# Modification of Epoxy Resins by Acrylic Copolymers with Side-Chained Mesogenic Units

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**ABSTRACT:** A series of acrylic copolymer modifiers with mesogenic side chain (LCGMB) were synthesized and used to modify E-51/DDM system. The dynamic mechanical behavior and impact strength of the modified systems were investigated. The results showed that the impact strength and modulus were influenced by the composition and the amounts of the modifiers. With addition of 10% (wt %) LCGMB (molar ratio of GMA : HEMA : MMA : BA = 4 : 10 : 26 : 60) based on the amount of the epoxy resin, the modified systems obtained 100% increase in impact strength, 10% increase in modulus, and a little increase in *Tg*. The toughening mechanism of the modified systems was also discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1787–1792, 1999

Key words: epoxy resins; modification; mesogenic units; acrylic copolymer

### INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting polymers that exhibit such desirable properties as tensile strength, high modulus, and excellent chemical and corrosion resistance. However, they show poor fracture toughness and low resistance to crack growth. To overcome these problems, reactive liquid rubbers or such thermoplastics as terminally functional engineering thermoplastics and liquid crystalline polymers were used to decrease the brittleness and to improve the toughness of the cured epoxy resins. The most common liquid rubbers were based on liquid butadiene-acrylonitrile copolymers, which are terminated with either carboxyl or amine end groups. These materials have been shown to increase the fracture toughness of matrix greatly, but they result in an undesirable lowering of the modulus of epoxy systems.<sup>1–3</sup> The use of thermoplastic particles as second phase toughening agents in epoxy resins has been explored more recently at little sacrifice of the modulus of the modified systems<sup>4–6</sup>; however, in most cases, only modest improvements in the fracture toughness have been reported. A drawback in the use of the thermoplastics as modifiers is poor processability, mainly caused by poor compatibility with the uncured epoxy resin.<sup>4,5</sup>

Therefore, our aim is to synthesize a series of modifiers for epoxy resins that would not only improve the fracture toughness, but would also keep the original high modulus of epoxy resin. In our laboratory, we synthesized a novel series of acrylic polymer modifiers (LCGMB) that contained the *n*-butyl acrylate flexible main chain with side-chained rigid mesogenic units. The sidechained rigid mesogenic units are designed to keep the high modulus and good thermal properties of the epoxy resins, the flexible main chain is intended to improve the toughness, and the pendant epoxy groups of the modifier were used as active functions while curing. This article reports

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LCGMB	$A_1$	$\mathrm{A}_2$	$A_3$	$A_4$	$B_3$	$\mathrm{B}_2$	B <sub>1</sub>
Molecular weight/mole epoxide	2,000	2,000	2,000	2,000	2,000	2,000	2,000
MMA (mol %)	6	20	33	46	25	15	10
BA (mol %)	80	66	53	40	66	66	66
Mesogenic units (mol %)	10	10	10	10	5	15	20
GMA (mol %)	4	4	4	4	4	4	4
State	Light yellow viscous. liq.						

Table I Composition and Physical Properties of LCGMB

the modification of 4,4'-diaminodiphenyl methane (DDM)-cured epoxy resin (E-51) with this novel modifier. The effect of the composition and the amount of LCGMB on the toughness of the cured epoxy resin were examined based on the dynamic mechanical behavior and impact strength of the modified systems.

#### **EXPERIMENTAL**

#### **Materials**

The epoxy resin was a commercial liquid bisphenol-A-type epoxy resin (E-51) with epoxide number of 0.51 (Yueyang Chemical Factory, China). The curing agent 4,4'-diaminodiphenol methane (Shanghai No. 2 Reagent Co.) was purified before use. The novel modifiers (LCGMB) were synthesized in our laboratory.

# Synthesis of Acrylic Copolymers with Side-Chain Mesogenic Units

The detailed procedure of the synthetic route has been developed in our laboratory and was described in another paper.<sup>7</sup> The structure of the modifiers was shown as follows. Physical properties of the modifiers LCGMB were summarized in Table I.



The infrared spectrum of a representative LCGMB sample, recorded at room temperature, is shown in Figure 1. The N—H stretching is in the 3500 cm<sup>-1</sup> region, and the 2840 cm<sup>-1</sup> and 2870 cm<sup>-1</sup> peak is attributable to methyl C—H stretch. The C=O stretching is in the 1760–1620 cm<sup>-1</sup> region. The 1,605, 1,580, 1,508, 1,460 cm<sup>-1</sup> peaks are assigned to the combined stretching and deformation aromatic C=C bands. The peaks in the 937 cm<sup>-1</sup> and 847 cm<sup>-1</sup> characterize the epoxy group.

#### Measurement

Mechanical properties of the cured resins were measured with a CHENGDE CHARPY XCJ-500 impact test machine according to China National Standard GB1043-79 (it is a non-notched impact test, and the sample size is  $55 \times 6 \times 4$  mm; testing temperature: 23°C). Dynamic mechanical analysis was performed with a JAPAN DDV-II-EA instrument between  $-150 \sim 200$ °C at a heating rate of 2°C/min and a frequency of 110 Hz. Infrared spectra were obtained with a computerized Nicolet–20SXB Fourier transform infrared spectrometer. The samples for the infrared studies were prepared by spreading melted the samples on the surface of KBr sheet.

#### **Curing Procedure**

A mixture of the epoxy resins and LCGMB was heated to  $60 \sim 80^{\circ}$ C to homogenize, and then the curing agent DDM was added into the mixture with stirring at  $50 \sim 60^{\circ}$ C, degassed at  $40^{\circ}$ C, poured into a mold, precured for 1 h at 120°C, and postcured for 3 h at 150°C. The amount (wt %) of the modifiers was calculated based on the amount of the epoxy resin. The curing agent was used stoichiometrically to the total epoxy contents of both the epoxy resin and the modifier.



Figure 1 Infrared spectrum of LCGMB sample recorded at room temperature.

#### **RESULTS AND DISCUSSIONS**

# Mechanical and Thermal Properties of the Modified Systems

# Effect of the Amount of LCGMB on the Mechanical and Thermal Properties of the Modified Systems

The  $T_g$  and impact strength of the modified systems as a function of the amount of LCGMB is shown in Table II. The results show that the impact strength of the modified systems increased with the amount of LCGMB increasing.

Compared to the pristine epoxy resin, the modified epoxy resins had 185% impact strength improvement at 5 wt % LCGMB; however, the impact strength of the modified systems tended to level off when the LCGMB content was above 10 wt %. Table II showed that  $T_g$  of the modified systems had the maximum value at addition of 15 wt % LCGMB.

It can be concluded that addition of the modifiers-acrylic copolymers with side-chained mesogenic units (LCGMB) significantly improve the mechanical properties of epoxy resin. The depen-

Table II Dependence of  $T_g$  and Impact Strength of the Modified Systems on Amounts of LCGMB in the Modified Systems<sup>a</sup>

Sample	$T_{g}$ (°C)	Impact Strength (kJ/m <sup>2</sup> )		
100  gE-51 + 25.3  gDDM	178.0	11.9		
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 5 \text{ gA}_2$	174.5	21.7		
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 10 \text{ gA}_2$	176.5	23.5		
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 15 \text{ gA}_2$	182.5	24.0		
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 20 \text{ gA}_2$	177.0	24.5		

 $^{\rm a}$  The systems were precured for 1 h at 120°C and postcured for 3 h at 150°C.

Sample	Content of Mesogenic Units in LCGMB (mol %)	$T_{g}$ (°C)	Impact Strength (kJ/m <sup>2</sup> )
100  gE-51 + 25.3  gDDM		178.0	11.9
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 15 \text{ gB}_3$	5	172.5	20.0
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 15 \text{ gA}_2$	10	182.5	24.0
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 15 \text{ gB}_2$	15	177.0	23.0
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 15 \text{ gB}_{1}$	20	166.5	21.6

Table III Dependence of  $T_g$  and Impact Strength for the Modified Systems on the Amounts of Mesogenic Units in LCGMB^a

<sup>a</sup> The systems were precured for 1 h at 120°C and postcured for 3 h at 150°C.

dence of the impact strength of the modified systems on the amounts of LCGMB differs significantly from that of the systems modified with acrylic elastomer,<sup>3,7</sup> but similar to that of the systems modified with engineering thermal plastics.<sup>4,6</sup> These results show that the side-chained mesogenic units play a important role in toughness.

### Effect of the Composition of LCGMB on the Mechanical and Thermal Properties of the Modified Systems

To make certain the modifier is compatible with the epoxy resins and to toughen the strengthen epoxy resin matrix, LCGMB was designed with a different composition. Effect of the composition of LCGMB on the mechanical and thermal properties of the modified systems was investigated when the amount of modifier in system was 15 wt %.

Table III shows the effect of its mesogenic unit amounts in LCGMB on the impact strength and  $T_g$  of the E-51/DDM/LCGMB. It was obvious that E-51/DDM/LCGMB system has the best modified result with 10 mol % mesogenic units in LCGMB—a 100% increase in the impact strength and a maximum  $T_g$  182.6°C. However, when the amounts of mesogenic units in LCGMB reached 20 mol %, the  $T_g$  of the modified system decreased to 166°C.

Figure 2 shows the effect of the amount of MMA in LCGMB on the impact strength and  $T_g$  of the modified systems. When the amount of MMA in LCGMB is about 30 mol %, the modified system had the best impact strength improvement.  $T_g$  of the modified system was independent of the amount of MMA in LCGMB.

Figure 3 shows that the impact strength of E-51/DDM/LCGMB system reached the maximum value when the amount of BA in LCGMB is

about 60 mol %. Tg of the modified systems was also independent of the amount of BA in LCGMB. When the amount of BA in LCGMB was over 80 mol %, a macro separation in the modified systems appeared. The best result can be obtained when the ratio between BA and MMA was 2 : 1.

### Dynamic Mechanical Analysis of the Modified Systems

Dynamic mechanical analysis (DMA) provides information about the microstructure of the modified systems. Figures 4 and 5 show the DMA curves of E-51/DDM/LCGMB as a function of the amount of LCGMB. The relaxation temperatures and modulus of these samples are summarized in Table IV.

The results of Table IV and Figure 4 showed that as compared with the unmodified system, the modulus of the modified systems was increased when



**Figure 2** Relation of content of MMA in LCGMB to impact strength and  $T_g$  for the modified systems (100 gE-51 + 25.3 gDDM + 15 gLCGMB).



Figure 3 Relation of content of BA in LCGMB to impact strength and  $T_g$  for the modified systems (100 gE-51 + 25.3 gDDM + 15 gLCGMB).

the amount of the LCGMB was below 15 wt %; however, when it reached 20 wt %, the modulus of the modified systems was decreased. With 10 wt % LCGMB in the modified system, the best result could be obtained which resulted in a 10% increase in the modulus as well as a 200% improvement in the fracture toughness. Figure 5 showed that the



Figure 4 Effect of content of LCGMB on modulus for the modified systems

 $\begin{array}{l} G_1:100 \ gE\text{-}51:25.3 \ gDDM \\ L_1:100 \ gE\text{-}51:25.3 \ gDDM:5 \ gA_2 \\ L_2:100 \ gE\text{-}51:25.3 \ gDDM:10 \ gA_2 \\ L_3:100 \ gE\text{-}51:25.3 \ gDDM:15 \ gA_2 \\ L_4:100 \ gE\text{-}51:25.3 \ gDDM:20 \ gA_2. \end{array}$ 



Figure 5 Effect of content of LCGMB on relaxation temperature for the modified systems

 $\begin{array}{l} G_1:100 \ gE\text{-}51:25.3 \ gDDM \\ L_1:100 \ gE\text{-}51:25.3 \ gDDM:5 \ gA_2 \\ L_2:100 \ gE\text{-}51:25.3 \ gDDM:10 \ gA_2 \\ L_3:100 \ gE\text{-}51:25.3 \ gDDM:15 \ gA_2 \\ L_4:100 \ gE\text{-}51:25.3 \ gDDM:20 \ gA_2. \end{array}$ 

peak position and magnitude of the  $\alpha$  relaxation peaks of the modified systems hardly changed, but all modified systems had several  $\beta$  relaxations:  $\beta_3$  $(-40 \sim -30^{\circ}\text{C}), \beta_2 (-10 \sim 10^{\circ}\text{C}), \beta_1(40 \sim 60^{\circ}\text{C}).$ The  $\beta_2$  relaxation peak, which appeared superimposed to the  $\beta_3$  relaxation peak, increased in magnitude with the amount of LCGMB increasing. The  $\beta_1$  relaxation is attributable to the relaxation of the hydroxy ether group (-CH<sub>2</sub>(CHOH)CH<sub>2</sub>O-) in the cured epoxy resin matrix.<sup>9</sup> Compared to the unmodified system, the new relaxation  $\beta_2$ ,  $\beta_3$  emerging in the range of  $-10 \sim 60^{\circ}$ C obviously are caused by the addition of LCGMB.  $\beta_2$  can be contributed to the relaxation of the flexible chain in the modifiers,  $\beta_3$  is attributable to the relaxation of the modifiers. The new transitions  $\beta_2$ ,  $\beta_3$  indicate the occurrence of phase separation to some extent in the modified systems. Furthermore, the improvement in the fracture toughness of the epoxy resin can be correlated with these relaxations below the  $\alpha$  relaxation in the modification with LCGMB. Such a correlation has been also reported in the modification of epoxy resins with reactive rubbers.<sup>2,3,8</sup> In the systems modified by LCGMB, it is noted that the modifier cannot only improve the fracture toughness, but can also increase the modulus of the modified systems, which is sharply different from the normal

	$T_{\beta}$ (°C)			m			Impact
Sample	$eta_1$	$eta_2$	$\beta_3$	$T_{\alpha}$ (°C)	$\begin{array}{c} \mathbf{E}_{100\tau} \\ \text{(Pa)} \end{array}$	$\begin{array}{c} \mathbf{E_{25\tau}}\\ (\mathrm{Pa}) \end{array}$	(kJ/m <sup>2</sup> )
100  gE-51 + 25.3  gDDM		-36		178.0	$4.65  ext{ E10}$	$2.28  ext{ E10}$	11.9
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 5 \text{ gA}_2$	-39	-2	59	175.0	$5.09  ext{ E10}$	$2.38  ext{ E10}$	22.2
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 10 \text{ gA}_2$	-36	11	57	177.0	$5.45  ext{ E10}$	$2.49  ext{ E10}$	23.5
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 15 \text{ gA}_2$	-35	8	54	182.5	4.96 E10	2.47 E10	24.0
$100 \text{ gE-}51 + 25.3 \text{ gDDM} + 20 \text{ gA}_2$	-36	18	41	177.0	$4.30  ext{ E10}$	$1.76  ext{ E10}$	24.5

<sup>a</sup> The systems of E-51/DDM/LCGMB were precured for 1 h at 120°C and postcured for 3 h at 150°C.

elastomer modifier. The increase in the modulus of the modified system demonstrates that the sidechained mesogenic units dissolving in the matrix can strengthen the epoxy resin matrix.

In conclusion, the acrylic copolymer with sidechained mesogenic units is an appropriate modifier for epoxy resins, which substantially increases both the fracture toughness and mechanical properties of the modified system. The dynamic mechanical analysis of the E-51/DDM/LCGMB proved the phase separation in the modified systems. The most suitable formulae of the modified system was 10 wt % LCGMB containing 60 mol % BA, 4 mol % GMA, 26 mol % MMA, and 10 mol % mesogenic units.

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