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A study on properties of epoxy resin toughened by functionalized polymer containing rigid, rod-like moiety

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Abstract

A series of novel reactive toughening agents defined as $LCEU_{PEG}$ containing both flexible chain and rigid, rod-like moiety were synthesized and used to modify the epoxy resin (E-51)/dicyandiamide (dicy) curing system. The curing reactivity, apparent activation energy E_a, curing mechanism, dynamic mechanical behavior, impact strength of E-51/$LCEU_{PEG}$/dicy systems was studied. The results show that the addition of $LCEU_{PEG}$ to epoxy resin and dicy curing system has apparently accelerated the curing reaction, reduced the apparent activation energy E_a of the curing reaction by about 60 kJ/mol, and decreased the curing temperature by about 50°C. In addition, the high modulus and good thermal properties are maintained, and the impact strength is enhanced by three to seven times compared with that of the unmodified sample. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

There has been increasing demand for the high performance composites with high resistance to fracture, high modulus, and good performance at elevated temperature. Epoxy resins are widely used in many applications. However, the improvement of toughness for cured epoxy resin is highly desirable to overcome their brittleness. One of the methods is by incorporating rigid, or reactive rubbery particles, or both of them [1,2]. However, modification by the addition of rubber is usually at the expense of T_g and modulus. Another way is by incorporating tough, high performance, and thermal stable engineering plastics, such as polyethersulfones [3] and polyetherimides [4]. Liquid crystalline polymers as fillers are also used to improve the toughness recently [5]. Much progress has been made by the approaches mentioned above.

It is well known that it is difficult to maintain high T_g and modulus of epoxy resin, while increasing its impact strength. For this reason, a series of reactive toughening agents containing both rigid, rod-like moiety and flexible spacer were synthesized to modify the dicy cured epoxy resin system in this article. The rigid, rod-like moiety is aimed to keep the high modulus and good thermal properties, while the flexible chains are used to improve the toughness. The curing reactivity, E_a, curing mechanism, dynamic mechanical properties, impact strength, as well as morphology of the fractured surfaces of the modified curing systems were investigated.

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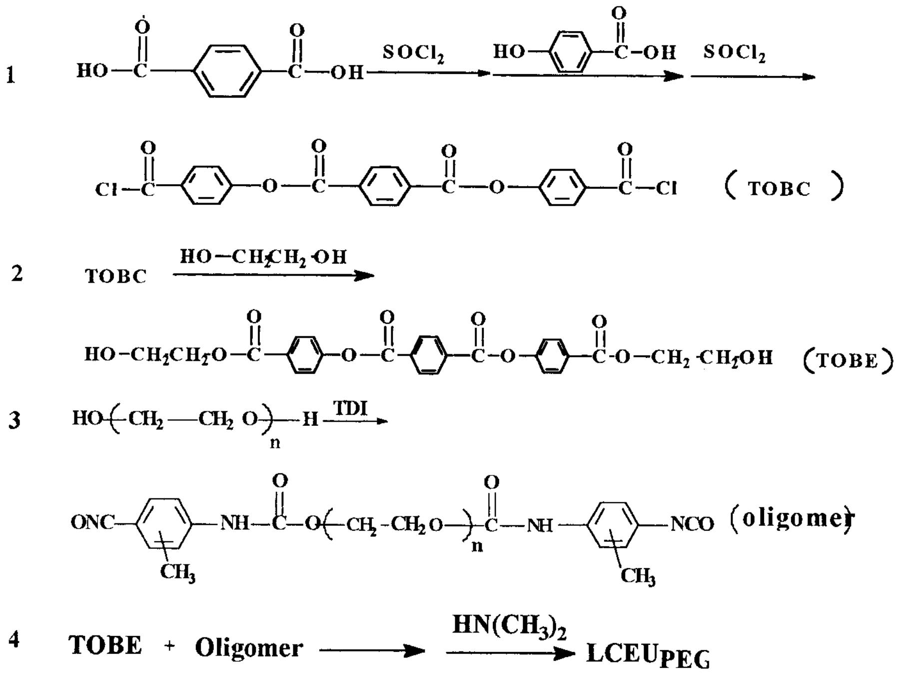
2. Experimental

2.1. Materials

Epoxy resin (diglycidyl ether of bisphenol A DGEBA (E-51, WEP = 196, purchased from Yueyang Chemical Plant, China, without further purification); toluene diisocyanate (TDI, 80% 2,4-mixture and 20% 2,6-mixture), dicyandiamide (dicy), *p*-phthalic acid, *p*-hydroxybenzoic acid, sulfurous chloride, diglycolethyene, purified with normal procedures); and four polyethylene glycols [PEG#200, PEG#400, PEG#600, PEG#1000] (used as supply).

2.2. Synthesis

The brief synthesis routes are presented as follows:



2.2.1. Preparation of terephthalyl chloride

Terephthalyl chloride was prepared by refluxing *p*-phthalic acid with sulfurous chloride for 4 h till the mixture turned clear. The product precipitated at 0°C, then isolated by filtration, recrystallized in petroleum ether and vacuum dried at 40°C, with yield of 81%.

2.2.2. Preparation of terephthalylbis(4-oxybenzoic) acid (TOBA) [6]

p-hydroxybenzoic acid (27.0 g) was dissolved in 400 ml, 0.1 M aqueous solution of sodium hydroxide, a solution of terephthaloyl chloride (17 g) in 170 ml terachloroethane was added drop-wise with stirring. The reaction mixture was stirred at room temperature for 6 h. The resulting white precipitate was soaked in 500 ml, 3 M HCl for 12 h. The product obtained by filtration and vacuum dried at 50°C for 12 h with yield of 90%.

2.2.3. Conversion of TOBA to terephthaloyl dioxydibenzoylchloride (TOBC) [6]

TOBA (40 g) was refluxed with thionyl chloride (500 ml) till the mixture turned clear. The TOBC precipitated from the solution at 0°C, and was isolated by filtration. The product was recrystallized from ether, and vacuum dried at 40°C with yield 70%.

2.2.4. Convert TOBC to terephthalylbis(4-oxybenzoyloxyhyroethyl) ester (TOBE)

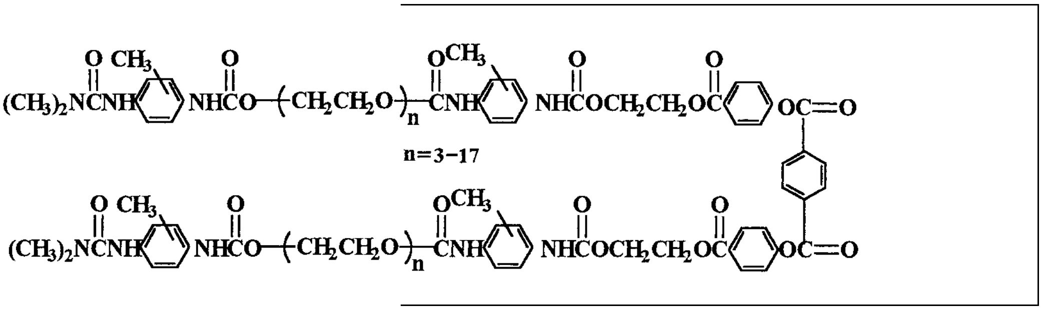
TOBC (44.3 g) was dissolved in 1,2-dichloroethane (200 ml) at 80°C, then diglycolethyene (15 g) was added. The mixture was stirred at 80°C for 3 h. The product precipitated was laid aside to room temperature. Filtrated and dried at 40°C under reduced pressure with yield 96%, melting point 210°C.

2.2.5. Preparation of the Oligemer [7]

Mixture of polyethylene glycol (1 mol) and toluene diisocyanate (2 mol) was reacted at 80°C for 4 h till the content of –NCO reached the half value of the initial. A viscous liquid was obtained.

2.2.6. Preparation of the LCEU$_{PEG}$

TOBE (0.1 mol) was dissolved in *N*,*N*-dimethylformamide (300 ml) at 80°C. Oligomer (0.2 mol) was added. The mixture was stirred at 80°C for 4 h. The solution was cooled to room temperature, and purged with excess dimethylamine. The solvent was removed by distillation under reduced pressure. Vacuum dried at 60°C for 10 h, the viscous pale yellow liquid product was obtained. Chemical formula of the resulting LCEU$_{PEG}$ is illustrated as follows:



When molecular weight of flexible spacer is 200, 400, 600, and 1000, LCEU$_{PEG}$ is denoted as LCEU$_{200}$, LCEU$_{400}$, and LCEU$_{600}$, and LCEU$_{1000}$, respectively. Physical properties: LCEU$_{200}$ (M_w = 1680, $\eta = 1.0 \times 10^5$ cP), LCEU$_{400}$ (M_w = 2080, $\eta = 1.35 \times 10^5$ cP), LCEU$_{600}$ (M_w = 2480, $\eta = 1.75 \times 10^5$ cP), LCEU$_{1000}$ (M_w = 3280, $\eta = 1.84 \times 10^5$ cP).

2.3. Apparatus

Differential Scanning Calorimeter, DSC-7, Perkin–Elmer, was calibrated with ultrafine Indium, the sample weight is about 10 mg; Rotational Viscosity Meter, RHEOTEST-2, former DDR, testing temperature: 25 ± 0.1°C, sample volume: 0.1 ml; Rheovibron DDV-II-EA, Toyo Baldwin, Japan, testing temperature range: $-150 \sim 250$°C, frequency: 11 Hz, sample size: $1.5 \times 0.2 \times 0.02$ cm^3, heating rate: 2°C/min; Impact Testing Machine, Charpry XCJ-500, China, tested according to China National Standard GB1043-79: non-notched-bar samples were used, testing temperature: 23 ± 0.1°C, sample size: $55 \pm 0.1 \times 6 \pm 0.1 \times 4 \pm 0.1$ cm^3; Scanning Electronic Microscopy (SEM), HITACHI-650X, Japan, the samples were shadowed with gold.

2.4. Curing procedure

In a 100 ml beaker, dicy and LCEU$_{PEG}$ were added to the liquid epoxy resin (E-51), the mixture was stirred for 5 min, then poured into the greased mould, degassed at 60°C for 2 h. All samples were cured at 120°C for 2 h, 140°C for 2 h and 160°C for 2.5 h.

3. Results and discussion

3.1. Curing reaction for E-51/dicy/LCEU$_{PEG}$ curing systems

3.1.1. Curing reaction temperature

The samples scanned by DSC at heating rate of 5°C/min, their peak temperature (T_p) of the curing reaction is shown in Table 1.

As shown in Tables 1 and 2, T_p are ranged within 142–153, 136–150, 135–147, and 133–145°C, respectively, for LCEU$_{1000}$, LCEU$_{600}$, LCEU$_{400}$, and LCEU$_{200}$ modified curing system. Compared with the unmodified system (T_p = 190°C), T_p has declined for 40–60°C. The results show that the addition of LCEU$_{PEG}$ significantly accelerate the curing reaction for E-51/dicy system. The curing reactivity increases with the increasing of LCEU$_{PEG}$ content and with the decreasing of their molecular weight (Fig. 1). This phenomena might result from the amount of reactive end-groups in the curing system increases with the increasing of the content of LCEU$_{PEG}$ and the decreasing of its the molecular weight.

3.1.2. Apparent activation energy

According to Kissinger's theory [8], $\ln V_T = \ln A - E_a/RT_p$ (where V_T is the heating rate in °C/min, R is gas constant, A is the frequency factor, T_p is peak temperature of the curing reaction obtained by DSC scanning at different heating rate and E_a is the apparent activation energy). Results are listed in Tables 3 and 4.

Table 1
Data of T_p for the curing systems

No.	E-51/dicy/$LCEU_{1000}$	T_p (°C)	No.	E-51/dicy/$LCEU_{600}$	T_p (°C)
A	100:6:10	153	E	100:6:10	150
B	100:6:15	151	F	100:6:15	145
C	100:6:20	149	G	100:6:20	142
D	100:6:30	142	H	100:6:30	136
0	100:6:0	190			

Table 2
Data of T_p for the curing reaction by DSC

No.	E-51/dicy/$LCEU_{400}$	T_p (°C)	No.	E-51/dicy/$LCEU_{200}$	T_p (°C)
I	100:6:10	147	M	100:6:10	145
J	100:6:15	143	N	100:6:15	141
K	100:6:20	139	O	100:6:20	136
L	100:6:30	135	P	100:6:30	133

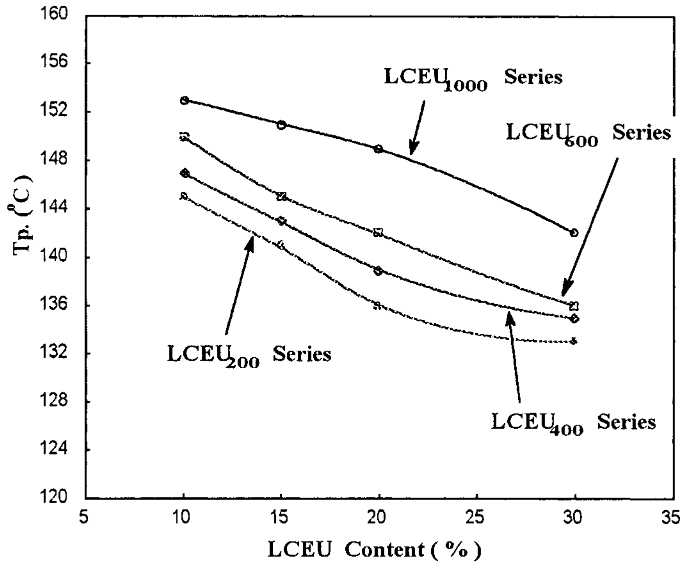


Fig. 1. Effect of $LCEU_{PEG}$ content and molecular weight on the reactivity of the curing systems.

Table 3
Data of E_a for the modified curing reaction

No.	E-51/dicy/$LCEU_{1000}$	E_a (kJ/mol)	No.	E-51/dicy/$LCEU_{600}$	E_a (kJ/mol)
A	100:6:10	66.9	E	100:6:10	79.4
B	100:6:15	65.3	F	100:6:15	73.6
C	100:6:20	63.6	G	100:6:20	74.6
D	100:6:30	74.6	H	100:6:30	73.9
0	100:6:0	146			

Table 4
Data of E_a for the modified curing reaction

No.	E-51/dicy/LCEU_{400}	E_a (kJ/mol)	No.	E-51/dicy/LCEU_{200}	E_a (kJ/mol)
I	100:6:10	79.8	M	100:6:10	70.7
J	100:6:15	80.7	N	100:6:15	79.5
K	100:6:20	79.1	O	100:6:20	80.6
L	100:6:30	84.8	P	100:6:30	81.4
0	100:6:0	146			

Table 5
Data of transition temperature for E-51/dicy/$\mathrm{LCEU}_{\mathrm{PEG}}$ curing systems

No.		0	A	B	C	D	E	F	G	H	0	I	J	K	L	M	N	O	P
T_g (°C)		177	154	146	133	121	156	148	135	125	176	157	150	137	129	159	153	145	141
T_β (°C)	$T_{\beta 1}$ (°C)	−47	−69	−67	−69	−65	−71	−71	−73	−73	−47	−71	−70	−69	−71	−65	−73	−69	−73
	$T_{\beta 2}$ (°C)		−56	−53	−57	−57	−55	−57	−60	−55		−55	−56	−60	−55	−55	−59	−53	−57

It may be seen, E_a of the modified curing reactions varies between 64 and 85 kJ/mol, decreased by 50 to 70 kJ/mol compared with the controlled system. The results show that the addition of $\mathrm{LCEU}_{\mathrm{PEG}}$ greatly accelerate the curing reaction of epoxy resin and dicy.

3.1.3. Curing mechanisms

The great difference in E_a suggests different curing mechanisms for $\mathrm{LCEU}_{\mathrm{PEG}}$ modified system and controlled system. The curing mechanisms of the modified system may be proposed as follows: (1) $\mathrm{LCEU}_{\mathrm{PEG}}$ (substituted urea) behaves to ease the opening of epoxy ring [9]. (2) The urea groups in $\mathrm{LCEU}_{\mathrm{PEG}}$ possess synergism effect on accelerating the curing reaction [10]. (3) The addition of $\mathrm{LCEU}_{\mathrm{PEG}}$ promotes the compatibility of dicy with epoxy resins, which may contribute to the curing reaction. It is well known that the reaction between epoxy resin and dicy only take place

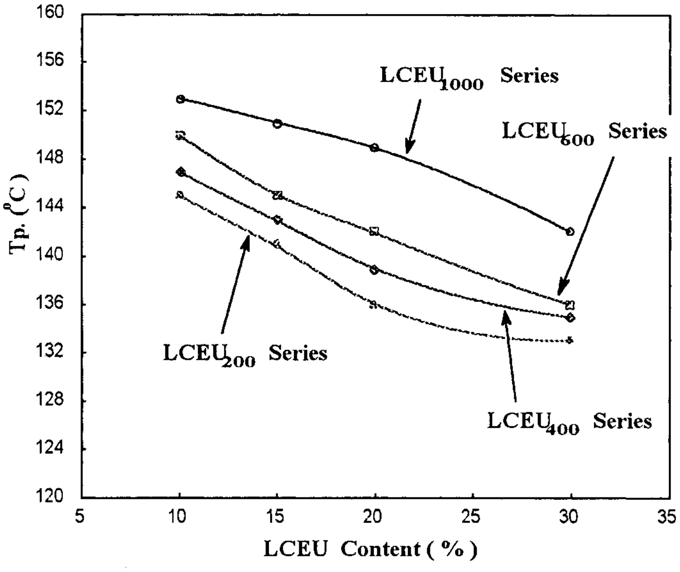


Fig. 2. Modulus vs. temperature for E-51/dicy/LCEU_{600} curing systems. 0: E-51/dicy/LCEU = 100:6:0; E: E-51/dicy/LCEU_{600} = 100:6:10; F: E-51/dicy/LCEU_{600} = 100:6:15; H: E-51/dicy/LCEU_{600} = 100:6:30.

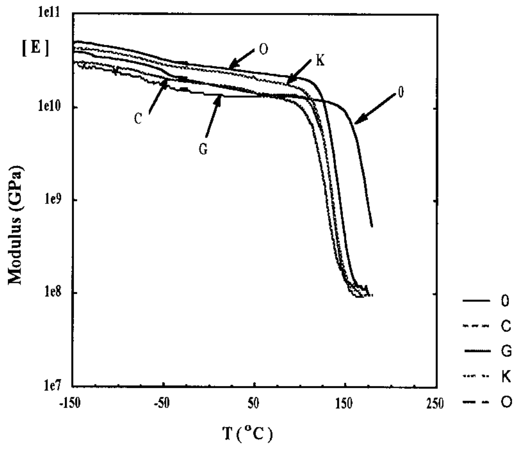


Fig. 3. Modulus vs. temperature for E-51/dicy/LCEU$_{PEG}$ curing systems. 0: E-51/dicy/LCEU = 100:6:0; C: E-51/dicy/LCEU$_{1000}$ = 100:6:20; G:E-51/dicy/LCEU$_{600}$ = 100:6:20; K: E-51/dicy/LCEU$_{400}$ = 100:6:20; O: E-51/dicy/LCEU$_{200}$ = 100:6:20.

at temperature near 190°C, since dicy is difficult to dissolve in liquid epoxy resin. However, ether chains in LCEU$_{PEG}$ caused the dicy to dissolve easier in epoxy resin. Thus caused the curing reaction temperature stepped down by 50°C as compared with that of the controlled sample.

3.2. Dynamic mechanical behavior

The dynamic mechanical properties of the modified curing systems were investigated at temperatures between −150 and 250°C, with RHEOVIBRON at a heating rate of 2°C/min and frequency of 11 Hz.

Fig. 2 shows the elastic modulus for LCEU$_{600}$ modified curing system, while Fig. 3 shows the elastic modulus of the curing system modified by LCEU$_{PEG}$ with various molecular weight of flexible chains. It may be seen that below 100°C, the elastic modulus of the modified curing system is approximate to that of the controlled sample. As we know when rubbery components are used to modify the epoxy resin, modulus is usually sacrificed at elevated temperature. However, toughening agents synthesized in this work consisted of flexible chains and rigid, rod-like unit. It is the rigid rod-like moiety that plays the great role in maintaining the high modulus properties of the cured epoxy resins.

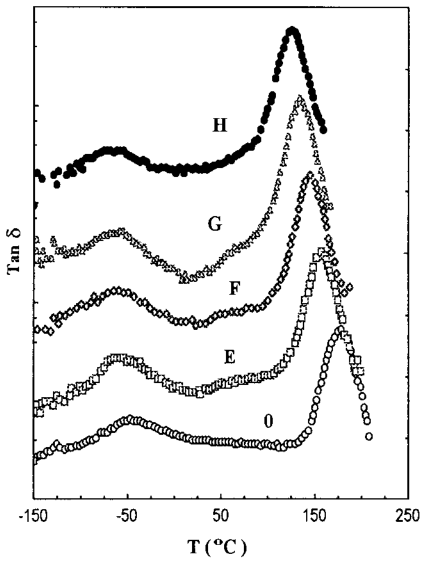


Fig. 4. Mechanical loss vs. temperature for E-51/dicy/LCEU$_{600}$ curing system. 0: E-51/dicy/LCEU = 100:6:0; E: E-51/dicy/LCEU$_{600}$ = 100:6:10; F: E-51/dicy/LCEU$_{600}$ = 100:6:15; G: E-51/dicy/LCEU$_{600}$ = 100:6:20; H: E-51/dicy/LCEU$_{600}$ = 100:6:30.

From Table 5 and Figs. 4 and 5, it can be seen that T_g of the modified curing system that appears to be slightly decrease with increasing content of LCEU$_{PEG}$, and increases with decreasing of the molecular weight of the flexible spacers in LCEU$_{PEG}$. Besides α- transition, there appears α-relaxation at around 60°C, which might be contributed by the addition of LCEU$_{PEG}$ to the epoxy resin. In addition, the position of β-transition gradually shifts to lower temperature, the width of the peaks is also broadened and even splits into double peaks. The influence of LCEU$_{PEG}$ content and its molecular weight on T_g is shown in

Table 6
Data of T_g and impact strength for E-51/dicy/LCEU$_{1000}$ and E-51/dicy/LCEU$_{600}$ curing systems

E-51/dicy/LCEU$_{1000}$	T_g (°C)	Impact strength (kJ/m^2)	E-51/dicy/LCEU$_{600}$	T_g (°C)	Impact strength (kJ/m^2)
100:6:0	176	4.0	100:6:0		4.0
100:6:5	–	8.2	100:6:5	–	14.6
100:6:10	154	26.8	100:6:10	156	25.9
100:6:15	146	25.2	100:6:15	148	25.1
100:6:20	133	29.2	100:6:20	135	26.3
100:6:30	121	31.4	100:6:30	125	25.1

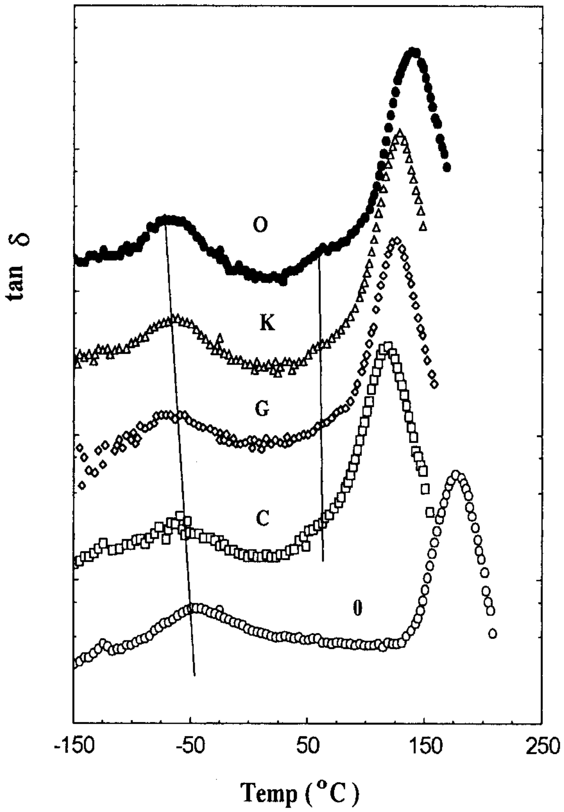


Fig. 5. Mechanical loss vs. temperature for $\mathrm{LCEU_{PEG}}$ modified curing systems. 0: E-51/dicy/LCEU = 100:6:0; C: E-51/dicy/$\mathrm{LCEU_{1000}}$ = 100:6:30; G: E-51/dicy/$\mathrm{LCEU_{600}}$ = 100:6:30; K: E-51/dicy/$\mathrm{LCEU_{400}}$ = 100:6:30; O: E-51/dicy/LCEU $_{200}$ = 100:6:30.

Fig. 6. With the same $\mathrm{LCEU_{PEG}}$, T_g decreases with the increase of its content, as for the same content of modifier, T_g decreases with the increase of its molecular weight, additionally, as the molecular weight of flexible chains in $\mathrm{LCEU_{PEG}}$ beyond 400, the curves essentially turn flat.

It has been suggested by Ochi and Shimbo that β-relaxation observed at about −40°C in the amine-cured epoxy resin system is the contribution from the

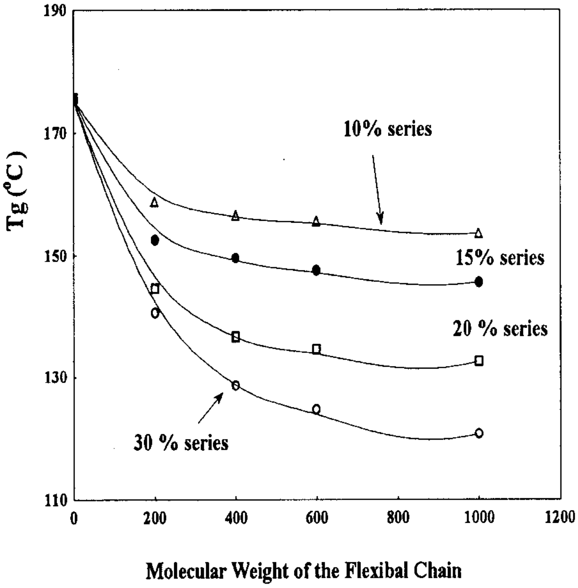


Fig. 6. Influence of M_w of the flexible chain in $\mathrm{LCEU_{PEG}}$ on T_g for the modified curing systems.

Fig. 7. SEM of the controlled sample, E-51/dicy = 100:6.

Table 7
Data of T_g and impact strength for E-51/dicy/$\mathrm{LCEU_{400}}$ and E-51/dicy/$\mathrm{LCEU_{200}}$ curing systems

E-51/dicy/$\mathrm{LCEU_{400}}$	T_g (°C)	Impact strength (kJ/m^2)	E-51/dicy/$\mathrm{LCEU_{200}}$	T_g (°C)	Impact strength (kJ/m^2)
100:6:0	176	4.0	100:6:0	176	4.0
100:6:5	–	12.5	100:6:5	–	8.0
100:6:10	157	17.0	100:6:10	159	14.5
100:6:15	150	12.2	100:6:15	153	12.2
100:6:20	137	9.2	100:6:20	145	7.3
100:6:30	129	8.2	100:6:30	141	3.0

segment of –$CH_2CH(OH)CH_2O$–, while β- relaxation observed at about −70°C in the anhydride-cured system is of the segment of –OCH_2CH_2O– generated during the curing reaction [11,12]. From the above results, it can be inferred that the toughening agent $LCEU_{PEG}$ has been incorporated into the cross-linked epoxy resin network, which leads to the formation of phase-separation structure, this kind of structure is favorable to enhancement of impact strength.

3.3. Impact fracture strength

From the data listed in Tables 6 and 7, it can be seen that the impact strength of the curing systems is greatly enhanced by the addition of $LCEU_{PEG}$. The improvement of impact strength is closely related to the content of $LCEU_{PEG}$ and the molecular weight of the flexible chains. Among these modifiers, $LCEU_{1000}$ and $LCEU_{600}$ are more effective, and the preferable content of them is between 10 and 15%. Under these conditions, not only impact strength is improved but also other good performance is maintained.

3.4. Morphology of the fractured surface [13]

The fracture surface of the unmodified epoxy resin

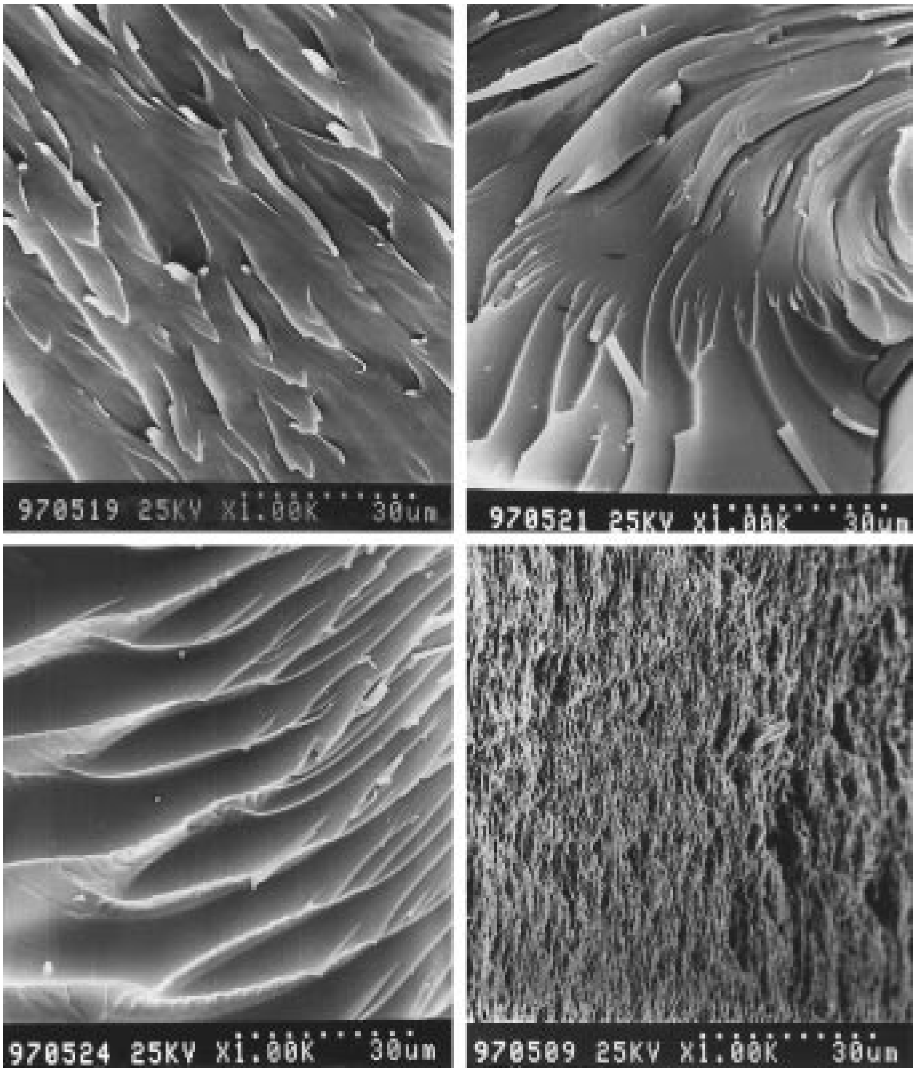


Fig. 8. SEM of the fractured surface of the modified curing samples. A: E-51/dicy/$LCEU_{200}$ = 100:6:10; B: E-51/dicy/$LCEU_{400}$ = 100:6:10; C: E-51/dicy/$LCEU_{600}$ = 100:6:10; D: E-51/dicy/$LCEU_{1000}$ = 100:6:10.

appears to be brittle fracture (Fig. 7). However, phase-separation appears on the fracture surfaces of the modified curing systems (Fig. 8), which indicates tough fracture. The fracture surface A appears rougher than that of the controlled sample, its impact strength gets considerable improvement correspondingly. The fracture surface of B appears branched, and also possesses high impact strength. Fracture surfaces of C and D show more branches resulted in the higher impact strength. The result shows that branches appearance on the fracture surface played an important role in improving impact strength.

In conclusion, $LCEU_{PEG}$ is an effective modifier for the epoxy resin–dicy curing system. With the addition of $LCEU_{PEG}$, curing reaction temperature is decreased by about 50°C; E_a by about 60 kJ/mol. $LCEU_{1000}$, and $LCEU_{600}$ are more effective than $LCEU_{400}$ and $LCEU_{200}$ as modifiers. The preferable content of the modifier in the curing system is 10–15% by weight. Modulus is maintained at a slight expense of T_g.

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