring epoxy monomer at  $150^{\circ}$ C under nitrogen gas, after the mixture had cooled to  $80^{\circ}$ C, CE was added and stirred vigorously for 5 min till CE was completely dissolved. Copper acetoacetate (0.05% of total weight of blends) and nonylphenol (2% of total weight of blends) catalyst were used in preparing all the samples. The samples were degassed under vacuum for a few minutes. The weight composition and the code names of the blends in this study are listed in Table I. The curing schedule were performed at  $171^{\circ}$ C for 1 h and postcured at  $200^{\circ}$ C for 4 h.

For fracture toughness study, the above-prepared blends in solution were degassed, and then poured into a mold that had been preheated to 150°C to

TABLE I Compositions of Liquid Crystalline Epoxy Modified CE/EP Resin Blends

				Cu	
Blend code	BADCy	DGEBA	LCE	$(AcAc)_2$	Nonylphenol
CE/EP	42	56	_	0.05	2
5 wt %-LC	40	53	5	0.05	2
10 wt %-LC	38	50	10	0.05	2
15 wt %-LC	35	48	15	0.05	2
20 wt %-LC	33	46	20	0.05	2

prevent fast cooling of the resin. The molds consisted of a sandwich of steel plates (12 cm by 24 cm) separated by a 6-mm spacer of PTFE and held together by binder clips. The mold surfaces were polished and a mold release applied prior to each use.

The mold filled with the CE/EP blends was placed in an oven set at a curing temperature of 170°C for 2 h. Then the temperature was raised to 200°C for 5 h of postcure. The molds were removed from the ovens and the sample plaques extracted. Each plaque was cut into bars of 40  $\times$  10 mm<sup>2</sup> and machine the bars into ASTM D638 Type V tensile specimens with a gauge width of between 2.5 and 3.5 mm.

## Instruments

Infrared spectra were recorded on a Nicolet NEXUS 470 Fourier transform infrared (FTIR) spectrometer using samples in KBr pellets. Dynamic study of curing behavior was undertaken with Pyris1 type differential scanning calorimetry (DSC) calorimeter (Perkin–Elmer), which was heated from room temperature up to 400°C at a heating rate of 10°C/min, in a nitrogen atmosphere. Pure indium was used as a standard for calorimetric calibration. A small quantity of the sample (8–12 mg) was used for the DSC studies in aluminum cell. An identical empty cell was taken as reference.

The morphologies of the cured blends were observed under a scanning electron microscope (SEM) (Tescan TS 5163 MM, Czech) at 20 kV accelerating voltage. The sample was fractured in liquid nitrogen, then mounted on a sample holder using an electrically conductive paint as an adhesive and coated with a thin gold layer by plasma sputtering to avoid a charging effect due to nonconductivity of the polymer.

Thermogravimetric analyses (TGA) were performed from room temperature to 800°C on powdered samples with masses between 8 and 15 mg using a Pyris 1 Thermogravimetric analyzer (Perkin– Elmer) at a heating rate of 10°C/min in a nitrogen atmosphere.

To investigate the dimensional stability of the cured blends thermal mechanical analysis was performed using TMA 2940 (TA Instruments) Thermal mechanical analysis (TMA) with the cured sheetshaped specimens. Each specimen was prepared in a cube shape with a dimension of  $5 \times 5 \times 0.5$  mm<sup>3</sup>. The frequency was 1 Hz and the scanning rate was  $10^{\circ}$ C/min from room temperature to  $300^{\circ}$ C.

The rheological variations of the blends during cure reaction were recorded on ARES-4A rheometers by TA Instruments: About 1 g of the blend was sandwiched between two round plates and softened at 50°C for 2 min, and then the plate distance was then adjusted to about 1 mm. For dynamic study, the temperature was raised at a rate of  $3^{\circ}$ C/min to 200°C. For isothermal study, the temperature was raised quickly at a rate of 100°C/min to the preset curing temperature. All the blends were tested under a parallel plate mode with a controlled strain of 1% to ensure that measurements were performed under linear viscoelastic conditions. The test multi-frequencies are set at 1, 2, 5, 10, and 20 rad/s.

Tests of the fracture mechanics were carried out on sharply notched three-point-bending specimens based on ASTM E 399-83-A3 with a crosshead speed of 1 mm/min. The fracture toughness ( $K_{IC}$ ) and the fracture energy ( $G_{IC}$ ) were then calculated according to the standard. In the mechanical tests, dumbbellshaped specimens based on ASTM D 638-82a type V were used to determine the tensile properties of LCE modified CE/EP blends on an Instron (Instron, High Wycombe, Bucks, UK) model 5565 tensile tester at a constant crosshead speed of 1.0 mm/min.

### **RESULTS AND DISCUSSIONS**

### Miscibility of LCE with CE/EP

Polarized optical microscope (POM) was used for the miscibility study of LCE with CE/EP blends during heating process. To keep the blends reacting at the lowest curing rate during this study, catalysts were not added and the heating rate was kept at 2°C/min, which is quite quicker compared with ordinary phase diagram analysis. However, this method could provide a primary knowledge of the structure change of the blends with LCE concentration at least.

At low temperature, the samples observed by POM were yellow opaque blends of liquid epoxy with crystalline LCE and some CE parts. Under POM, it can be seen some color patterns of crystals. Increasing the temperature, some of the color patterns would disappear while the residue would change their dimensions and distort under shear at the crystal-LC transformation. Further heating the sample would result in the transition of LC to isotropic and the POM observation window being black.

To understand the effect of LCE weight percentage on the miscibility of blends and mesogenic state transition, a broad LCE to CE/EP ratio were studied other than the composition listed in Table I. As one can see from the phase diagram of the LCE modified CE/EP blends (Fig. 1), the mesogenic phase is quite narrow at low LCE content, and the LC phase broadened with the increase of LC content. At the same time, the temperatures of both melting and clear point rose with the increase of LC concentration.



Figure 1 Phase diagram of LCE modified CE/EP blends.

The reaction mechanism of cyanate ester resin coreacted with epoxy resin have been studied for a long time as published in numerous literatures. The curing reactions between cyanate esters and epoxy resin have been proposed by Bauer pathways<sup>22</sup> (Scheme 2) that involve: (1) cyanurate formation through trimerization of cyanate ester, (2) insertion of glycidyl ether epoxide into aryl cyanurate, (3) rearrangement of aryl cyanurate into alkyl isocyanurate, and (4) oxazolidinone formation through the reaction of epoxy and cyanate ester.

To study the effects of LCE on the cure reaction of cyanate ester and epoxy functions groups, we used FTIR to study blends with different LCE/CE mole ratio. The consumption of cyanate ester group was clearly demonstrated by the decrease of the characteristic epoxy peak at 2230  $\text{cm}^{-1}$  together with the epoxy group at 915  $\text{cm}^{-1}$ .

The appearance of cyanurates and Oxazolidinone groups at 1565 and 1760 cm<sup>-1</sup> attributed to the homopolycyclotrimerization of cyanate ester and its coreaction with epoxy group. The hydroxyl group as a result of side-reaction of epoxy and cyanate group showed a peak at 3400 cm<sup>-1</sup>. Figure 2 shows the FTIR results of cured EP/CE and LCE/CE blends of ratio 2 : 1 and 1 : 2 as examples.

By using phenyl ring vibrations at 1610 cm<sup>-1</sup> as inner standard, the peak area of triazine to Oxazolidinone could be calculated to study the effects of CE/LCE ratio on curing reaction. As shown in Table II, the ratio of Oxazolidinone to triazine intensity increased with the increment of epoxy or LCE content due to the coreaction of triazine with epoxy group. For DGEBA/BADCy blends, when the sample contains excess DGEBA epoxy resin (molar ratio of EP/CE = 1 : 0.5), the peak ratio of cyanurate to oxazolidinone is less than 0.1. Therefore, the oxazolidinone formation is the dominant curing reaction for samples containing excess epoxy resin. On the other hand, when the samples contain excess cyanate ester (molar ratio of EP/CE = 1 : 2), the peak ratio of cyanurate to oxazolidinone is greater than 0.67. The formation of cyanurate is clearly the dominant curing reaction in this case.

However, compared with the CE/EP blends, LCE/CE blends have a different result when the LCE content was increased, i.e., the ratio of oxazolidinone to triazine intensity dropped down sharply. This result might indicate an incomplete reaction of epoxy groups with the triazine groups.

To understand the above incomplete reaction results, both of the morphology and mechanical



**Scheme 2** Coreaction scheme proposed between cyanate ester and epoxy groups.



**Figure 2** Comparison of FTIR spectra for LCE/CE and EP/CE blends.

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Ratio of E	P to CE	Cyanurate triazine 1565 cm <sup>-1</sup>	Oxazolidinone 1760 $\text{cm}^{-1}$	Ratio of triazine to oxazolidinone
EP/CE	1:0.5	0.15	2.41	0.06
	1:1	0.62	2.14	0.29
	1:2	2.32	3.49	0.67
LCE/CE	1:0.5	0.43	0.49	0.88
	1:1	1.05	0.97	1.08
	1:2	1.96	1.11	1.77

 TABLE II

 The Ratio of Cyanurate Triazine to Oxazolidinone in Different CE/EP (LCE)

 Composition

properties of LCE modified CE blends were studied. Figure 3 shows the fracture surfaces of LCE modified CE blends with different LCE concentration. At low LCE content as in LCE/CE = 1 : 2 (mole), LCE were completely dissolved in CE matrix and form a homogenous phase structure. Increase of the LCE





**Figure 3** Morphologies of the LCE modified CE systems with different LCE/CE mole ratio. (a) LCE/CE = 1 : 2, (b) LCE/CE = 1 : 1, and (c) LCE/CE = 2 : 1.



Figure 4 DSC scanning of LCE modified CE/EP blends at a heating rate of  $10^{\circ}$ C/min.

content as in LCE/CE = 1 : 1 (mole) resulted in a phase separation of LCE from CE-rich matrix, as one can see from Figure 3, dispersed particles with diameter about 10  $\mu$ m appeared in CE-rich matrix. Further increase the LCE content as in LCE/CE = 2 : 1 (mole), particles with larger diameter about 20  $\mu$ m were founded in CE-rich matrix [Fig. 3(c)]

Related to the miscibility of LCE with CE, the above incomplete reaction of epoxy group might be attributed to the phase separation of LCE from CE-rich phase, which prevented the epoxy groups in LCE particle to react with triazine groups. Mechanical properties of these blends demonstrated the above phase separation, as we studied the tensile strength of these three samples, the results are 62, 51, and 44 MPa for LCE/CE = 1 : 2, LCE/CE = 1 : 1, and LCE/CE = 2 : 1 composites, respectively. Apparently, too much amount of LCE would deduce its immiscibility with CE resin, and result in a phase separation and incomplete cure reaction, thus the mechanical properties were also deteriorated by this redundant LCE content.

Therefore, we would focus on the blends with lower LCE concentration in the following studies.

## Chem-rhelogical behaviors of LCE modified CE/EP blends

The dynamic DSC scanning of the blends of LCE/ CE/EP with LCE content ranged from 5 to 20% were shown in Figure 4. For CE/EP, the exothermic reaction give a peak at about 290°C, while addition of LCE shifted the peak to low temperature, take 10 wt %-LC as an example, as 256°C. At the same time, both the starting and ending of exothermal peak shifted to lower temperatures with the increase of LCE content. It indicates that the curing reaction rate increased with increment of LCE content, which suggests that the addition of LCE accelerates the curing reaction of CE/EP. There may be two reasons that can be used to explain this phenomenon: first, the incorporation of azomethine group would low down the curing temperature in cyanate ester/epoxy resin blends as previously reported in epoxy resin blends where the LCE could also increase the curing rate<sup>20,21</sup>; second, as previously reported by Carfagna et al.,<sup>23</sup> LC epoxy could accelerate the curing rate of blends due to their mesogenic structures.

Associated with the DSC study is the rheological study, as many a time, CE/EP blends are used with processing concerns. Figure 5 shows the dynamic rheological study of 20 wt %-LC blends at heating rate of 3°C/min as an example. At low temperatures, elastic modulus was larger than that at medium temperature range of about 70 to  $150^{\circ}$ C, which might be a result of unmelted LCE as solid particle fillers. The beginning of exponential growth of elastic modulus took place near 170°C at this heating rate, and gelled at about 180°C shortly after the growth as the multifrequency scanning of tan  $\delta$  crossed over here. Therefore, the LCE modified CE/EP blends still had a broad processing window of low viscosity.

For isothermal study, Figure 6 gives an example of 20 wt %-LC blends cured at 170°C. At the beginning of curing reaction, the blend showed a quite low viscosity as about 0.05 Pa s, which is approximately the value of complex viscosity at 1 Hz. It can be seen from Figure 6, at the beginning, loss modulus G' are larger than elastic modulus G' at all frequencies, while G' grew quickly at the exponential growth stage. The crossover points of G' and G'' at about 750 s at 170°C for 20 wt %-LC, at about the same time, the multi-frequency scanning of tan  $\delta$  also crossed over. This result demonstrated the gelation might be



**Figure 5** Dynamic rheological study of 20 wt %-LC blends at heating rate of 3 $^{\circ}$ C/min at different frequencies.

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**Figure 6** Isothermal study of the rheological behavior of 20 wt %-LC blends at different frequencies.

either the crossover point of G' and G'', or the point of tan  $\delta$  at different frequencies, though the later is more credible for most systems.

#### Thermal properties of LCE modified CE/EP

TMA was used to study the glass transition temperature and thermal expansion coefficient of LCE modified CE/EP blends. Table III shows  $T_g$  and CTE values below and above  $T_g$ . Apparently, The TMA  $T_g$  of rigid-rod LCE modified CE/EP blends were higher than that of CE/EP blends,  $T_g$  increased with the increment of LCE content, indicating that the presence of LCE in rigid structures have a positive effect on the glass transition.

The coefficient of thermal expansion of CE/EP is the highest (54  $\mu$ m/m<sup>-1</sup>/K<sup>-1</sup>) among the test samples before  $T_g$ , and is also higher than that of LCE modified CE/EP blends above  $T_g$ . With the addition of LCE, all the CTE below  $T_g$  decreased when the LCE content was increased, which might be resulted from the rigid-rod structure of LCE confining the molecular motion of CE/EP below  $T_g$ . Therefore, LCE would be a good modifier for electronic materials, which need low CTE to control dimension stability and lower inner stress.

TABLE III Glass Transition Temperature and Coefficient of Thermal Expansion of LCE Modified CE/EP Blends

		CTE ( $\mu m/m^{-1}$ , $K^{-1}$ )		
Sample	$T_g(^{\circ}C)$	$\overline{\alpha_1}$ , below $T_g$	$\alpha$ , above $T_g$	
CE/EP	171	53.6	176.9	
5 wt%-LC	173	49.4	185.4	
10 wt%-LC	177	45.9	170.6	
15 wt%-LC	182	43.7	168.0	
20 wt%-LC	193	42.0	172.6	



**Figure 7** TGA thermograms of full cured LCE modified CE/EP blends.

As to the TGA study in nitrogen, the starting temperatures of weight loss (5% weight loss) are from 364 to 377°C. Figure 7 presents the thermograms obtained for the five systems. It was observed that all LCE modified EP/EP systems manifested almost identical decomposition pattern, and their curves were nearly superposable throughout the temperature region below 450°C. Maximum decomposition temperatures of the systems are also the same, while the residue char yields have differences. Increment of LCE content increased the char yields of blends at 600°C (Table IV), as the proportion of C/H increases with the substitution of DGEBA by the LCE resin, this proportion affects the char yield and may have a positive effect on flame retardance for electronic materials.

# Morphology and mechanical properties of LCE modified CE/EP

It had been reported<sup>24</sup> and also found in our previous works that a fibrillar or grooved fracture surface was observed in the crack fracture of LCE based

TABLE IV							
<b>Thermal Properties</b>	of	LCE Modified	CE/EP	Blends			

Sample	$T_d (^{\circ}C)^{a}$	PDTmax (°C) <sup>b</sup>	Char yield (%) <sup>c</sup>
CE/EP	377	426	19.2
5 wt%-LC	370	420	21.0
10 wt%-LC	364	421	23.0
15 wt%-LC	375	422	24.4
20 wt%-LC	368	424	25.5

<sup>a</sup> Five percent decomposition temperature under a nitrogen atmosphere.

<sup>b</sup> Maximum decomposition temperature.

<sup>c</sup> At 600°C under a nitrogen atmosphere.



DATE: 01/18/07 50 µm Vega @Tescan Device: TS5136MM Fudan University Image

**Figure 8** SEM imagine of oriented site of the LCE modified CE/EP blends (20 wt %-LC).

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thermoset. Before curing reaction, LC molecular dispersed well in thermoset resins, however, the curing reaction results in self-oriented alignment of LC molecules in the blend due to its rigidity of mesogen component, and then microfibers was formed, followed by skin-core structure with thermoset wrapped the microfibers in the cured thermoset resins.

In this work, we also investigated the effects of LC concentration on the phase structures. At low LCE content, like 5 wt %-LC, the LC was dissolved into CE/EP completely and formed a homogenous structure. Increase of the LC content results in the formation of fibrillar structures in some oriented sites in blends with LCE content above 15%. Figure 8 shows the morphology of fractured surfaces of 20 wt %-LC blend as an example. In this photo, the oriented sites of LC fibril were magnified to show its structure.

To understand the relation between the phase morphology and the mechanical properties, the tensile and fracture toughness properties of CE/EP and its blends with LCE were investigated. The mechanical properties of all the systems cured at  $170^{\circ}$ C for 2 h and postcured at  $200^{\circ}$ C for 4 h are presented in Table V with error about 5%. Compared with the CE/EP system, the results revealed the increase of fracture toughness, tensile strength, modulus, and strain to break for the cured blends with liquid crystalline modifiers.

As for Young's modulus, it was increased for LCE modified systems in comparison with the neat CE/ EP system, which showed a trend like those of the tensile strengths and elongations. Also, Young's modulus was generally highest for the 20 wt %-LC system. Because Young's modulus represents the extent of resistance to deformation for a sample in the initial stage of a tensile test, during which the sample would be unbroken, it is connected to the degree of tightness of the network rather than the degree of crosslinking of the sample. For higher content of LC modified systems, a higher degree of mesogenic structure formed can lead to a higher value of Young's modulus for the whole sample.

For the fracture properties, adding LC would lead to an increase in both the fracture toughness (by 10– 30%) and the fracture energy (by 15–40%); this shows the same trend as that of the tensile strength and elongation at break. For the 20 wt %-LC system, both the fracture toughness and fracture energy were the highest. This was attributed to the formation of mesogenic fibril structure. These mechanical test results can be well related to their morphologies due to the toughening effect of LC molecules.

#### CONCLUSIONS

A LCE resin with azomethine groups was employed to modify a blend of BACDy cyanate ester resin and DGEBA epoxy resin. The curing rates of blends were measured simultaneously with DSC and rheometers. The results showed that the curing rate of CE/EP was affected by the composition in the blend, the curing rate increased with the increment of LCE content. Too much amount of LCE would induce phase separation from CE matrix during its blending with CE resin, thus results in an incomplete reaction of LCE. The mechanical properties were improved due

 TABLE V

 Mechanical Properties of Fully Cured LCE Modified CE/EP Systems

Sample	Fracture toughness $K_{IC}$ (MPa m <sup>1/2</sup> )	Fracture energy $G_{IC}(J m^{-2})$	Modulus (GPa)	Tensile strength (Mpa)	Elongation at break (%)
CE/EP	0.29	254	3.06	41.6	2.16
5 wt%-LC	0.32	293	3.13	48.5	3.05
10 wt%-LC	0.34	328	3.16	55.6	3.37
15 wt%-LC	0.35	347	3.22	58.3	3.48
20 wt%-LC	0.36	364	3.35	62.4	3.86

to the formation of oriented fibril structure by LC molecules. Thermal expansion coefficients were lowed down with the increase of LCE content. The thermal degradation temperatures show little differences, while only the residue char yields were slightly increased with the addition of LCE.

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