Application of a Series of Novel Chain-Extended Ureas as Latent-Curing Agents and Toughening Modifiers for Epoxy Resin

BAO-LONG ZHANG,[1] HUI-QI ZHANG,[1,2] YING-CAI YOU,[1] ZONG-JIE DU,[1] PEI-YUAN DING,[1] TAO WANG,[1] JI-FU HUANG[1]

[1] Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

[2] Department of Applied Chemistry, Tianjin University, Tianjin 300072, People's Republic of China

ABSTRACT: A series of novel chain-extended ureas (U_i) containing poly(ethylene glycol) (PEG) spacers with different molecular weights were synthesized and the reactive mechanism, reactive activity, impact strength, dynamic mechanical behavior, morphology, and storage properties of the epoxy resin/chain-extended urea system were studied. Experimental results revealed that the impact strength of the epoxy resin modified with chain-extended urea containing a PEG flexible spacer with molecular weight of 1000 is 9.5 times higher than that of the epoxy resin/dicyandiamide system. Results also show that the molecular weight of PEG in chain-extended ureas hardly has any influence on the reactive activity of the chain-extended ureas. The storage life of the epoxy resin/U_i system can be delayed to 38 h at 50°C. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 339–347, 1998

Key words: epoxy resin; chain-extended ureas; toughening modifier; latent-curing agent; poly(ethylene glycol)

INTRODUCTION

Epoxy resins have excellent adhesion, mechanical, and electrical properties and are widely utilized in the fields of coatings, adhesives, castings, etc. However, it is well known that the commonly used epoxy resins are rather brittle when cured with stoichiometric amounts of common curing agents such as aliphatic or aromatic polyamides, dicarboxylic acids, anhydrides, boron trifluoride, and tertiary amines, and their low impact resistance greatly limits the use of these resins in structural applications. In addition, epoxy resins usually must be admixed with curing agents in order to promote the cure before use. A disadvantage of epoxy resin compositions is that when a common curing agent is mixed with epoxy resin a measurable amount of curing occurs at room temperature, even if the composition normally requires heating for the final cure. For this reason, most epoxy resin compositions are marketed commercially as two-part systems, the curing agent being kept separate from the part containing the epoxy resin, until just prior to actual application. For many applications, there would be a great advantage in an epoxy resin composition which can be marketed as a one-part system, where the curing agent is already present and which can be brought to a rapid cure by the application of heat. Such a system, containing the curing agent, should have a long life at usual room temperatures. Therefore, the synthesis of novel curing

agents which can meet the above requirements (called latent-curing agents) and at the same time can improve the impact strength of epoxy resins is a significant goal.

This article reports the synthesis of a series of novel chain-extended ureas U_i containing poly-(ethylene glycol) (PEG) flexible spacers with different molecular weights and their application as the latent-curing agents as well as toughening modifiers for the epoxy resin. The effect of the molecular weight of PEG flexible spacers in U_i and the content of U_i on the properties of epoxy resin/U_i system was examined.

EXPERIMENTAL

Materials

Epoxy resin (E-51) with an epoxide number of 0.51 was purchased from Yueyang Chemical Factory (Hunan Province, China). Poly(ethylene glycol)s (PEG) with molecular weights of 106, 400, 600, and 1000 were all dehydrated in a vacuum for 48 h at 70°C before use. Toluene diisocyanate (TDI) (80/20) was purified by distillation under a vacuum. Tetrahydrofuran was first refluxed over sodium and then distilled. The pure dimethylamine was obtained by heating the aqueous solution of dimethylamine.

Synthesis of Chain-extended Ureas

Chain-extended ureas with PEG flexible spacers (Scheme 1) were synthesized according to the methods described by Wissman et al.[1] and Liang,[2] and their properties are summarized in Table I.

Measurements

The reactive activity of U_i was examined by a CDR-1 type differential scanning calorimeter (DSC) (Shanghai Balance Factory) at a heating rate of 1, 2, 5, and 10°C/min, respectively. Dynamic mechanical analysis was performed with a DDV-II-EA instrument (TMI Toyo Baldwin Co.) between −150 and 250°C at a heating rate of 5°C/min at a frequency of 110 Hz. The Charpy impact strength of the cured resins was determined by an XCJ-500 Charpy impact tester at 23°C. Scanning electron micrographs were taken with a Hitachi X-50 instrument. The storage properties of the epoxy resin composites with chain-extended ureas
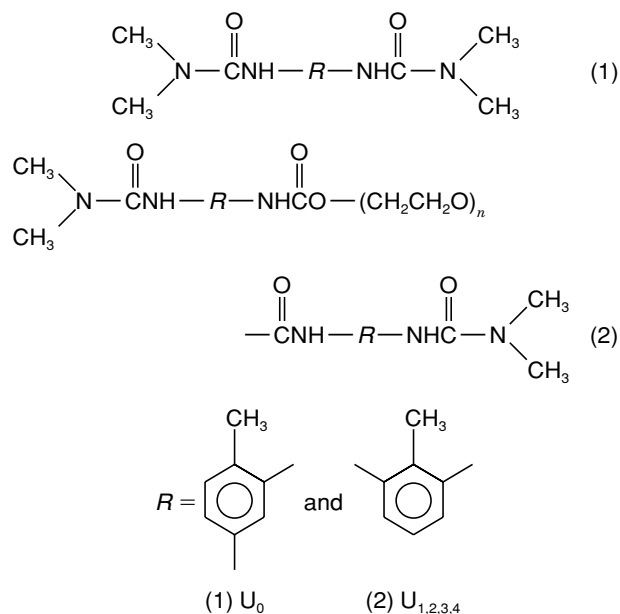
Scheme 1   The chemical structures of the ureas.

were measured with a Reheotext-2 type cone-and-plate rotary viscosimeter at 50°C.

Curing Procedure

A mixture of U_i and the epoxy resin (E-51) was degassed at room temperature. The resulting mixture was then poured into a mold and cured for 2 h at 100°C. The content of U_i was calculated based on the amount of the epoxy resin.

RESULTS AND DISCUSSION

Reactive Mechanism of E-51/U_i System

The use of ureas as curing agents for epoxy resins has been the subject of extensive studies.[3–5] Iwakura and Izawa[3] analyzed the reaction between phenyl glycidyl ether (PGE) and substituted ureas of the type C_6H_5 NHCONRR′, where $R = C_2H_5$, C_4H_9, CH_3, or H and $R = C_2H_5$, C_4H_9, or C_6H_5 and gave the following curing mechanism of the epoxy resin with ureas:
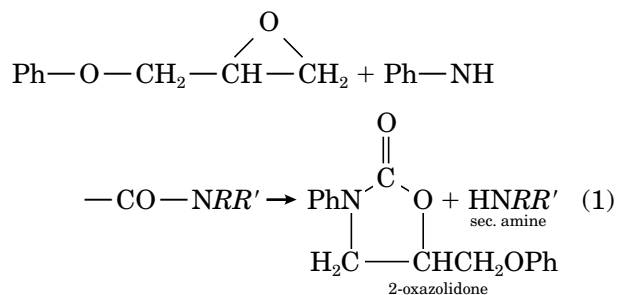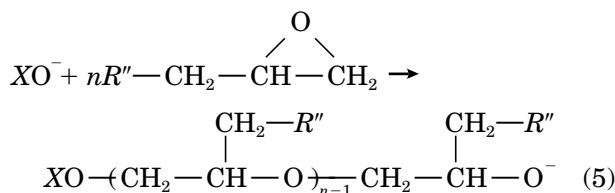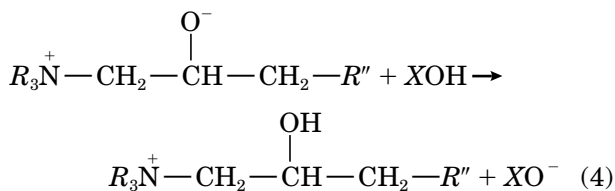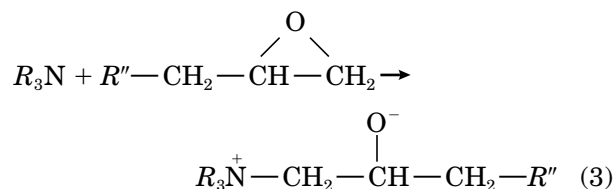
Table I   Physical Properties of the Synthesized Ureas

Properties	Urea Code (U_i)				
	U_0	U_1	U_2	U_3	U_4
Molecular weight of PEG	0	106	400	600	1000
Color	White	White	White	Light yellow	Light yellow
State	Powder	Powder	Viscous liquid	Viscous liquid	Viscous liquid
Melting point (°C)	185	78	—	—	—
Viscosity ($cp \times 10^{-4}$)[a]	—	—	29.13	5.52	1.68
Yield (%)	94	92	91	90	90

[a] Measured with a Reheotext-2 type cone-and-plate rotary viscosimeter at 25°C.

$$R'' - CH_2 - \overset{O}{\overset{\diagup \diagdown}{CH} - CH_2} + HNRR' \rightarrow$$

$$R'' - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_2 - NRR' \quad (2)$$

$$R_3N + R'' - CH_2 - \overset{O}{\overset{\diagup \diagdown}{CH - CH_2}} \rightarrow$$

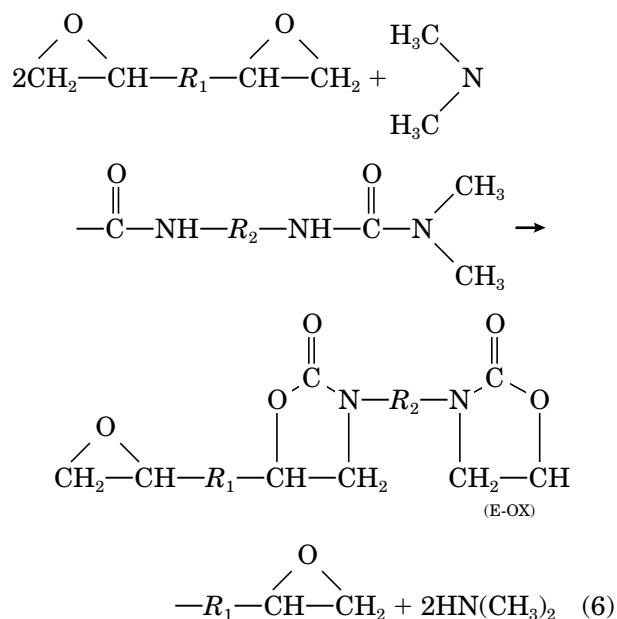$$\overset{+}{R_3N} - CH_2 - \underset{\underset{O^-}{|}}{CH} - CH_2 - R'' \quad (3)$$

$$\overset{+}{R_3N} - CH_2 - \underset{\underset{O^-}{|}}{CH} - CH_2 - R'' + XOH \rightarrow$$

$$\overset{+}{R_3N} - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_2 - R'' + XO^- \quad (4)$$

$$XO^- + nR'' - CH_2 - \overset{O}{\overset{\diagup \diagdown}{CH - CH_2}} \rightarrow$$

$$XO \overset{}{(CH_2 - \underset{\underset{CH_2 - R''}{|}}{CH} - O)_{n-1}} CH_2 - \underset{\underset{CH_2 - R''}{|}}{CH} - O^- \quad (5)$$
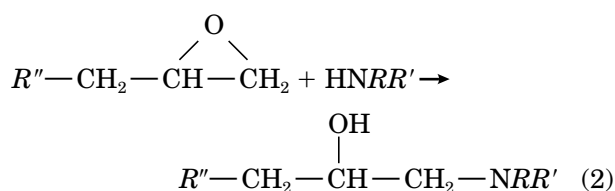
Experimental studies carried out by Byrne et al.[4] and Fasce et al.[5] further confirmed that the progress of the reaction between the epoxy and ureas takes place along steps (1)–(5) shown above. Therefore, we can deduce that the reaction mechanism between epoxy resin E-51 and diurea (U_i) is same as the above mechanism. In a great excess of the epoxy resin, the reaction between the epoxy resin E-51 and diurea (U_i) first leads

to the formation of epoxy resin containing oxazolidone (E-OX) and dimethylamine along step (6) as shown below and then dimethylamine will lead to a rapid polymerization of E-51 and E-OX along steps (2)–(5):

$$2CH_2 - \overset{O}{\overset{\diagup \diagdown}{CH}} - R_1 - \overset{O}{\overset{\diagup \diagdown}{CH - CH_2}} + \overset{H_3C}{\underset{H_3C}{\diagup}} N$$

$$- \overset{O}{\overset{\|}{C}} - NH - R_2 - NH - \overset{O}{\overset{\|}{C}} - N \overset{CH_3}{\underset{CH_3}{\diagdown}} \rightarrow$$

$$\underset{CH_2 - CH - R_1 - CH - CH_2}{\overset{O}{\overset{\diagup \diagdown}{}}} \overset{O \underset{\overset{\|}{C}}{} \quad O \underset{\overset{\|}{C}}{}}{O \diagdown \underset{N - R_2 - N}{} \diagup O} \underset{CH_2 - CH}{\overset{O}{\overset{\diagup \diagdown}{}}}$$

(E-OX)

$$- R_1 - \overset{O}{\overset{\diagup \diagdown}{CH - CH_2}} + 2HN(CH_3)_2 \quad (6)$$

Reactive Activity of E-51/U_i System

The reactive activity of the E-51/U_i system was measured with DSC and the results are listed in Table II.

The results show that the reactive activity of the epoxy resin composites with ureas containing PEG flexible spacers is higher than that of E-51/U_0 system, which comes from the increase of compatibility between E-51 and ureas containing PEG flexible spacers. The results also show that

Table II Temperatures of DSC Peaks (T_p) and Kinetic Data Determined by Kissinger's Method[6] for E-51/U_i [100/15 (g/mmol)] System

U_i	U_0	U_1	U_2	U_3	U_4
T_p (°C)[a]	147	140	141	141	139
Ea (kJ/mol)[b]	47.2	44.1	44.4	43.8	41.8

[a] DSC scanning rate: 5°C/min.
[b] Activation energy of curing reaction.

the reactive activity of the E-51/$U_{(1,2,3,4)}$ system, within the limits of error, is almost the same regardless of the different molecular weight of the PEG flexible spacers contained in chain-extended ureas.

The effect of the concentration of U_4 on the storage life of the E-51/U_4 system is shown in Figure 1. It can be seen that the storage life of the E-51/U_4 system increases as the concentration of U_4 decreases and is 38 h at 50°C when the ratio of E-51/U_4 is 100/3.7 g/mmol.

Dynamic Mechanical Analysis of the Cured Resins

Dynamic mechanical analysis can give information on the microstructure of the cured resins. Fig-
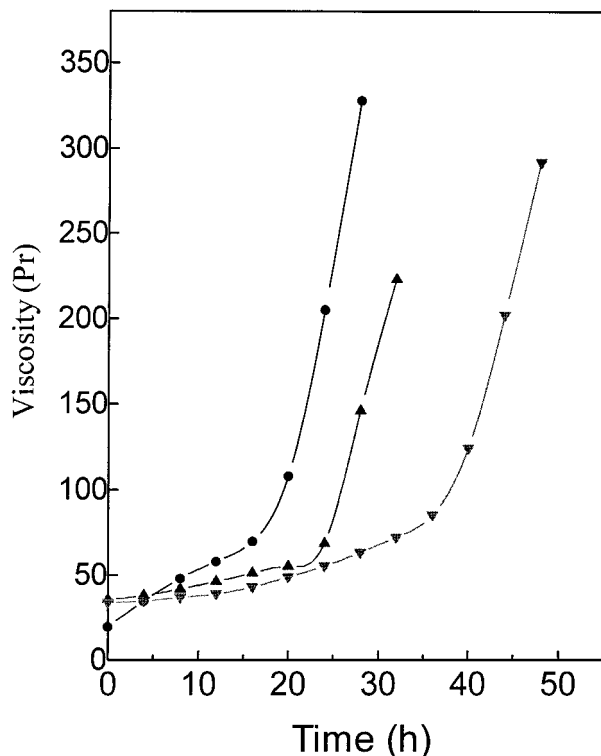

Figure 1 Dependence of the viscosity of E-51/U_4 system on time. E-51/U_4 [g/mmol]: (●) 100/14.6; (▲) 100/7.4; (▼) 100/3.7.
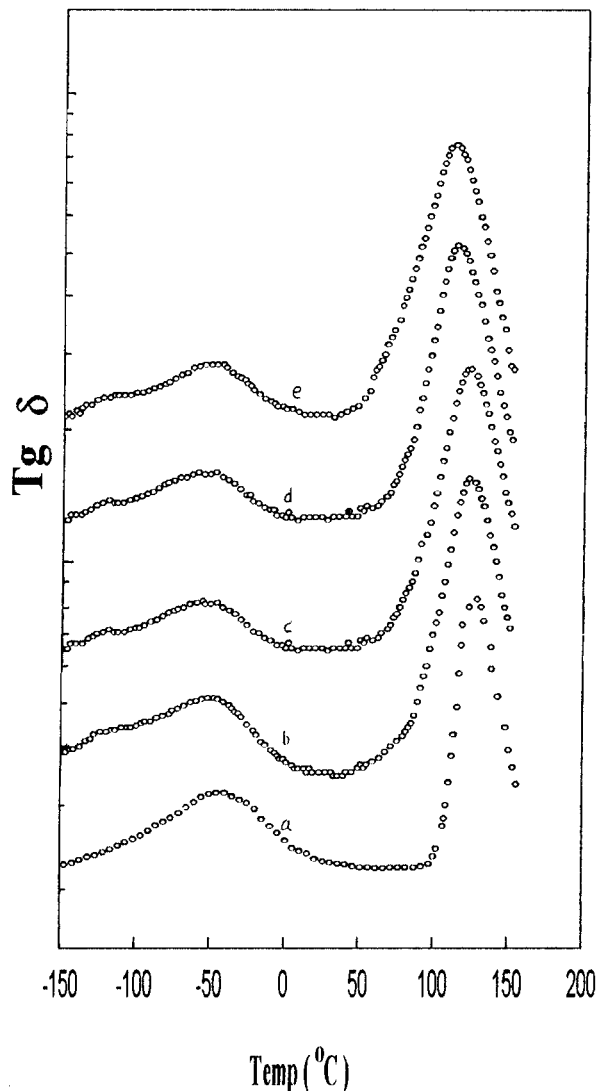

Figure 2 Dynamic mechanical spectra of the cured E-51/U_1 system: (a) U_0; (b) U_1; (c) U_2; (d) U_3; (e) U_4.

ure 2 shows the dynamic mechanical spectra of the cured E-51/U_i system as a function of the molecular weight of PEG flexible spacers in chain-extended ureas. The relaxation temperatures and modulus of the samples are summarized in Table III. It can be seen that all the samples of the cured epoxy resins modified with chain-extended ureas have three relaxation peaks, that is, the α-relaxation peak, the β-relaxation peak, and the γ-relaxation peak, while the cured E-51/U_0 system has only an α-relaxation peak and a β-relaxation peak. This suggests that the γ-relaxation is attributed to the vibration of the segment chain —CH_2CH_2O— in PEG flexible spacers. It has also been verified that the α-relaxation and the

Table III   Relaxation Temperatures and Modulus for the Cured E-51/U_i [100/14 (g/mmol)] System

U_i	T_α (°C)	T_β (°C)	T_γ (°C)	$E (\times E^{-10}) (-130°C)$	$E (\times E^{-10}) (20°C)$
U_0	127	−49		4.14	2.08
U_1	123	−50	−122	2.65	1.40
U_2	121	−52	−121	4.33	2.49
U_3	117	−52	−123	3.92	1.87
U_4	113	−48	−118	4.16	2.12

β-relaxation are attributed to the glass transition of the cured epoxy resin and the vibration of the segment chain $-CH_2CH(OH)CH_2N-$, respectively.[7−9] The results also show that the α-relaxation temperatures (T_g) of the cured E-51/U_i system decrease with increasing molecular weight of the PEG flexible spacers in chain-extended ureas. Meanwhile, the molecular weight of PEG flexible spacers in chain-extended ureas hardly has an influence on the β-relaxation and γ-relaxation temperatures of the cured E-51/U_i system. In addition, the modulus of the cured E-51/U_i system, within the limits of error, almost keeps constant with increasing molecular weight of the PEG flexible spacers in chain-extended ureas.

Figure 3 shows the dynamic mechanical spectra of the cured E-51/U_4 system as a function of the content of U_4, and the corresponding relaxation temperatures and modulus of the samples are summarized in Table IV. It can be seen that in the modification with less than 20% of U_4 the α-relaxation temperatures (T_g) of the cured E-51/U_4 system increase rapidly with increasing content of U_4; when the content of U_4 exceeds 20%, however, the α-relaxation temperatures (T_g) of the cured E-51/U_4 system decrease slightly with increasing content of U_4. A similar result was also obtained in a previous article.[10] It can also be seen that the modulus of the cured E-51/U_4 system, within the limits of error, also keeps constant with increasing content of U_4.

Impact-resistance Properties of E-51/U_i System

Figure 4 shows that the impact strength of the cured E-51/U_i [100/14 (g/mmol)] system increases with increasing the molecular weight of PEG flexible spacers in chain-extended ureas in the range studied and the impact strength of the cured E-51/U_4 system is almost 2.3 times higher than that of the cured E-51/U_0 system and 9.5 times higher than that of the cured E-51/dicyandiamide [100/8 (g/g)] system.[10]

It is very clear that the addition of the chain-extended ureas significantly improves the mechanical properties of the epoxy resin. However,
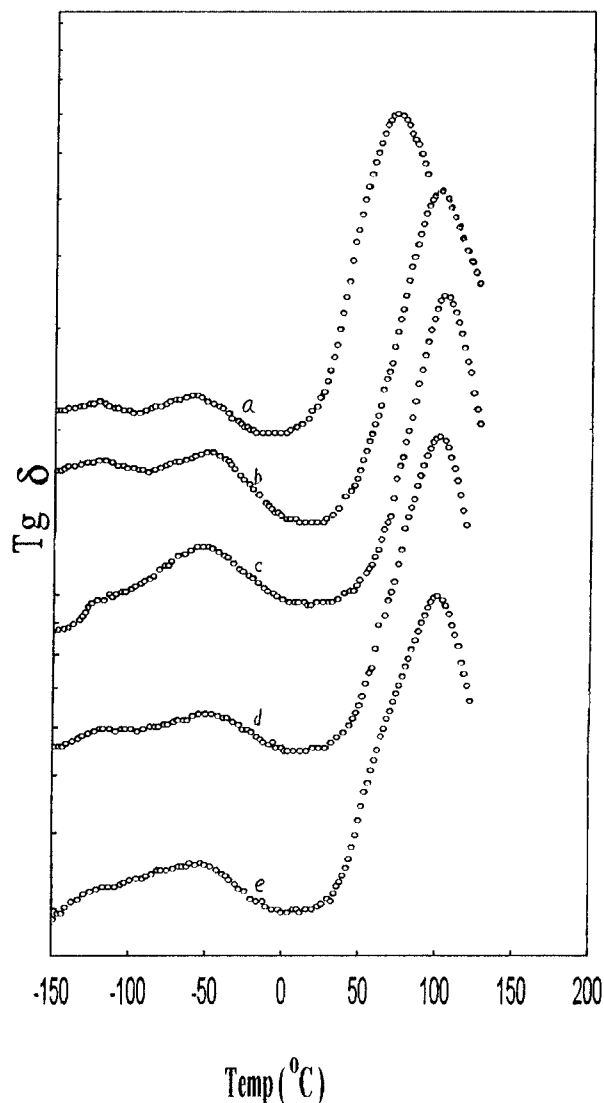

Figure 3 Dynamic mechanical spectra of the cured E-51/U_4 system as a function of the content of U_4: (a) 10%; (b) 15%; (c) 20%; (d) 25%; (e) 30%.

Table IV   Relaxation Temperatures and Modulus as a Function of the Concentration of U_4 in the Cured E-51/U_4 System

U_4/E-51 (g/100 g)	T_α (°C)	T_β (°C)	T_γ (°C)	E ($\times E^{-10}$) (-130°C)	E ($\times E^{-10}$) (20°C)
10	71	-59	-120	4.57	2.49
15	102	-49	-120	3.66	1.95
20	105	-50	-122	3.12	1.44
25	100	-51	-120	3.14	1.42
30	99	-55	-120	4.54	2.21

another consideration should be how to reduce the cost and use the smallest amount of chain-extended ureas to obtain the best toughening effect. Indeed, the impact strength of the cured E-51/U_i system will be strongly dependent on the amount of U_i. It can be seen from Figure 5 that the impact strength of the cured E-51/U_4 system increases with increasing the content of U_4; however, it tends to level off when the content of U_4 exceeds 25%. This means that there is a limit of the content of U_4 to improve the mechanical properties of the epoxy resin.

Morphology of the Cured Resins

The toughening mechanism can be explained in terms of the morphological behavior because the morphological examination can give interesting information on the microstructure of the cured resins. Figure 6 shows the scanning electron micrographs of the cured E-51/U_i system. It can be seen that the morphologies of the epoxy resins modified with chain-extended ureas are quite different from that of the cured E-51/U_0 system. The morphology of the cured E-51/U_0 system shows
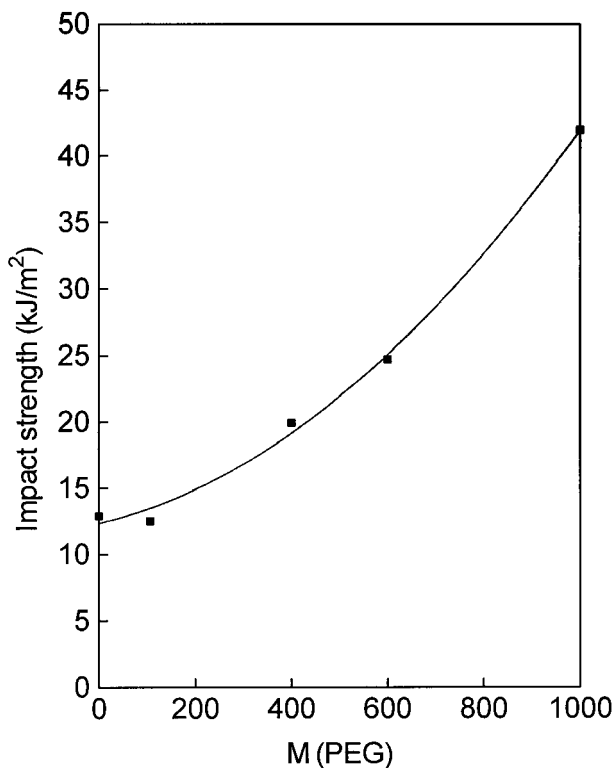
Figure 4   Relations of the impact strength to the molecular weight of PEG contained in U_i for the cured E-51/U_i [100/14 (g/mmol)] system.
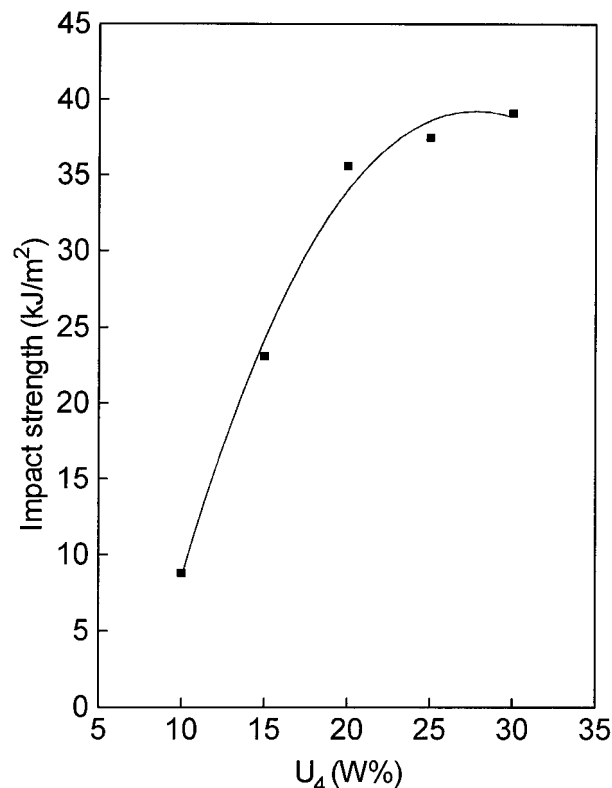
Figure 5   Relations of the impact strength to the content of U_4 in the cured E-51/U_4 [100/content of U_4 (g/g)] system.
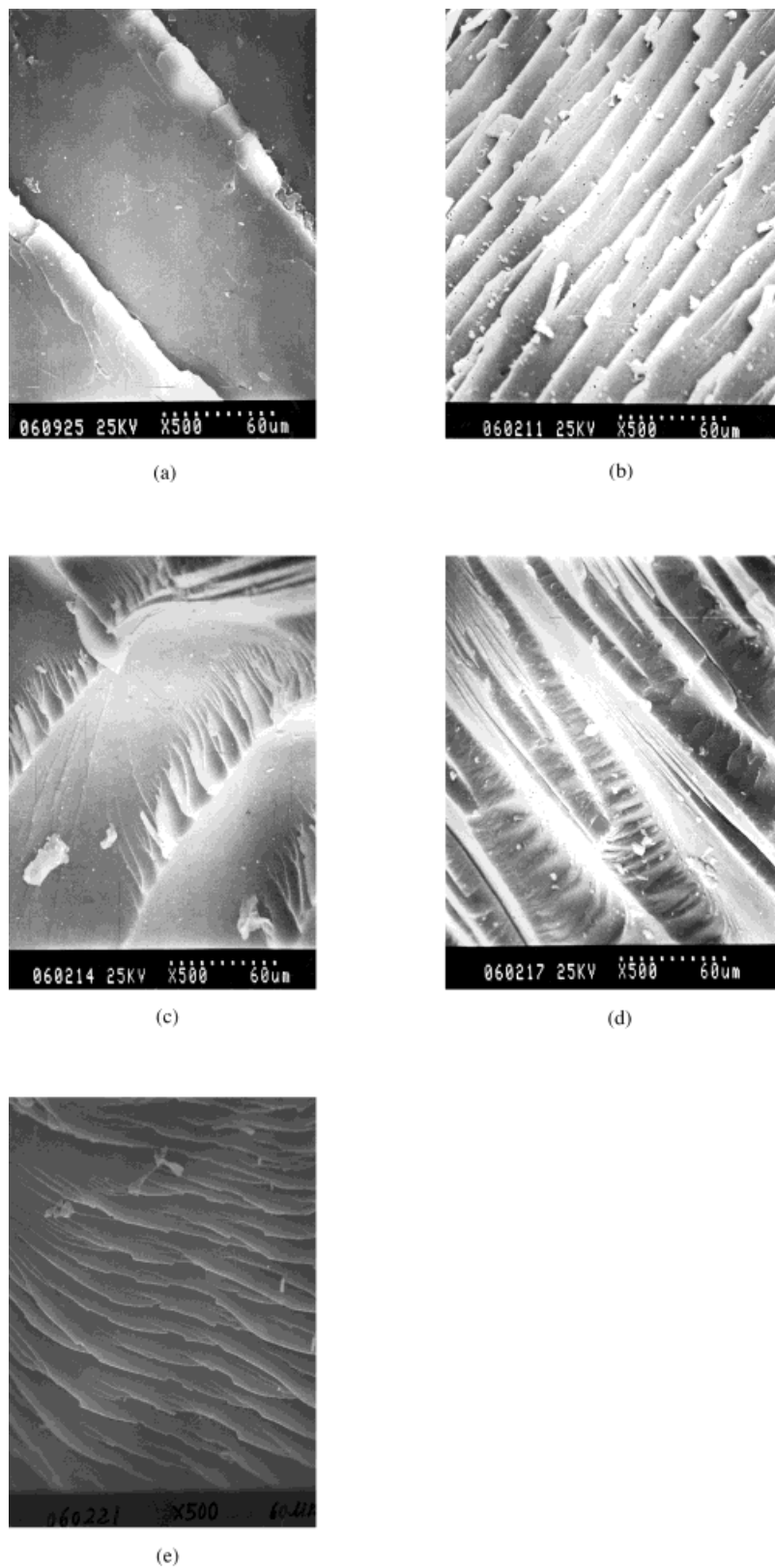
(a)

(b)

(c)

(d)

(e)

Figure 6 Scanning electron micrographs of the fracture surfaces of the impact specimen for the cured E-51/U_i [100/14 (g/mmol)] system: (a) U_0; (b) U_1; (c) U_2; (d) U_3; (e) U_4.
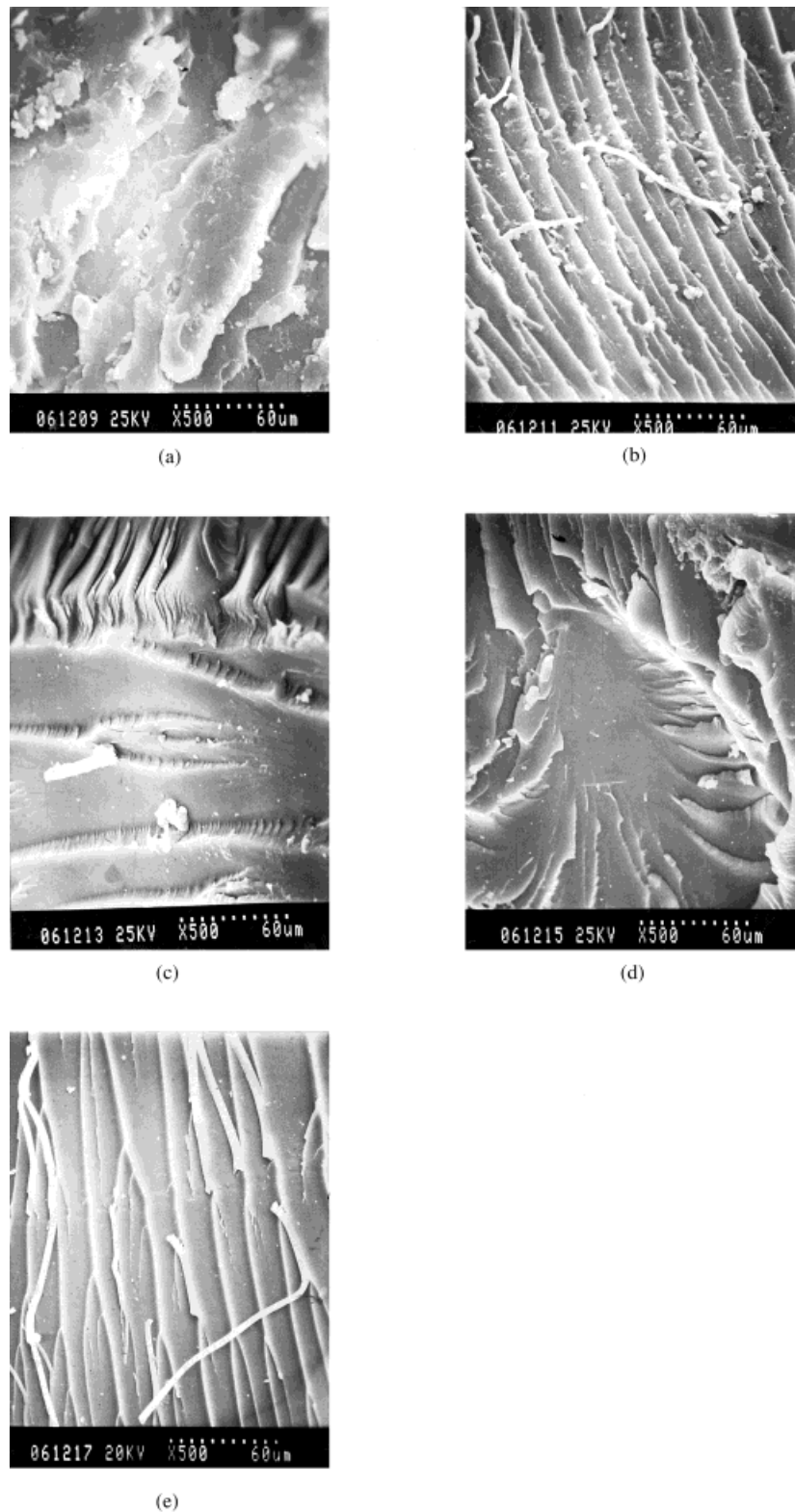
Figure 7 Scanning electron micrographs of the fracture surfaces of the impact specimen for the cured E-51/U_4 system. E-51/U_4 (g/g): (a) 100/10; (b) 100/15; (c) 100/20; (d) 100/25; (e) 100/30.

the characteristic of brittle fracture, while for the morphologies of the epoxy resins modified with chain-extended ureas (especially U_2, U_3, U_4) the characteristic of the toughening fracture can be clearly observed. This fits the impact-resistance properties of the cured epoxy resins modified with the chain-extended ureas very well.

Figure 7 shows the scanning electron micrographs of the cured E-51/U_4 system. The morphological behaviors also correspond to the toughness of the cured epoxy resins.

CONCLUSIONS

A series of novel chain-extended ureas containing PEG flexible spacers were synthesized. The effect of the molecular weight of PEG flexible spacers in chain-extended ureas and the content of the chain-extended ureas on the reactive activity of the E-51/U_i system and the impact resistance of the cured epoxy resins was investigated in detail. From experimental results, the following conclusions are obtained:

1. The chain-extended ureas containing PEG flexible spacers can act as the latent-curing agents for the epoxy resin (E-51), and the storage life of the E-51/U_i system might be delayed to 38 h at 50°C.

2. The chain-extended ureas containing PEG flexible spacers can also act as effective toughening modifiers for the epoxy resin (E-51). The impact strength of the cured E-51/U_i system increases with increasing molecular weight of the PEG flexible spacers in chain-extended ureas in the range studied and the addition of U_4 (less than 25%) greatly increases the impact resistance of the cured epoxy resins at minimal expense of mechanical properties.

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