

Blends of Liquid Crystalline Polyester–Polyurethane and Epoxy: Preparation and Properties

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ABSTRACT: A novel liquid crystalline polyester–polyurethane (LCPU) that contains polyester mesogenic units was synthesized in the present work. Through a careful investigation of the structure and morphology of the LCPU, it was found that the home-synthesized LCPU is a highly birefringent thermotropic nematic liquid crystal. After being blended with bisphenol-A epoxy, the liquid crystalline polymer can, simultaneously, improve the impact strength and

the glass transition temperature as well as the tensile strength and the tensile modulus of the blends. It was proved to be an efficient toughening agent for epoxy without the expense of other properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 783–787, 2003

Key words: blends; liquid-crystalline polymers (LCP); resins

INTRODUCTION

To modify the brittleness of epoxy resins, elastomers or rubbery thermoplastics are often incorporated as toughening agents through blending. However, this used to result in decreased strength and heat resistance of the matrix, failing to provide an overall improvement of the performance.^{1,2} In recent years, the application of liquid crystalline polymers in toughening epoxy has attracted considerable interest. Carfagna et al., for example, suggested that the addition of a small amount of a liquid crystalline polymer into epoxy could enhance the ductility of the matrix without sacrificing its glass transition temperature and other mechanical properties.³ Zhang et al. synthesized a series of reactive toughening agents containing both a flexible oligomer and a rigid liquid crystalline unit.⁴ It was demonstrated that the impact strength of epoxy was increased by three- to sevenfold, while the dynamic modulus and thermal properties were maintained. Considering the evident advantages of liquid crystalline polymers over conventional polymers in toughening epoxy, a novel liquid crystalline polyester–polyurethane (LCPU) was synthesized in the present work through the reaction of a liquid crystal-

line polyester, polyhexamethylene-bis-(4-oxybenzoates)–terephthaloyl (PHBHT), with the oligomers of 2,4-tolyene diisocyanate (TDI) and diethylene glycol (see Scheme 1). It was hoped that the —NCO groups on the chains of the LCPU might take part in the curing reaction with epoxy after blending and thus enhance the interfacial interaction in the blends containing epoxy. To examine the role of this home-made liquid crystalline polymer, the structure and properties of the blends of LCPU and epoxy resin were evaluated (Scheme 1).

EXPERIMENTAL

Materials

Methyl-4-hydroxybenzoate, 1,6-hexandiol, TDI, 4,4'-diaminodiphenylsulfone (DDS), and diethylene glycol (Aldrich) were used without further purification. Terephthaloyl dichloride, with a melting point of 81°C, was synthesized and purified by subliming in our laboratory. Bisphenol-A epoxy resin (CYD128, 100 g epoxy resin contains 0.52 mol epoxy groups) was supplied by the Yueyang Petrochemicals Co. (China).

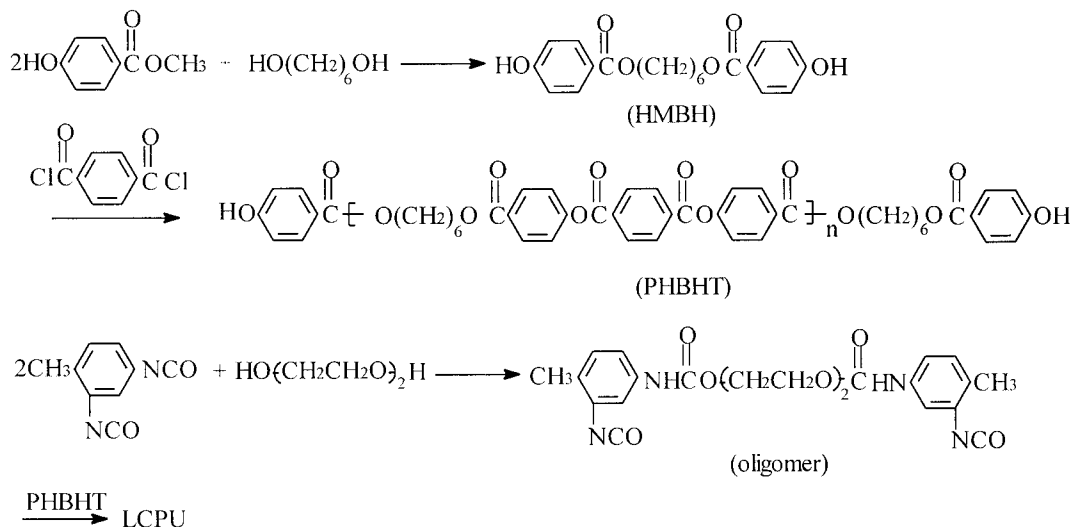
Synthesis of hexamethylene bis(4-hydroxybenzoate) (HMBH)

HMBH was synthesized according to Ref. 5 by molten-state transesterification of methyl-4-hydroxybenzoate and 1,6-hexandiol. The product yield was 85%, m.p. 183°C. ¹H-NMR (DMSO): δ 10.2(2H, Ar—OH), δ 7.8(4H,Ar), δ 6.8(4H,Ar), δ 4.2(4H,—O—CH₂—),

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Scheme 1

δ 1.7(4H,CH₂), δ 1.4(4H,CH₂). IR(KBr): 3390, 2941, 1681, 1607, 1592, 1511, 1284, 961, 853, 770 cm⁻¹. ANAL. Found: C, 66.89 wt %; H, 6.12 wt %. Calcd for C₂₀H₂₂O₆: C, 67.06 wt %; H, 6.14 wt %.

Synthesis of PHBHT

HMBH (6 mmol) and terephthaloyl dichloride (5 mmol) were dissolved in 1,1,2,2-tetrachloroethane (50 mL) and then a minimum amount of pyridine was added dropwise. The mixture was stirred at 80°C for 2 h and at 150°C for 10 h, respectively. After the reaction, the mixture was poured into a beaker filled with 100 mL of 95% methanol, filtered, washed with water, and eventually dried in a vacuum oven at 80°C. The yield was 95% and the product (melting point, 224°C) was characterized by the typical infrared absorptions at 3407, 2939, 1719, 1502, 1266, 975, 873, 760, and 717 cm⁻¹.

Synthesis of LCPU

2,4-TDI (2.1 mmol), diethylene glycol (1 mmol), and PHBHT (2 mmol) were dissolved in 1,1,2,2-tetrachloroethane (30 mL). The mixture was stirred at 140°C for 4 h, and then the product was washed with petroether, filtered, and dried in a vacuum oven at 80°C. The yield was 85% and the product (melting point, 196°C) was characterized by the typical infrared absorptions at

3344, 2949, 2276, 1737, 1714, 1537, 1502, 1274, 872, 761, and 717 cm⁻¹.

Preparation of LCPU/epoxy blends

LCPU and bisphenol-A epoxy resin were put in a flask at a certain proportion and stirred at 230°C for 10 min. When the system was cooled to 100°C, DDS was added. Then, the mixture was poured into a mold that had been heated to 120°C. The blends were subsequently cured at 160°C for 2 h and at 180°C for 2 h, respectively.

Characterization

Intrinsic viscosities of the polymers were determined by an Ubbelohde viscometer with a phenol/1,1,2,2-tetrachloroethane mixture (1:1) as a solvent at 30°C. ¹H-NMR spectra and infrared (IR) spectra were recorded on a Varian INOVA500 and a Perkin-Elmer Spectrum One Fourier transform infrared spectrom-

TABLE I
Intrinsic Viscosity (η_{iv}) and Thermal Properties of the Polymers

Polymers	η_{iv} (dL/g)	T_m (°C)	ΔH_m (J/g)
PHBHT	0.385	224	12.96
LCPU	0.426	196	7.09

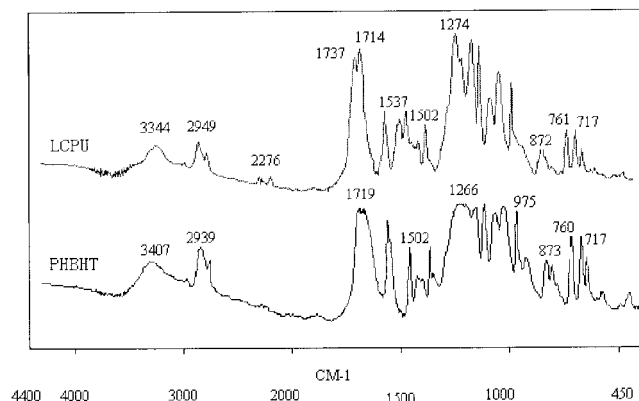


Figure 1 FTIR spectra of PHBHT and LCPU.

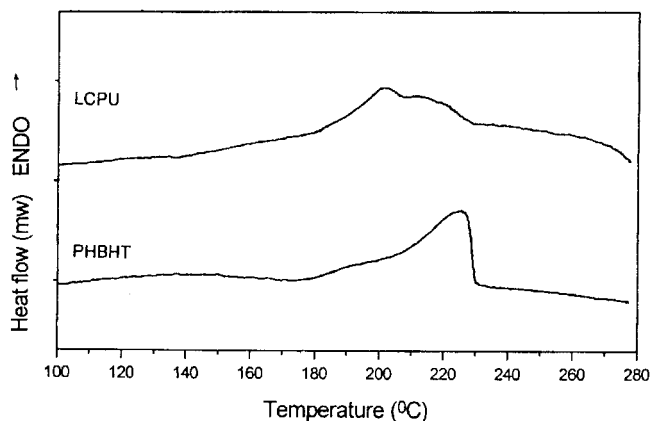


Figure 2 DSC heating curves of PHBHT and LCPU.

ter, respectively. Differential scanning calorimetry (DSC) measurements were conducted on a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20°C. Phase transitions and optical anisotropies were observed by an Olympus BH-2 polarizing microscope equipped with a heating stage. Tensile strength and moduli were determined with a Shenzhen Reger RGT-5 universal testing system. Charpy unnotched impact strength measurements were carried out on an XJJ-5 impact tester.

RESULTS AND DISCUSSION

As both PHBHT and LCPU are insoluble in the usual organic solvents, their intrinsic viscosities, η_{iv} , had to be measured in a component solvent of phenol/1,1,2,2-tetrachloroethane. From Table I, it is seen that the η_{iv} of LCPU is 0.426 dL/g, significantly higher than the value of PHBHT (0.385 dL/g). Clearly, it can be attributed to the molecular weight increase as a

result of the reaction between PHBHT and the oligomers produced by diethylene glycol and TDI.

Figure 1 shows the IR spectra of PHBHT and LCPU. For PHBHT, the peak at 3407 cm^{-1} is assigned to terminal O—H stretching of phenol groups, and the adsorption at 1719 cm^{-1} results from ester groups adjacent to benzene rings. For LCPU, the peaks at 3340 and 1537 cm^{-1} are due to N—H groups, generated by the reaction of the terminal phenol groups of PHBHT with —NCO in the aforesaid oligomers.

Thermal properties of the polymers are illustrated in Figure 2 and Table I. The DSC heating curves of PHBHT and LCPU show endotherms at 240°C ($\Delta H_m = 12.96$ J/g) and 190°C ($\Delta H_m = 12.03$ J/g), respectively. Both the melting temperature, T_m , and the melting enthalpy, ΔH_m , of LCPU are lower than those of PHBHT, due to the addition of flexible diethylene glycol and structurally unsymmetrical TDI. Similar to the case of liquid crystalline polyurethane,^{6,7} the clearing temperature of the nematic phase and the cold-crystallization transition of LCPU were not detected by DSC. Besides, LCPU started to be decomposed when the temperature exceeded 280°C.

The examination of PHBHT and LCPU under a polarizing optical microscope indicated that they are highly birefringent and liquid crystalline. A threaded nematic texture was observed in two cases: PHBHT starts to melt and to form bright regions at a temperature higher than 224°C (Fig. 3), and the clearing point of the liquid crystalline domains becomes detectable above 300°C. For LCPU, the liquid crystalline threaded texture begins to appear at 200°C, but turns dark at 280°C due to the pyrolysis of the polymer.

Figure 4 and Table II show the glass transition temperatures, T_g 's, of the blends. Evidently, incorporation of LCPU can remarkably increase the T_g of the matrix. In general, the T_g of epoxy represents the upper limit

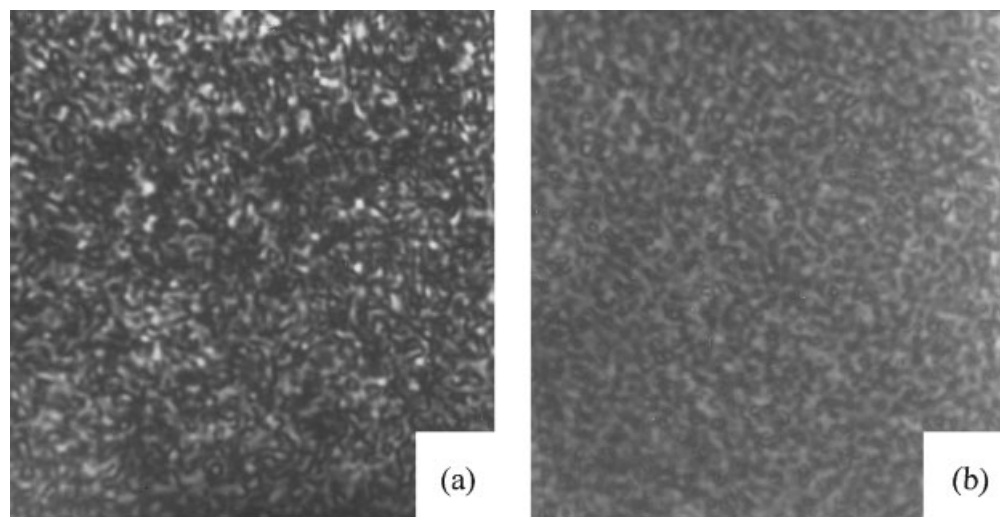


Figure 3 Optical micrographs of (a) PHBHT and (b) LCPU at 260°C.

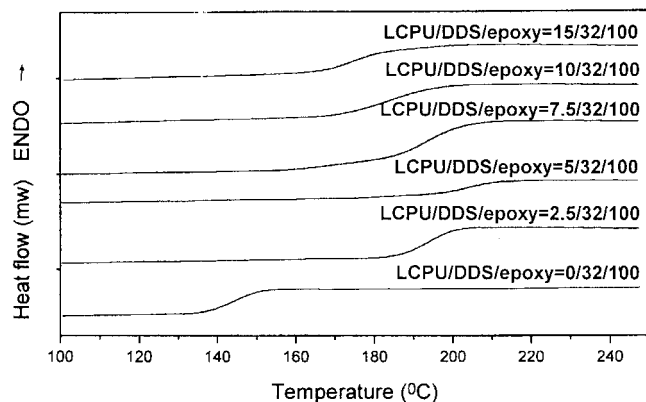


Figure 4 DSC curves of LCPU/epoxy blends.

of its working temperature. Conventional toughening methods by means of rubbery materials would reduce the T_g of epoxy,^{1,2,8,9} being unfavorable for the application under high-temperature conditions. Therefore, the T_g data of the blends strongly suggest that the current LCPU might bring about different effects on the properties' improvement of epoxy.

To evaluate this consideration, the mechanical performance of the blends was measured (see Table II). It can be seen that tensile strengths and tensile moduli of the blends increase with an increasing LCPU content. At a loading of LCPU/DDS/epoxy = 5.0/32/100, a maximum of impact strength appears, which is 3.5 times higher than that of the neat epoxy system. It should be noted that both the impact strength and the T_g of the blends decrease slightly when the ratio of LCPU/epoxy is over 5%. This might be a result of the changes in the microstructure of the blends as a function of the blending ratio. As shown by the optical micrographs in Figure 5, the bright domains of the liquid crystalline are well dispersed in the epoxy in the case of an LCPU/epoxy ratio of 5% [Fig. 5(b)] due to the reaction of the terminal —NCO groups of LCPU with the phenol groups of epoxy. When the LCPU content is further increased, however, phase separation appears [Fig. 5 (c)]. Consequently, the decrease in the interfacial area and the phase separation between LCPU and epoxy limits the increase of the impact strength and the T_g of the blends.

TABLE II
Thermal and Mechanical Properties
of LCPU/epoxy Blends

Blending composition (LCPU/DDS/epoxy) (wt)	T_g (°C)	Impact strength (kJ/m ²)	Tensile strength (MPa)	Tensile modules (GPa)
0/32/100	144	12.0	58.4	1.02
2.5/32/100	193	17.5	70.2	1.09
5.0/32/100	204	42.8	78.7	1.15
7.5/32/100	199	33.9	80.3	1.18
10/32/100	198	30.6	86.1	1.55

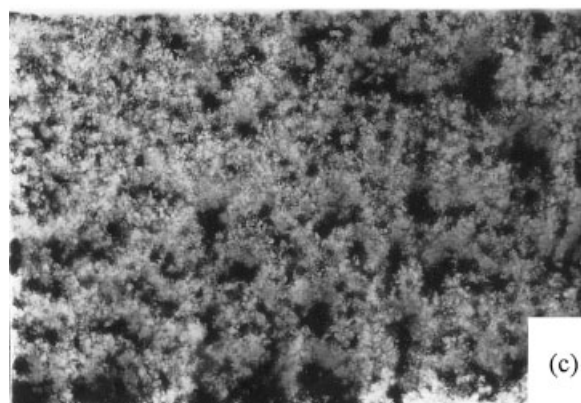
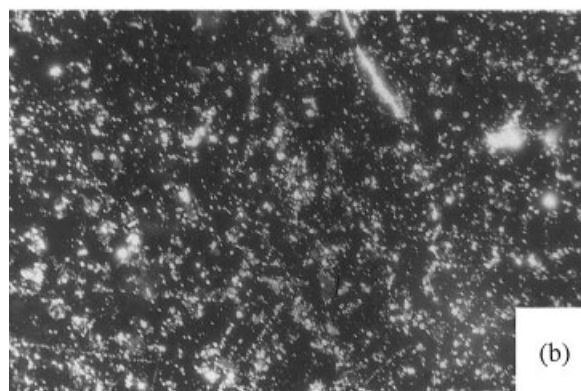
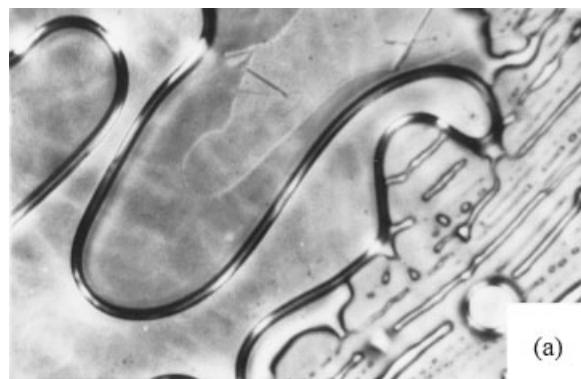


Figure 5 Optical micrographs of epoxy resin and LCPU/DDS/epoxy blends at 260°C. Compositions of the blends: (a) LCPU/DDS/epoxy = 0/32/100; (b) LCPU/DDS/epoxy = 5/32/100; (c) LCPU/DDS/epoxy = 10/32/100.

The curing reaction kinetics of LCPU and epoxy resin blends was carefully investigated by DSC measurements. It was found that the addition of LCPU enhances the curing reaction rate and decreases the apparent activation energy of the curing reaction.¹⁰ Compared with unfilled LCPU, the improved impact strength for the blend of the LCPU/epoxy resin is due mainly to the reaction between LCPU and the epoxy resin.

CONCLUSIONS

Blending of the home-synthesized LCPU with epoxy is an effective way to improve the overall properties

(thermal and mechanical properties) of the latter, especially at a relatively low LCPU fraction. Further works are needed to identify the micromechanisms involved in the simultaneous enhancement of the performance of epoxy, which would help to give full play to the liquid crystalline polymer.

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