A Study on the Properties of Epoxy Resin Toughened by a Liquid Crystal-Type Oligomer

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ABSTRACT: A series of novel reactive toughening agents ($LCEU_{PPG}$) containing both a flexible spacer and rigid liquid crystalline unit were synthesized to modify the bisphenol epoxy resin/dicyandiamide curing system. The curing reactivity, apparent activation energy, curing mechanism, dynamic mechanical behavior, and impact strength of the modified system were systematically studied. Compared with the unmodified system, the results indicate that $LCEU_{PPG}$ have greatly accelerated the curing reaction between epoxy resin and dicyandiamide, reduced the apparent activation energy of the curing reaction, enhanced the impact strength 3–7 times, and maintained high dynamic modulus and good thermal properties. In addition, SEM observation of the fracture surfaces showed a two-phase microstructure in the modified systems. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 177–184, 1999

Key words: epoxy resin; toughening; morphology

INTRODUCTION

Because of its outstanding physical properties, including high strength, high modulus, effective solvent, and temperature resistance, epoxy resin is widely used. However, its brittleness limits its application to projects requiring high-impact strength,[1] so people have done a lot of work to improve its toughness. The incorporation of elastomeric modifier is a successful method. During the curing process the rubber component precipitated from the epoxy matrix and formed a fine and homogeneous dispersed phase which acted as stress-concentrating sites and initiated energy-absorbing processes such as shear yielding and cavitation.[2] However, as the crosslinking density of the matrix increases, its ability to be plastically deformed strongly decreases, and the dispersed rubber particles can no longer induce the energy dissipation process.[3] As a result, tough, ductile, and thermally stable engineering thermoplastics such as polyethersulfones,[4] polyetherimides,[3] poly(aryl ether ketone)s,[5,6] poly(phenylene oxide),[7] and aromatic polyesters[8] were used to improve the toughness of highly crosslinking resins. Liquid crystalline polymers[9] were also used as a modifier for this purpose. Improvements in toughness have been achieved, but the solvent is needed to mix the modifier with the epoxy resin homogeneously, which makes processing difficult.

This article describes the synthesis of a series of novel reactive toughening agents containing both a rigid liquid crystalline unit and flexible spacer. They were used to modify the epoxy resin/dicyandiamide (E-51/dicy) curing system. The rigid chain was used to retain the high dynamic modulus and good thermal properties of the epoxy resins, while the flexible spacer was to improve

Table I   Data of T_p for LCEU$_{PPG}$ Modified Curing Reaction

No.	E-51/dicy/LCEU$_{1000}$	T_p (°C)	No.	E-51/dicy/LCEU$_{2000}$	T_p (°C)	No.	E-51/dicy/LCEU$_{4000}$	T_p (°C)
0	100 : 6 : 0	190						
1	100 : 6 : 10	160	5	100 : 6 : 10	171	9	100 : 6 : 10	176
2	100 : 6 : 20	155	6	100 : 6 : 20	168	10	100 : 6 : 20	174
3	100 : 6 : 30	152	7	100 : 6 : 30	166	11	100 : 6 : 30	172
4	100 : 6 : 40	148	8	100 : 6 : 40	163	12	100 : 6 : 40	170

T_p, peak temperature of DSC curve.

the impact strength. The curing reactivity, dynamic mechanical behavior, impact strength, and fracture morphology of bisphenol epoxy resin (E-51)/dicyandiamide (dicy) systems modified with LCEU$_{PPG}$ were investigated.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A epoxy resin (E-51, epoxy equivalent 196, Yueyang Chemical Plant, China), toluene diisocyanate (TDI) (80% 2,4- and 20% 2,6-mixture, Japan), three polypropylene glycols [PPG#1000, PPG#2000, PPG#4000] (Tianjin Third Oil Chemical Plant), dicyandiamide (dicy), p-phathalic acid, and p-hydroxybenzoic acid, sulfurate chloride (were purchased from the chemical agent company in Tianjin, China).

Apparatus

A differential scanning calorimeter (DSC) (DSC-7, Perkin–Elmer Co.), rotation viscometer (Rheotest-2, former DDR), rheovibron dynamic viscoelastomer (DDV-II-EA, Toyo Baldwin Co.), impact testing machine (CHARPRY XCJ-500, China), and scanning electronic microscopy (SEM) (Hitachi-650X, Japan) were used.

Synthesis

Synthetic routes are shown as shown in Structure 1.[1]

TOBC was synthesized by the reaction of p-phathalic acid and p-hydroxybenzoic acid in step **1** according to Guthrie and coworkers.[10] TOBE was prepared by the reaction of TOBC with glycol in 1,2-dichloroethane at 80°C for ~ 2 h in step **2**, (m.p. = 210°C). In step **3,** oligomer was synthe-

sized according to Sandler and Berg.[11] In step **4,** LCEU$_{PPG}$ was prepared by the reaction of TOBE with oligomer in *N,N*-dimethylformaldehyde (DMF) and functionalized with $HN(CH_3)_2$. A viscous liquid was obtained by removing the solvent. The structure of LCEU$_{PPG}$ is presented in Structure 2.[2]

When the molecular weight of the flexible chain is 1000, 2000, or 4000, LCEU$_{PPG}$ corresponds to LCEU$_{1000}$, LCEU$_{2000}$, and LCEU$_{4000}$. Physical properties: LCEU$_{1000}$ (M_w = 3280, η = 1.94 · 10^5 cP), LCEU$_{2000}$ (M_w = 5280, η = 3.34 · 10^5 cP), and LCEU$_{4000}$ (M_w = 9280, η = 6.76 · 10^5 cP).

Curing Procedure

Epoxy resin (E-51) was poured into a beaker, then dicyandiamide and LCEU$_{PPG}$ were added at room temperature without solvent, the mixture was stirred for ~ 5 min to homogenize, and this was added to a stainless mold, filmed with grease, and degassed for 2 h at ~ 60°C. This was pro-cured for 2 h at 120°C, then 2 h at 140°C, and post-cured for 2.5 h at 160°C. The content of dicydiamide in the curing systems is 6% (wt), and the content of LCEU$_{PPG}$ (wt %) is varied.

Table II   Data of E_a of the Curing Reaction

No.	E_a (kJ/mol)	No.	E_a (kJ/mol)	No.	E_a (kJ/mol)
0	146				
1	92.3	5	86.4	9	94.7
2	83.9	6	77.4	10	89.9
3	74.6	7	79.5	11	92.2
4	73.8	8	80.7	12	89.9

Structure 1

RESULTS AND DISCUSSION

Curing Reaction for E-51/dicy/LCEU$_{PPG}$ Curing Systems

Reactivity

The curing reaction temperature was obtained and listed in Table I by DSC at a scanning rate of 5°C/min.

As shown in Table I, DSC peak temperature (T_p) for the E-51/dicy curing systems modified by LCEU$_{1000}$, LCEU$_{2000}$, and LCEU$_{4000}$ were 148–160°C, 163–171°C, and 170–176°C, respectively. The decrease of DSC T_p showed that the addition of LCEU$_{PPG}$ could accelerate the curing reaction between bisphenol epoxy resin and dicyandiamide. Its accelerating ability increased with increasing of the concentration of LCEU$_{PPG}$ in the curing systems, and decreased with increasing molecular weight of flexible spacer in LCEU$_{PPG}$. The larger the molecular weight of flexible spacer in LCEU$_{PPG}$, the lower its accelerating ability, and the higher the curing temperature.

Structure 2

Figure 1 Dynamic elastic modulus versus temperature for E-51/dicy/LCEU$_{1000}$ curing system. (0) E-51/dicy/LCEU = 100 : 6 : 0; (1) E-51/dicy/LCEU$_{1000}$ = 100 : 6 : 10; (2) E-51/dicy/LCEU$_{1000}$ = 100 : 6 : 20; (3) E-51/dicy/LCEU$_{1000}$ = 100 : 6 : 30; (4) E-51/dicy/LCEU$_{1000}$ = 100 : 6 : 40.

Apparent Activation Energy (E_a)

E_a could be obtained from the equation $\ln V_T = \ln A - E_a/RT_p$ according to Kissinger,[12]

Figure 2 Effect of molecular weight on the dynamic modulus of the modified curing systems. (0) E-51/dicy/LCEU = 100 : 6 : 0; (2) E-51/dicy/LCEU$_{1000}$ = 100 : 6 : 20; (6) E-51/dicy/LCEU$_{2000}$ = 100 : 6 : 20; (10) E-51/dicy/LCEU$_{4000}$ = 100 : 6 : 20.

Figure 3 Effect of LCEU$_{PPG}$ addition on T_g for the modified curing systems.

where V_T is the heating rate in °C/min, R is the gas constant, A is the frequency factor, T_p is the DSC peak temperature in K, and E_a is the apparent activation energy in kJ/mol. Plotting $\ln V_T$ versus $1/T_p$, the E_a of various curing systems is listed in Table II (the series number is the same as in Table I).

It could be seen that E_a values of the modified curing systems dropped 50 to 70 kJ/mol, which contributed to the significant accelerating of the curing reaction and the great decreasing of curing reaction temperature.

Curing Mechanisms

The apparent activation energy E_a of the modified curing systems is $\sim$ 70–90 kJ/mol, while E_a of the controlled sample (E-51/dicy) is 146 kJ/mol, so they would display different curing mechanisms. The curing mechanisms may be as follows: (1) the structure of LCEU$_{PPG}$ is a kind of substituted urea, which is favorable for epoxy ring opening[13]; (2) the urea functional group in the LCEU$_{PPG}$ has a synergism, which accelerates the curing reaction of E-51/dicy[14]; (3) dicyandiamide is insoluble in the epoxy resin and the curing reaction occurs only when the temperature is close to the melt point of dicyandiamide. However, both epoxy and dicy have good compatibility with LCEU$_{PPG}$, so the addition of LCEU$_{PPG}$ improved the solubility of dicy in the epoxy resin. These result in the dropping of curing reaction temperature by $\sim$ 40°C and the decreasing of apparent E_a for $\sim$ 60 kJ/mol.

Dynamic Elastic Modulus

Figure 1 shows that the dynamic elastic modulus of the modified systems formulated as No. 2, No. 3, and No. 4 was higher than that of the controlled sample (E-51/dicy) below 100°C. Generally, dynamic modulus would be decreased with the addition of the flexible toughening agent. However, due to the novel modifier containing not only the flexible spacer but also the rigid liquid crystalline unit, the high dynamic modulus could be maintained. The flexible spacers are aimed to improve impact strength, and the rigid unit is intended to retain high dynamic modulus and thermal properties of the cured resin. The rigid liquid crystalline unit played a great role in maintaining or enhancing the high dynamic modulus of epoxy resin modified by $LCEU_{PPG}$.

As shown in Figure 2, the dynamic modulus of the modified systems decreased with increasing molecular weight of $LCEU_{PPG}$. However, the dynamic modulus of the curing system modified with $LCEU_{1000}$ was still higher than that of the controlled sample, even the amount of the modifier was up to 20%.

Relaxation and Transition Mechanisms of the Curing Systems

Data of relaxation temperature are listed in Table III.

The influence of content of $LCEU_{PPG}$ and flexible molecular weight in the modifier on T_g is shown in Table III and Figure 3. It can be seen that glass transition temperatures of the modified curing systems slightly decreased with the increasing of content of $LCEU_{PPG}$, which was due to the incorporation of flexible spacer into the epoxy resin network. However, as the molecular weight of $LCEU_{PPG}$ increases, T_g only slightly increases. It may be that the increasing of the flexible molecular weight in $LCEU_{PPG}$ leads to the reduction of the number of reactive groups per molecule and decreasing its reactivity. To fully cure the epoxy resin, the curing temperature should be raised. However, the increase of curing temperature resulted in the increasing of reaction rate between epoxy and dicyandiamide, as well as the forming of tighter networks and higher glass transition temperature than that of the control sample.

To investigate the influence of $LCEU_{PPG}$ on the dynamic mechanical behavior of the modified systems, the $LCEU_{1000}$ modified system was chosen as an example (Fig. 4). Compared with the con-

Figure 4 Mechanical loss versus temperature for $LCEU_{1000}$ modified curing system. (0) E-51/dicy/LCEU = 100 : 6 : 0; (1) E-51/dicy/$LCEU_{1000}$ = 100 : 6 : 10; (2) E-51/dicy/$LCEU_{1000}$ = 100 : 6 : 20; (3) E-51/dicy/$LCEU_{1000}$ = 100 : 6 : 30; (4) E-51/dicy/$LCEU_{1000}$ = 100 : 6 : 40.

Dynamic Mechanical Behavior

The dynamic mechanical properties between −150–250°C for the modified curing systems were investigated by using a Rheovibron dynamic viscoelastomer at a heating rate of 2°C/min and a frequency of 11 Hz.

Table III   Data of Transition Temperature for E-51/dicy/LCEU$_{PPG}$

Value (°C)	Number												
	0	1	2	3	4	5	6	7	8	9	10	11	12
T_g	175.6	156.7	148.6	147.6	139.7	161.8	160.6	159.2	157.0	168.7	164.6	162.6	160.7
T_β	−47.1	−54.3	−51.6	−55.3	−56.0	−47.2	−52.2	−51.3	−49.3	−56.3	−56.7	−55.4	−54.8
T_γ	−122.3	−123.0	−125.4	−123.2	−123.1	−123.4	−121.1	−121.3	−123.3	−123.1	−123.4	−121.6	−121.4

trolled sample, β relaxation temperature shifted to lower temperature and shoulder peaks appeared on the left side of α relaxation peaks for all the modified curing systems. The decrease of T_g and appearance of α-shoulder peak may be the result of the addition of LCEU$_{PPG}$ which incorporated into the tight epoxy resin network.

The β relaxation of the dicy-cured system occurred at $\sim$ −47°C, which agreed with the results of Ochi and Shimbo.[15,16] The β relaxation was the contribution of the hydroxyether group [—CH$_2$(CHOH)CH$_2$O—] in the amine-cured epoxy resins network. However, β relaxation of the modified systems shifted to a lower temperature, which may be the contribution of the flexible ether segment in LCEU$_{PPG}$. From these results it could be concluded that LCEU$_{PPG}$ incorporated into the epoxy crosslinking network and led to the formation of a two-phase microstructure in the modified systems, which contributed to the improvement of impact strength. It also could be confirmed further by impact test and SEM observation. Gamma relaxation at $\sim$ −120°C may correspond to the crankshaft rotation in the epoxy matrix.

Investigation of Impact Strength and T_g

Impact strengths of the cured samples were determined according to China National Standard GB1043-79 (Non-notched-bar impact test, sample size: 55 × 6 × 4 mm; testing temperature: 23°C); data are listed in Table IV.

From the data listed in Table IV, it can be seen that the impact strength improved 3–7-fold and there was a slight decrease of T_g by adding LCEU$_{PPG}$ for the E-51/dicy curing systems. Figure 5 shows the influence of the amount of LCEU$_{2000}$ on T_g and impact strength of modified system. Even with 10% addition of LCEU$_{2000}$, the impact strength can be improved 5 times than that of the controlled sample, so LCEU$_{PPG}$ is an effective modifier in enhancing impact strength for the epoxy resin E-51/dicy curing system.

Morphology of the Fracture Surfaces

The fracture surfaces of the impact samples were observed by scanning electron micrographs (SEM). Figure 6(a) showed the SEM micrograph of the unmodified system, which displayed the typical brittle fracture features. SEM micrographs of the modified systems were showed in Figure 6(b–d). A two-phase network was observed with the epoxy-rich phase as the continuous matrix and the LCEU$_{PPG}$ as dispersion phase composed of spherical particles. The dispersed particles act as stress concentrators during fracture, which induce delocalized plastic deformation of the matrix around the particles, and dis-

Table IV   Data of T_g and I_s for the Modified Curing Systems

E-51/dicy/LCEU$_{1000}$	T_g (°C)	I_s (kJ/m^2)	E-51/dicy/LCEU$_{2000}$	T_g (°C)	I_s (kJ/m^2)	E-51/dicy/LCEU$_{4000}$	T_g (°C)	I_s (kJ/m^2)
100 : 6 : 0	175.6	4.0						
100 : 6 : 10	156.7	18.0	100 : 6 : 5	—	16.5	100 : 6 : 10	168.7	18.7
100 : 6 : 15	—	18.3	100 : 6 : 10	161.8	18.8	100 : 6 : 15	—	16.1
100 : 6 : 20	148.6	18.4	100 : 6 : 20	160.6	27.6	100 : 6 : 20	164.6	14.6
100 : 6 : 30	146.6	19.7	100 : 6 : 30	159.2	21.2	100 : 6 : 30	162.6	12.9
100 : 6 : 40	139.7	16.4	100 : 6 : 40	157.0	8.6	100 : 6 : 40	160.7	—

T_g, glass transition temperature; I_s, impact strength.

sipate fracture energy. Sizes of the particles are 0.4–1.0 μm. It is important that impact strength cannot be effectively improved as the particle size is greater than 1 μm.

CONCLUSION

From the experiments we conclude that LCEU$_{PPG}$ is a very effective modifier for the bisphenol A

Figure 6. SEMs of the fracture surfaces for various E-51/dicy/LCEU$_{PPG}$ curing system. (a) E-51/dicy = 100:6; (b) E-51/dicy/LCEU$_{1000}$ = 100:6:10; (c) E-51/dicy/LCEU$_{2000}$ = 100:6:10; (d) E-51/dicy/LCEU$_{4000}$ = 100:6:10.

epoxy resin and dicyandiamide curing system. The addition of LCEU$_{PPG}$ can improve the impact strength by 3 to 7 times, accelerate the curing reaction, drop the curing reaction temperature ~ 40°C, and reduce the apparent reactive energy for ~ 50 kJ/mol. Dynamic modulus can be maintained or enhanced, and T_g is only slightly decreased. The emerged phase-separation structure is contributed to the significant enhancement of the impact strength.

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