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Studies on the properties of epoxy resins modified with chain-extended ureas

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Abstract

Two kinds of reactive toughening accelerators for epoxy resin, amine-terminated chain-extended urea (ATU) and imidazole-terminated chain-extended urea (ITU) were synthesized from polyurethane prepolymer. Compared with the unmodified system, the curing activity, dynamic mechanical behavior, impact property and fracture surface morphology of the modified systems were systematically investigated. Results show that the curing activity of modified epoxy resin E-51/dicyandiamide (dicy) systems is so greatly enhanced that the apparent activation energy of curing reaction decreases from 130.2 kJ/mol for the unmodified system to 75–85 kJ/mol for the modified systems. The curing reaction mechanism of E-51/dicy system accelerated by ITU is different from that of the system accelerated by ATU, and a little different from that of the system accelerated by imidazole. Furthermore, the impact strength of the cured systems modified with ITU are 2–3 times higher than that of the unmodified system, while the glass transition temperatures are little altered, and the fracture surfaces of all modified systems display tough fracture feature. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Chain-extended urea; Toughening

1. Introduction

Epoxy resin is one of the most important thermosetting polymer materials. It has many excellent properties, such as high thermal stability, adhesion, mechanical and electrical properties, and is widely utilized in the field of coatings, adhesives, castings, etc. However, it is well known that the commonly used epoxy resin is generally rather brittle when cured with stoichiometric amount of common curing agents such as aliphatic or aromatic amides, dicarboxylic acids, anhydrides, boron trifluoride, because of its highly crosslinked structure. Its poor fracture toughness greatly limits the use of this resin in structural applications. Improving the toughness of this resin is very important for epoxy technology. Lots of efforts have been made to improve the toughness of the cured epoxy resin. One approach is the modification with some reactive liquid rubbers, such as carboxyl-terminated butadiene-acrilonitrile liquid rubber (CTBN) or amine-terminated butadiene-acrilonitrile liquid rubber (ATBN) [1–10]. The end groups present in such elastomeric moieties are able to react with the oxirane ring of the epoxy resin, making the two phases chemically bound, and seems quite successful. However, these rubbers lack heat resistance because of the double bond, and thus the modification with these rubbers leads to low thermal stability of the cured epoxy resin over the high temperature region. In order to maintain its high thermal stability over a broad range of temperature, researchers take silicone rubber instead of CTBN and ATBN to modify epoxy resin. Another problem appears that the silicone rubber [11,12] separates from the epoxy resin if it is directly blended with epoxy resin, because silicone rubber lacks compatibility with epoxy resin. Compatibilizer can be added to the system to improve the dispersibility. Nevertheless, most of these works are at the cost of the modulus or hardness of epoxy resins. In addition, the curing temperature for the above-modified system is usually very high and the reactivity very low.

This paper reports two kinds of chain-extended ureas containing PPG flexible spacer, which were synthesized and used to modify the dicyandiamide-cured epoxy resin system. The reactivity, dynamic mechanical behavior, impact property and morphology for the curing systems were examined.

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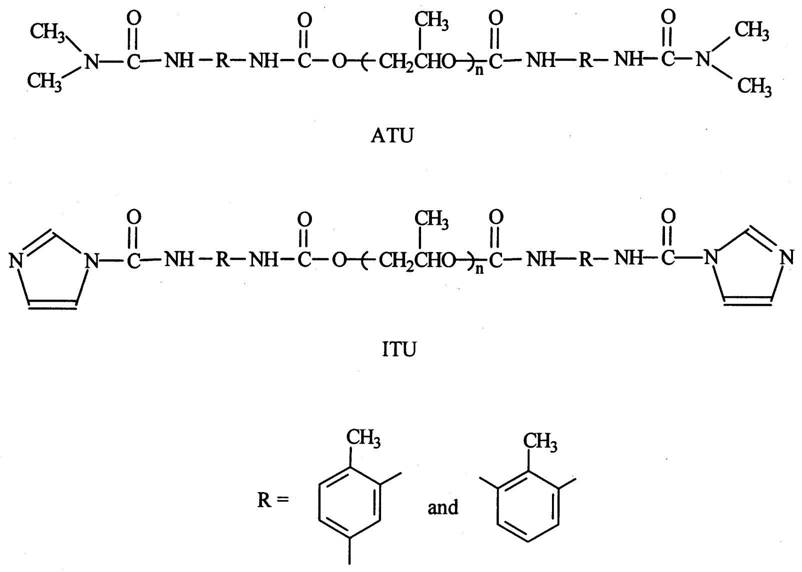


Scheme 1.

2. Experimental

2.1. Materials

The base material used in this study is a standard epoxy E-51, which is a diglycidyl ether of bisphenol A epoxy resin with epoxide number of 0.51, supplied by Yueyang Chemical Factory, Hunan Province, PRC. The curing agent is dicyandiamide. Polypropylene glycol PPG1000 with molecular weight of 1000 was dehydrated in vacuum for 48 h at 70°C before use. Toluenediisocyanate (TDI) (80/20) was purified by distillation under vacuum. The pure dimethylamine was obtained by heating the aqueous solution of dimethylamine. Imidazole was purified by recrystallization from benzene.

2.2. Synthesis of chain-extended urea

Synthesis of the chain-extended urea was conducted via a two-stage process. In the first stage, polyurethane prepolymer was synthesized by the reaction of 1 mol of PPG1000 and 2 mol of toluenediisocyanate. Terminal of reaction was confirmed by determination of the isocyanate group content by means of titration. In the second stage of the process, the prepolymer was terminated with dimethylamine and imidazole, respectively, to prepare chain-extended ureas with flexible spacers (chemical structures of the chain-extended ureas; Scheme 1), properties of which are summarized in Table 1.

Table 1
Physical properties of the synthesized chain-extended ureas

Code of ureas	ATU	ITU
Color	Light yellow	Yellow
State	Viscous liquid	Viscous liquid
Yield (%)	98	99

2.3. Curing procedure

A mixture of epoxy resin (E-51), dicyandiamide and modifier was degassed in vacuum at 40°C for about 8 h. The resulting mixture was then cast into a preheated mold coated with silicone resin and cured according to the following curing cycle: 1 h/80°C + 4 h/120°C for modified systems and 1 h/120°C + 4 h/150°C + 1 h/180°C for the controlled system. The mold was removed from the oven and allowed to cool gradually to room temperature. All formulations were made by approximately 100 parts by weight epoxy resin with different parts of modifier and curing agent. Since all the formulations were based on 100 parts of epoxy resin, the modifier or curing agent will be referred to on parts per hundred epoxy resin.

2.4. Measurements

The curing reactivity was examined by differential scanning calorimetry (DSC: CDR-1, Shanghai Balance Factory, PRC) at a heating rate of 1, 2, 5 and 10°C/min, respectively. Prior to the examination, epoxy resin, curing agent and modifier was mixed fully. About 10–15 mg of the mixture was used for testing. Dynamic mechanical analysis was performed with a viscoelastomer (Rheovibron DDV-II-EA, TMI TOYO BALDWIN Co. Ltd, Japan) at a frequency of 110 Hz and over the temperature range of −150–250°C with a heating rate of 2°C/min. The thickness of the specimens was about 0.2 mm, width 1.5–3.0 mm and length 3.0–4.0 cm. The impact strength of the cured resins was determined by a Charpy impact-testing machine (XCJ-500, Chende, PRC) according to China National Standard GB 1043-79. The specimen described in GB 1043-79 is with

Table 2
DSC peak temperatures (°C) for the curing systems at different heating rate

No.	Formulation	DSC peak temperature (°C)			
		10°C/min	5°C/min	2°C/min	1°C/min
0	E-51/dicy = 100/6	197	190	175	168
1	E-51/dicy/ITU = 100/6/5	149	133	118	108
2	E-51/dicy/ITU = 100/6/10	142	127	114	103
3	E-51/dicy/ITU = 100/6/15	138	123	110	98
4	E-51/dicy/ITU = 100/6/20	132	121	107	94
5	E-51/dicy/ATU = 100/6/10	152	140	127	114

a thickness of 4.0 mm and width of 6.0 mm. The morphology of the fracture surfaces was observed by a scanning electron microscope (SEM: X-650, Hitachi Co. Ltd., Japan) at an accelerating voltage of 20 kV. The surface was coated with a thin layer of gold to reduce charge built-up on the surface and improve conductivity.

3. Results and discussion

3.1. Reactivity of the curing system

The curing procedures of the curing systems were investigated by DSC, and the DSC peak temperatures are presented in Table 2.

As shown in Table 2, at the heating rate of 5°C/min, DSC peak temperature (T_p) for the controlled system is as high as 190°C. However, at the same heating rate, with 10% amount of modifier, DSC peak temperature decreases to 127°C for the imidazole-terminated chain-extended urea (ITU)-modified system and 140°C for the amine-terminated chain-extended urea (ATU)-modified system. Moreover, DSC peak temperature for the same heating rate decreases with an increase of the ITU content. The decrease of DSC peak temperature reveals that the addition of ATU or ITU can accelerate the curing reaction between bisphenol epoxy resin and dicyandiamide greatly. The difference of T_p between the ITU-modified system and ATU-modified system indicates the different reactivity between them.

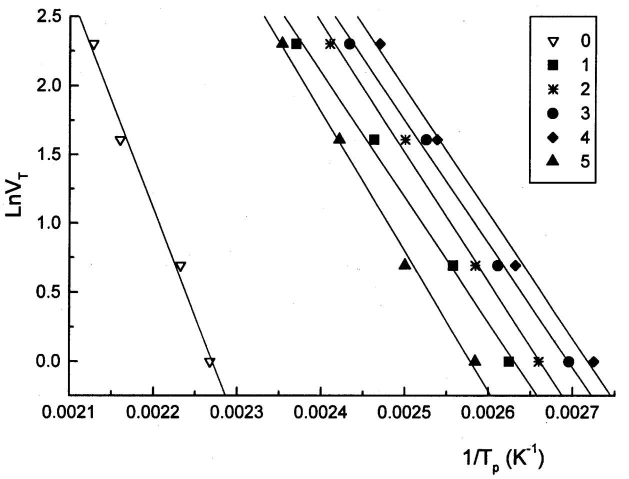


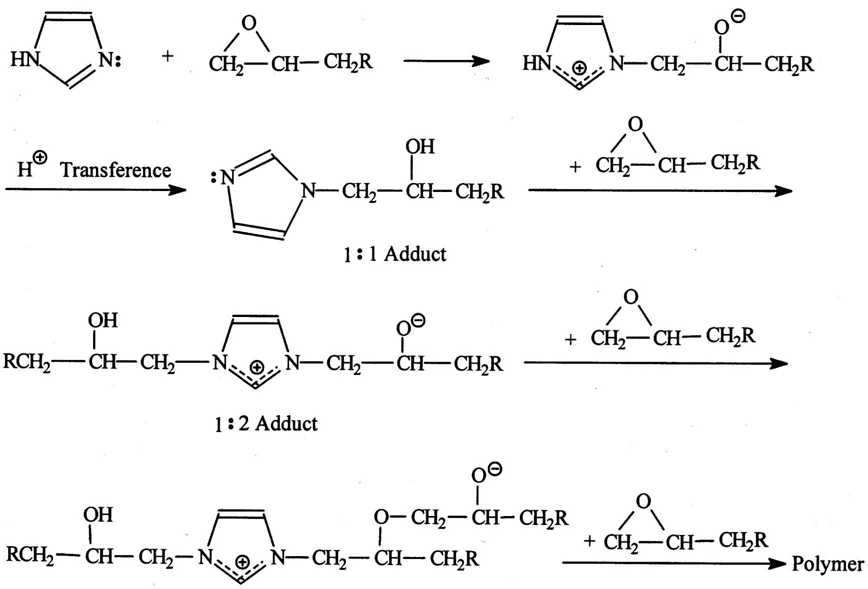
Fig. 1. Dependence of ln V_T on $1/T_p$ for the curing systems.

The reactivity can be characterized with apparent activation energy. Kissinger [13] has put forward a theory, which allows the determination of apparent activation energy. His theory shows that the relationship between DSC peak temperature T_p in K and the heating rate V_T is of the following form: $\ln V_T = \ln A - E_a/RT_p$, where R is a gas constant, A the frequency factor, and E_a is the apparent activation energy. A plot of ln V_T against $1/T_p$ should be linear with slope $= -E_a/R$. The data in Table 2 are plotted in this way in Fig. 1 and good linearity are obtained. The kinetic data derived from the plots are given in Table 3.

It can be seen from Table 3 that the curing activity of the modified E-51/dicyandiamide (dicy) systems are so greatly enhanced that the apparent activation energy of curing reaction decrease from 130.2 kJ/mol for the unmodified system to 75–85 kJ/mol. The curing reaction mechanism of E-51/dicy system accelerated by ITU is different from that of the system accelerated by ATU, and a little different from that of the system accelerated by imidazole. The curing reaction mechanism of E-51/dicy system accelerated by ATU is attributed to the urea group [14]. As for ITU-modified system, not only the urea group but also the N atom of 3-position in the imidazole ring of ITU can accelerate the E-51/dicy system greatly. Bareton et al. reported that [15] the curing reaction procedure of epoxy resin with imidazole is divided into two steps (epoxy curing procedure accelerated with imidazole; Scheme 2). First, the alkyloxyl anion is provided through addition of the 3-position N atom of imidazole on the epoxide group and followed by rapid transference of proton on 1-position to generate 1:1 adduct. Secondly, 1:1 adduct reacts with epoxide group leads to

Table 3
Kinetic data of the curing systems determined by Kissinger's method

No.	E_a (kJ/mol)	ln A	Correlation coefficient γ
0	130.2	35.54	−0.9951
1	75.4	23.85	−0.9974
2	77.9	24.94	−0.9977
3	74.5	24.14	−0.9978
4	75.4	24.64	−0.9976
5	84.1	26.09	−0.9977



Scheme 2.

the formation of another alkyloxyl anion (1:2 adduct), and the second alkyloxyl anion attacks the epoxide to form the third alkyloxyl anion, and so on, finally to epoxy network. Thus on the DSC curve, there are two peaks which are attributed to the two reaction steps. ITU modifier synthesized in this paper takes advantage of the great curing activity of imidazole. However, only single peak appearing on the DSC curves of the ITU-modified systems indicates one step in the curing procedure. Compared with imidazole, there is no proton on 1-position N atom of imidazole ring in ITU, so the first step of 1:1 adduct formation no long exist during the curing reaction procedure of ITU-modified system. Because of the specialty in the chemical structure of ITU, which containing urea group and imidazole ring, the two groups can synergistically contribute to the reactivity of ITU, but the effect of imidazole ring is dominant. Thus the curing activity of E-51/dicy system accelerated with ITU is higher than that of ATU.

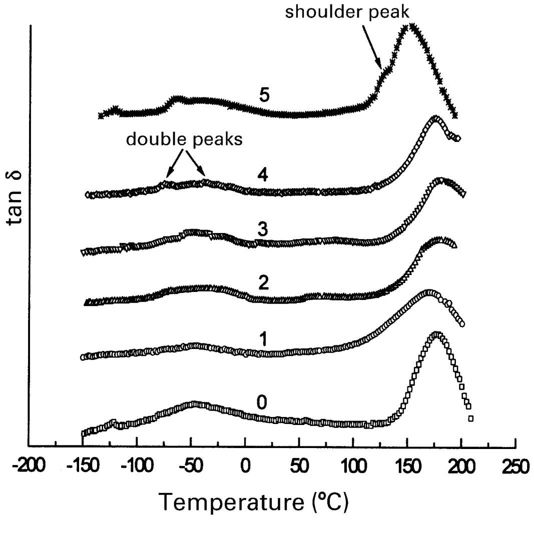


Fig. 2. Dynamic mechanical spectra for the controlled and modified systems.

3.2. *Dynamic mechanical analysis for the cured system*

Dynamic mechanical analysis can give information on the microstructure of the cured resins. Fig. 2 shows the dynamic mechanical spectra for tan δ of the cured E-51/dicy systems. The relaxation temperatures and moduli of the samples are summarized in Table 4. It can be seen that all spectra of the cured systems exhibit α- and β-relaxation peak. The α-relaxation can be clearly attributed to the glass transition of the cured epoxy resin. Compared with the unmodified system, the temperature range of β-relaxation for the modified systems becomes broad, and for 20% ITU-modified system, the β-relaxation splits into two separate relaxations, indicating that the β-relaxation of the modified systems corresponds to the vibration of two kinds of segments. It has been suggested by Ochi and Shimbo [16,17] that β-relaxation observed at about −40°C in the amine-cured epoxy resin system is caused by a flexible segment of $-CH_2CH(OH)CH_2N-$, while β-relaxation

Table 4
Data of relaxation temperatures and moduli for the cured systems

No.	T_γ (°C)	T_β (°C)	T_α (°C)	E (−120°C)	E (30°C)
0	−122.3	−47.3	175.6	5.67×10^{10}	2.56×10^{10}
1		−47.4	169.7	5.09×10^{10}	2.54×10^{10}
2		−47.4	178.4	5.49×10^{10}	2.22×10^{10}
3		−49.4	179.1	5.55×10^{10}	2.92×10^{10}
4		−75.1, −47.7	175.4	5.73×10^{10}	2.35×10^{10}
5	−121.3	−53.3	150.7	5.37×10^{10}	2.29×10^{10}

Table 5
Influence of the amount of ITU and dicyandiamide on the impact strength

No.	Formulation	Impact strength (kJ/m^2)
0	E-51/dicy = 100/6	4.0
1	E-51/dicy/ITU = 100/6/5	12.8
2	E-51/dicy/ITU = 100/6/10	14.0
3	E-51/dicy/ITU = 100/6/15	15.1
4	E-51/dicy/ITU = 100/6/20	14.0
5	E-51/dicy/ATU = 100/6/10	29.7
6	E-51/dicy/ITU = 100/2/10	13.9
7	E-51/dicy/ITU = 100/4/10	15.0
8	E-51/dicy/ITU = 100/8/10	13.1

observed at about −70°C in the anhydride-cured system is the contribution from the segment of $-OCH_2CH_2O-$ generated during the curing reaction. In this study, because of the addition of chain-extended urea, there are two kinds of segments, $-CH_2CH(OH)CH_2N-$ and $-CH_2CH(CH_3)O-$ in the cured systems. Both of them may make contribution to the β-relaxation, so the temperature range of β-relaxation for the modified systems becomes broad. Furthermore, for the modified systems, the temperature range of α-relaxation also becomes broad, and for 10% ATU-modified system, shoulder peak appears in the α-relaxation of the tan δ curve, giving the indication of micro-phase-separation. Considering the glass transition temperature, it decreases to 150.6°C for the ATU-modified system, while it is little changed for the ITU-modified systems. The high glass transition temperature of ITU-modified system is unambiguously due to the high cross-linking density of network resulting from the high reactivity of ITU. In addition, for the ITU-modified system, within experimental error, modulus almost maintain constant with an increase of ITU content, and this is also due to the high cross-linking density of network.

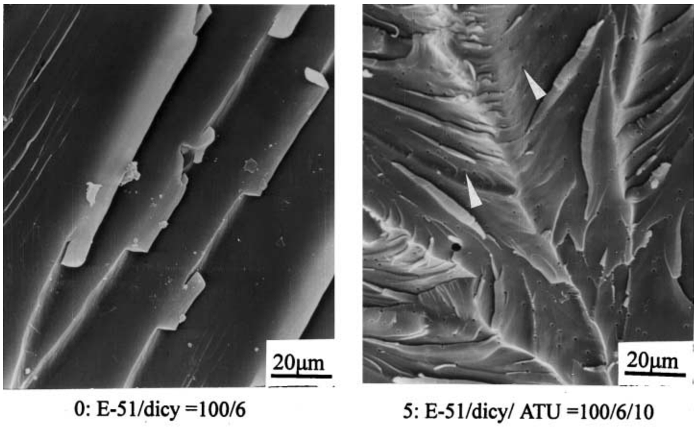
3.3. Impact-resistance property of the cured system

The most common approach used to enhance the toughness of epoxy resins is to add a softer second phase to epoxy resin [18]. The dispersed rubber phase plays an important role in the toughness improvement of the material. Rubber particles, by acting as stress concentrators, allow the matrix between the particles to undergo both shear and craze deformation. In this study, the chain-extended ureas with flexible spacers act as the softer phase. The impact-resistance property of the cured epoxy resins with different amount of modifier and curing agent was evaluated on a Charpy impact testing machine, and the results are listed in Table 5.

It is very clear that the addition of the chain-extended ureas significantly improves the toughness of the cured epoxy resin. For the ATU-modified system, the impact strength is almost eight times as much as that of the controlled system, while for the ITU-modified systems, the impact strength improves 2–3 times. Levita et al. [19] as well as Pearson and Yee [20] found that cross-linking density has a great influence on toughening, and toughness exhibits a maximum for intermediate cross-linking density. The cross-linking density of ITU-modified systems is so high that the impact strength is relatively low compared with ATU-modified system, which has moderate cross-linking density. Combined with the values of glass transition temperature and modulus, the modification of epoxy resin with ITU is successful. In addition, the experimental results show that, with 10% amount of ITU, the impact strength changes slightly but randomly when dicyandiamide content increases from 2 to 8%.

3.4. Morphology of the fracture surface

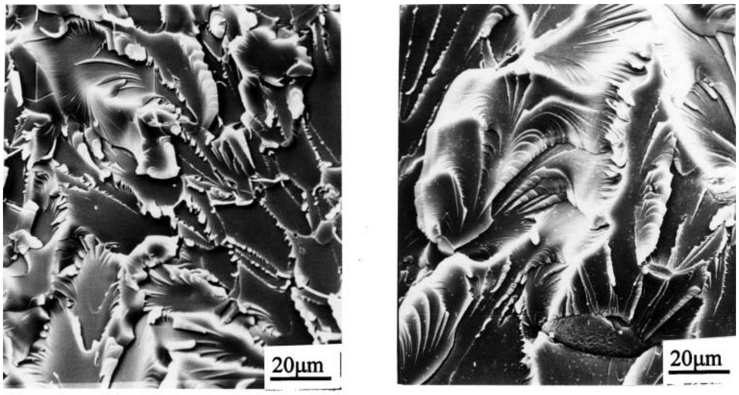
The fracture surfaces of the impact specimens were observed by SEM. The toughening mechanism can be explained in terms of the morphological behavior because the morphological examination can give interesting information on the microstructure of the cured resins. Numerous experimental studies have been devoted to elucidating the mechanism by which an added flexibilizer improves epoxy toughness, and various conceptual theories have been



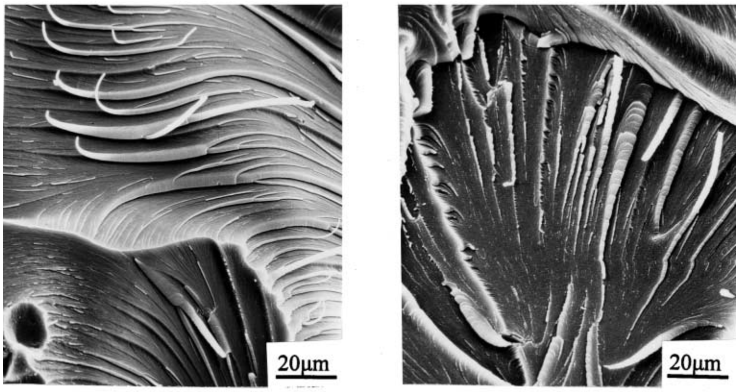
0: E-51/dicy =100/6

5: E-51/dicy/ ATU =100/6/10

Fig. 3. SEM micrographs of the controlled and 10% ATU-modified systems. The holes or indentations, resulting from cavitation during fracture, are highlighted by arrowheads in the right micrograph.



1: E-51/dicy/ITU=100/6/5 2: E-51/dicy/ ITU =100/6/10



3: E-51/dicy/ ITU =100/6/15 4: E-51/dicy/ ITU =100/6/20

Fig. 4. SEM micrographs of the modified systems with different ITU content.

proposed. Several researchers [21–24], for example, have proposed that a flexibilizer helps to promote crazing of the epoxy matrix in close vicinity to flexibilizer dispersions, whereas Kunz-Douglass and co-workers [25,26] attribute rubber toughening to the elasticity of the flexibilizer. A mechanism that combines shear yielding and enhanced epoxy crazing has been suggested by Bucknall and Yoshii [27]. Flexibilizer cavitation, followed by shear yielding, is presently the most widely accepted explanation for epoxy toughening [4,6,9,28–31].

The SEM micrographs of the fracture surfaces of the epoxy specimens are shown in Figs. 3 and 4. It can be seen that the morphologies of the epoxy resins modified with chain-extended ureas with flexible spacers are quite different from that of the unmodified system. The fracture surface of the unmodified system is very smooth and with uniform crack direction, and reveals the characteristic of brittle fracture. As for the modified systems, the fracture surfaces present rough and irregular appearance, and the fracture stripes divert to different directions, which can disperse stress, indicating the characteristic of toughening fracture. Some plastically deformed materials and crack branching resulting from shear yielding are observed for 15% ITU content. However, morphology of the fracture surface for ATU-modified system is different from that of ITU-modified system. Holes or indentations can be seen in the micrograph of ATU-modified system, resulting from cavitation during fracture, while the ITU-modified epoxy appears topologically homogeneous. Difference between the two kinds of specimens is due to the extent of phase-separation during the curing process. If phase separation is rapid relative to gelation, then the resulting morphology will reveal phase-separation. The lower reactivity of ATU-modified system results in lower rate of gelation, and then the more extent of phase-separation. Overall, the above results unambiguously support that the micromechanism of shear yielding is the principal toughening mechanism and responsible for the enhancement of toughness. This is in very good agreement with the impact resistance property of the cured epoxy resins modified with the chain-extended ureas.

4. Conclusions

Two kinds of chain-extended ureas containing PPG flexible spacers were synthesized and used to modify epoxy resin E-51/dicyandiamide system. The curing activity, dynamic mechanical behavior, impact property and fracture surface morphology of the modified systems were systematically investigated. From experimental results, the following conclusions are obtained:

1. The chain-extended ureas can greatly accelerate the curing reaction between epoxy resin E-51 and dicyandiamide. The apparent activation energy of curing reaction decreases from 130.2 kJ/mol for the unmodified system to 75–85 kJ/mol.
2. The curing reaction mechanism of E-51/dicy system accelerated by ITU is different from that of the system accelerated by ATU, and a little different from that of the system accelerated by imidazole.
3. The chain-extended ureas containing PPG flexible spacers can also act as an effective toughening modifier for the epoxy resin. The impact strength of the cured systems modified with ITU are 2–3 times higher than that of the unmodified system, while the glass transition temperatures are little changed, and the fracture surfaces of all modified systems display tough fracture feature.

Acknowledgements

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