Modification of an *o*-Cresol Formaldehyde Epoxy Resin by the Thermotropic Liquid Crystalline Polymer

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ABSTRACT: Two novel liquid crystalline polymers, poly-diethyleneglycol bis(4-hydroxybenzoate) terephthaloyl and block copolymer (PDBH), were synthesized by condensation reaction. The blends of the two liquid crystalline polymers and *o*-cresol formaldehyde epoxy resin were prepared by linear phenol-formaldehyde resin as curing reagent. Both mechanical and thermal properties of the blends containing liquid crystalline polymer were improved to a certain extent. By adding 5 wt % PDBH, the impact strength, bending strength, and the glass transition temperature were enhanced by 128%, 23.84%, and 28°C, respectively, compared with the unmodified version. The results of curing kinetics showed that the curing reaction active energy of the modified system by PDBH decreased from 79.70 to 70.26 kJ/mol. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1626–1631, 2005

Key words: *O*-cresol formaldehyde epoxy resin; liquid crystalline polymer; toughening; curing kinetics

INTRODUCTION

o-Cresol formaldehyde epoxy resin (O-CFER) was exploited to cater to the rapid development of semiconductor and electron industry. A three-dimensional network structure with highly crosslinking density was formed in the O-CFER curing due to the fact that each benzene ring in O-CFER contains an epoxy group. O-CFER contains abundant phenolic frameworks, which present excellent heat stability, mechanical strength, electrical insulation, and water and chemical inertness. Another character of O-CFER is that its epoxy value is nearly stable with variation of the softening point. Moreover, the low intrinsic viscosity endows its dominant craftwork stability and craftwork processability. Therefore, O-CFER has been used as the packaging material of the integrated circuit, electron parts of an apparatus, and feeble electricity goods in the field of semiconductor industry. However, its highly crosslinked structure results in significant brittleness and thus limits its application. To overcome this weakness, two common approaches for modifying epoxy are the introduction of functionalized reactive rubbers or thermalplastics.[1] Reactive rubbers such as carboxyl-terminated butadiene acrylonitrile, amine-terminated butadiene acrylonitrile, or epoxy-terminated butadiene acrylonitrile have been used to improve the toughness of O-CFER. However, the pressure of the rubbery phase usually results in inferior properties such as lower glass transition temperature (T_g) and elastic modulus under wet or hot conditions. Toughening epoxy resin by thermalplastics presents significant problems in cure process due to the large viscosity difference between the thermalplastics and the epoxy resin.

As a novel kind of toughening agent, thermotropic liquid crystalline polymer (TLCP) has attracted considerable interest in the aspect of modifying epoxy resin recently.[2–6] It can not only improve the toughness and strength of epoxy resin but also modify the heat resistance. Most of the current reported liquid crystalline polymers are liquid crystalline polyester or polyurethane. It is difficult to modify *o*-cresol formaldehyde epoxy resin due to the poor compatibility of these liquid crystalline polymers and *o*-cresol formaldehyde epoxy resin. So we synthesized the liquid crystalline polyester polydiethyleneglycol bis(4-hydroxybenzoate) terephthaloyl (PDBT) and its block copolymer, PDBH, whose main chain includes polar groups to improve the interfacial interaction of TLCP and *o*-cresol formaldehyde epoxy resin. The synthesis route of PDBT and PDBH is shown in Scheme 1. To examine the role of this homemade liquid crystalline polymer, the structure and properties of the blends of PHDH or PDBT and *o*-cresol formaldehyde epoxy resin were evaluated.

EXPERIMENTAL

Materials

Methyl 4-hydroxybenzoate, diethyleneglycol, tetrabutyl tianate, tetrabutyl ammonium chloride, cyclopen-

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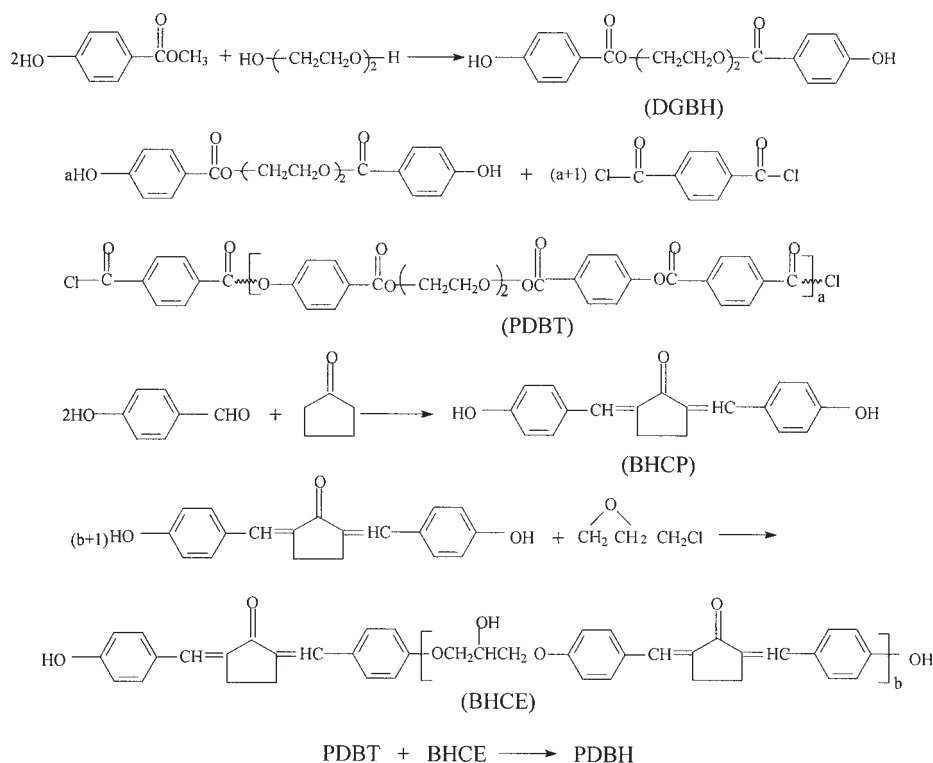
Scheme 1 Synthesis route of PDBT and PDBH ($a = 6$, $b = 2$).

tanone, and p-hydroxybenzaldehyde were used without further purification. Terephthaloyl dichloride was synthesized and purified by sublimation in our laboratory. Epichlorohydrin and 1,1,2,2-tetrachloroethane were dried with a molecular sieve. O-CFER (100 g resin contains 0.49 mol epoxy groups) was supplied by Yueyang Petrochemicals Co. Linear phenol-formaldehyde resin (LPR, 100 g resin contains 0.98 mol hydroxy groups) was supplied by Zhongdianhuawei Electron Limited Co. (China).

Synthesis of monomers and polymers

The monomer diethyleneglycol bis (4- hydroxybenzoate) (DGBH) was synthesized according to Ref.[6]. A total of 7 g diethyleneglycol and 22 g methyl 4-hydroxybenzoate was dissolved in 40 mL 1,1,2,2-tetrachloroethane. The mixture was poured into a three-neck flask equipped with a water-separator and condensor. A total of 0.3 mL tetrabutyl titanate was added dropwise to the above solution slowly with electromagnetic stirring until the solvent approached the reflux temperature. The reaction didn't terminated until the calculated quantity of CH_3OH had been collected. The final product was washed with distilled water and methylbenzene after the solvent and excessive methyl 4-hydroxybenzoate were distilled out un-

der normal and reduced pressure, respectively. Yield was 80%; melt point was 105°C.

PDBT was synthesized as follows. 0.04 mol DGBH (13.84 g) and 0.04(a + 1)/a mol terephthaloyl dichloride were dissolved in 60 mL 1,1,2,2-tetrachloroethane. The mixture was stirred at 80–100°C for 2 h and then at reflux temperature for 10 h. Afterward, the mixture was poured into a beaker filled with 50 mL anhydrous alcohol, washed, filtered, and eventually dried in a vacuum oven at 100°C. The product (yield 90%) was characterized by FTIR, DSC, and POM.

Bis(4-hydroxybenzylidene) cyclopentanone (BHCP) was synthesized according to Refs.[7,8]. To a mixture of 1.68 g (0.02 mol) cyclopentanone and 4.88 g (0.04 mol) p-hydroxybenzaldehyde, 15 mL piperidine was added slowly dropwise so that the temperature did not rise above 40°C. Then the mixture was stirred at 80°C for 6 h. The reactant was diluted with 50 mL pyridine and poured into 500 mL cold water acidified with HCl. After being filtered, the final product (yield 75%) was washed two times with no-water alcohol and dried in a vacuum over 100°C. IR (KBr) was 3418, 1730, 1607, 1512, 1456, 1285, 1200, 1077 and 1019 cm^{-1}.

Bis(4-hydroxybenzylidene) cyclopentanone epichlorohydrin (BHCE) was synthesized as follows. 0.02 mol (1.85 g) epichlorohydrin and 0.02(b + 1)/b mol BHCP were poured into a three-neck flask equipped with
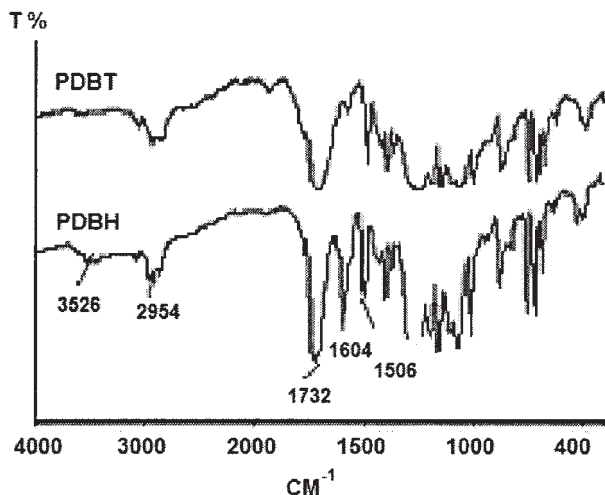
Figure 1 FTIR spectra of PDBT and PDBH.

Figure 2 DSC heating curves of PDBT and PDBH (20°C/min).

stirrer and attemperator. A total of 40 mL DMF and 2 mL 30% NaOH was added to the above mixture and 0.2 mL tetrabutyl ammonium chloride was dissolved to the solution. The mixture was stirred for 5 h at 50°C and then poured into a 100-mL beaker, washed with distilled water, and adjusted to pH 2 with HCl. The above solution was stirred for 2 h at high speed, filtered, and washed with distilled water three times. The obtained product was dried in a vacuum oven at 100°C. The yield was 85%, IR (KBr): 3435, 2925, 1679, 1599, 1511, 1456, 1256, and 1158 cm^{-1}.

The block copolymer PDBH was synthesized as follows. 10.0 g PDBT and equal mole BHCE were dissolved in 60 mL 1,1,2,2-tetrachloroethane. The mixture was poured into a three-neck flask equipped with stirrer and reflux condenser and was stirred at 80–100°C for 2 h and then reacted reflux for 20 h. After the solvent was removed, the product was washed with distilled water and anhydrous alcohol two times, respectively, and finally dried in a vacuum oven at 100°C. The structure and properties of the copolymer were characterized by FTIR, DSC, and POM.

Preparation of PDBH or PDBT/O-CFER/LPR blends

TLCP (PDBH or PDBT) and O-CFER were put into a flask at a certain proportion and stirred at 240°C.l The mixture was cooled to room temperature after TLCP was dissolved in O-CFER. A certain amount of LPR was added to the above system. The mixture was stirred at 140–160°C for 20 min so that LPR dissolved completely. The mixture was poured into a mold that had been heated at certain temperature and then the mold was degassed in a vacuum oven at 150°C. The blends were heated and cured at 180°C for 2 h and at
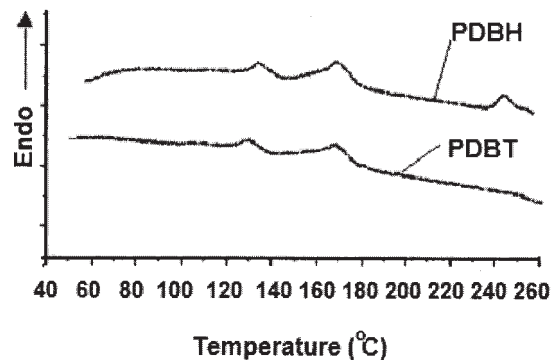
200°C for 2 h, respectively. IR of the cured blends indicated that the curing reaction was almost complete because the peak at 909 cm^{-1} (s,O-H) nearly disappeared.

Characterization and measurement

FTIR spectra of the synthesized monomers and polymers were measured with a Perkin-Elmer Spectrum One infrared spectrometer. Thermal properties of the polymer were examined in nitrogen using a Perkin-Elmer DSC-7 thermal analyzer at a heating rate of 20°C/min. The anisotropic and isotropic temperatures were determined with a polarizing microscope of Leica DMLP equipped with a heated stage. Charpy unnotched impact strength measurements were carried out on an XJJ-5 impact tester; the dimensions of the samples were 80 × 10 × 4 mm. Bending strength was determined with a Shenzhen Reger RGT-5 universal testing system.

RESULTS AND DISCUSSION

Characterization of liquid crystalline polymers

Figure 1 shows the IR spectra of PDBH and PDBT. For
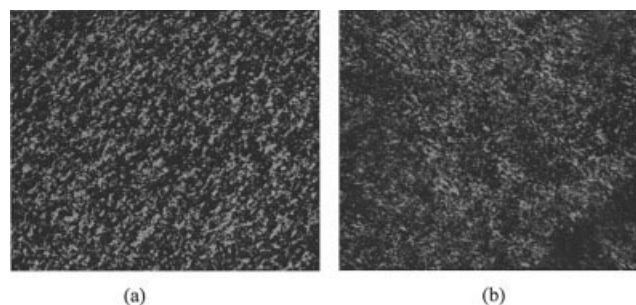

Figure 3 Polarized optical micrographs of PDBT and PDBH. (a) PDBT at 189°C; (b) PDBH at 185°C.
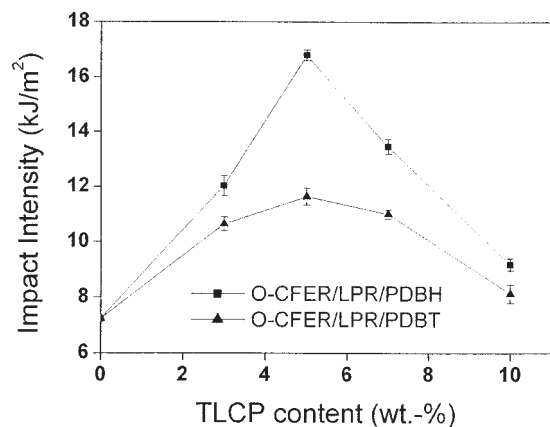
Figure 4 Impact strength as a function of TLCP content.

PDBH, the peak at 3526 cm^{-1} is assigned to terminal O-H stretching of phenol groups. The peak at 2954 cm^{-1} is the characteristic absorption of –CH$_2$- and the absorption at 1732 cm^{-1} results from ester group adjacent to benzene rings. The peaks at 1604 and 1506 cm^{-1} are due to the stretching of C = C in the main chain and C = C in the benzene rings, respectively. For PDBT, the O-H peak isn't distinct, owing to being terminated by chloride.

Thermal properties of the polymers are shown in Figure 2. For PDBH, there are three peaks at 139, 178, and 240°C, which are representative of the glass transition (T_g), nematic liquid crystalline phase transition (T_{KN}), and clearing point of liquid crystalline (T_{NI}), respectively. The block copolymer PDBH presents a liquid crystal phase from 178 to 240°C. For PDBT, there are only two peaks at 130 and 172°C, which are representative of the glass transition (T_g) and nematic liquid crystal phase transition (T_{KN}), respectively, but the clearing point of liquid crystal (T_{NI}) isn't distinct.

Figure 3 shows the POMs of PDBH and PDBT at 189 and 189°C, which present highly birefringent and nematic liquid crystal behavior. The polymer starts to
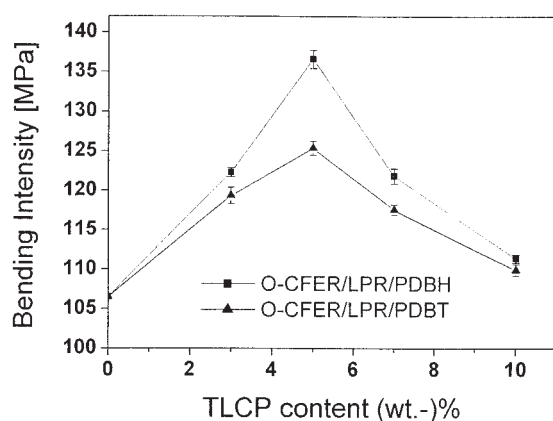
TABLE I
Glass Transition Temperature (T_g) of Blends for Different TLCP content

TLCP (wt %)	0	3	5	7.5	10
O-CFER/LPR/PDBH	98.0	124.5	126.1	123.2	120.3
O-CFER/LPR/PDBT	98.0	117.9	120.9	118.4	115.7

melt and form bright regions at a temperature higher than 178°C for PDBH and 172°C for PDBT, respectively, and the threaded nematic texture was observed. When the temperature is higher than 240°C for PDBH and 230°C for PDBT, the field of vision turns to be dark due to the liquid crystal phase disappearance of the polymers.

The properties of O-CFR/LPR/PDBH and O-CFR/LPR/PDBT blends

Mechanical properties, especially impact strength, were very important for epoxy resin. Figure 4 shows the dependence of impact strength of the blends on weight percent of PDBH or PDBT. When the content of TLCP is lower than 5 wt %, the impact strength increases gradually with increasing content. The impact strength of the O-CFER/LPR/PDBH blend attains the maximum at 5 wt % PDBH, which is 2.28 times that of the unmodified system, namely from 7.37 to 16.80 kJ/m^2. For the O-CFER/LPR/PDBT system, the impact strength is lower than the former but higher than in the unmodified version, 11.64 kJ/m^2 for 5 wt % PDBT. When the content of TLCP was higher than 5 wt %, the impact strength decreases gradually with increasing TLCP content. Figure 5 shows the dependence of the bending strength of the blends on the weight percent of PDBH or PDBT. Similar to impact strength, the bending strengths of 5 wt % PDBH and 5 wt % PDBT modified curing systems are 136.6 and 125.2 MPa, while that of the unmodified curing
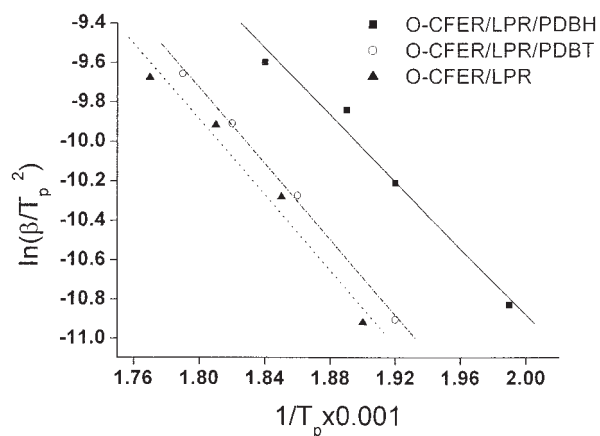

Figure 5 Bending strength as a function of TLCP content.

Figure 6 Curing kinetics curves of the blends

TABLE II
Curing Kinetics Data of the Blends

Curing system	E_a (kJ/mol)	n	A (K · S^{-1}) ($\times 10^7$)	K ($\times 10^{-3}$)		
				413K	433K	453K
O-CFER/LPR	79.70	1.09	1.52	1.26	3.71	9.80
O-CFER/LPR/PDBT	80.0	1.12	1.88	1.47	4.32	11.5
O-CFER/LPR/PDBH	70.26	1.14	0.35	4.53	11.7	27.6

system is 106.5 MPa. This indicates that the mechanical properties of o-cresol formaldehyde epoxy resin have been improved due to the addition of 5 wt % TLCP, and the effectiveness of adding PDBH is more remarkable than that of PDBT.

It is necessary that epoxy resin should possess good heat resistance in many cases. Generally, glass transition temperature (T_g) of epoxy resin represents the upper limit of its working temperature; therefore, T_g of blends was an important parameter of the heat resistance. The T_g of blends with the different content of PDBH and PDBT is listed in Table I. When the content of PDBH and PDBT was 5 wt %, the T_g of blends increased from 98 to 126.1 and 120.9°C, respectively. The reason why TLCP can improve T_g of the blends was mainly attributed to the rigid segments in PDBH or PDBT. The rigid segments possess the properties of enduring high temperature, so the addition of PDBH or PDBT improved the heat resistance clearly.

Curing kinetics

There are many methods for studying the curing reaction of epoxy resin such as DSC, solid state ^{13}C-NMR, and FTIR methods [9–12] DSC and FTIR are the common methods to study the curing reaction both in characterizing the curing behavior and in the crosslinked reaction process of epoxy resin. In this paper, DSC was utilized to investigate the curing kinetics at different heating rate of 5, 10, 15, and 20°C/min according to nonisothermal experiments. The curing reaction active energy (E_a) could be obtained from the equation $\ln(\beta/T_P^2) = \ln(AR/E_a) - E_a/RT_p$ on the basis of Kissinger, where β is the heating rate, R the gas constant, A the frequency factor, T_p the DSC peak temperature in K, and E_a the apparent activation energy in kJ/mol by plotting in $\ln(\beta/T_P^2)$ versus $1/T_p$. Figure 6 shows the relation between $\ln(\beta/T_P^2)$ and $1/T_p$ of unmodified and modified systems (10 wt % PDBH or 10 wt %PDBT). This indicates that E_a of the PDBH modified system decreased to 70.26 from 79.70 kJ/mol of the unmodified system, but E_a of the PDBT modified system shows less change compared with the unmodified system. The reaction order (n) and the reaction rate constant K could be calculated from the

equations $d\ln\beta/day(1/T_p) = -E_a/nR$ and $K = A\exp(-E_a/RT)$ according to the Crane and Arrhenius formulas. The results are listed in Table II.

From the data listed in Table II, the curing reaction is a 1st-order reaction according to the n values being near unity. The reaction rate constant (K) increased with gradual improvement of the curing reaction temperature. At the same temperature, the K value of O-CFER/LPR/PDBH system was higher than that of O-CFER/LPR system although the frequency factors (A) were opposite. This marks the significant acceleration of the curing reaction and the great decrease of the curing reaction temperature with the decreasing E_a. For the O-CFER/LPR/PDBT system, the curing reaction active energy (E_a) and the reaction rate constant (K) are not distinctly different compared to that of the neat epoxy resin curing system.

The reason why the curing reaction activation energy (E_a) decreased for PDBH is mainly that the carbonyl group of the heterocyclic cyclopentanone is an electron-withdrawing group and has little steric hindrance compared with the carbonyl group adjacent to benzene rings. When phenol –OH group of the LPR curing reagent reacted with the epoxy group of the O-CFER, the carbonyl group of the cyclopentanone caused a synergistic effect with the phenol –OH, so the addition of PDBH was favorable for the ring-opening reaction of the epoxy resin and decreased the curing reaction activation energy (E_a).

CONCLUSIONS

1. Two liquid crystalline polymers, PDBH and PDBT, were synthesized by polycondensation reaction in solution. The nematic liquid crystalline phase range, observed by POM, was from 178 to 240°C for PDBH and from 172 to 230°C for PDBT, respectively.

2. The mechanical and thermal properties including the impact strength, bending strength, and the glass transition temperature of the modified system were enhanced remarkably compared with the unmodified system, and the modification effect of O-CFER/LPR/PDBH blend containing block copolymer PDBH is superior to that of O-CFER/LPR/PDBT blend.

3. The results of curing reaction kinetics showed that the reaction activation energy (E_a) decreased and the reaction rate constant (K) increased by adding a small amount of PDBH into the O-CFER/FPR system.

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