The Effect of Urea Bond on Structure and Properties of Toughened Epoxy Resins

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ABSTRACT: In this article, modified poly(oxypropylene) diamines were synthesized and used as a new flexible curing agent for epoxy resins. The purpose of modification is to introduce urea group into epoxy resins. The reaction rate, mechanical properties, glass transition temperature (T_g), and fracture surface morphology of these toughened epoxy resins were investigated. Because of urea groups, the reactivity between poly(oxypropylene) diamines and epoxy resins was significantly enhanced. At the same time, the urea groups resulted in strong intersegmental hydrogen bonding between modified poly(oxypropylene) chain, which reduced the compatibility of poly(oxypropylene) with epoxy resins and resulted in higher T_g of toughened epoxy. The modified sample had tensile strength of 15.8 MPa and ultimate elongation of 118% at room temperature, whereas the unmodified sample only had 6.2 MPa and 70%. The scanning electron microscope analysis showed that the modified system displayed tough fracture feature, whereas the unmodified system showed typical brittle fracture. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2195–2201, 2010

Key words: epoxy resin; toughness; urea; modification

INTRODUCTION

Epoxy resins are a most important class of thermosetting resins for many engineering applications, including coating, structural decoration, and electronic encapsulation. However, commoly used epoxy resins have inherent brittleness and poor crack resistance because of their highly crosslinked structure. This often limits the usefulness of epoxy resin for many applications especially that require flexibility. The most common approach to toughen epoxy resins is the introduction of liquid rubber as toughening additives, such as carboxyl-terminated butadiene-acrylonitrile liquid rubber or amine-terminated butadiene-acrylonitrile liquid rubber.[1–6] The rubber moieties significantly improve the toughness of cured epoxy resins. 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.

Recently, low-molecular-weight polyether diamines, such as poly(oxypropylene) diamines including Jeffamine D-230, D-400, and D-2000, have been widely used as curing agents for DGEBA epoxy resins.[7–10] Poly(oxypropylene) diamines are also used with other diamine, which have rigid functionality. These mixed diamines include *m*-phenylene diamine and D-230,[11] diethyl toluene diamine and D-230 or D-400,[12] Iso-phorone diamine and D230.[13] Usually, epoxy-based materials with higher ultimate elongation require much more additive of poly(oxypropylene) diamines in the formulation. However, with the increase of molecular weight and content of poly(oxypropylene) diamines, the mechanical properties of toughened epoxy resins, such as tensile strength, reduce to a very low level. How to maintain high ultimate elongation without sacrificing tensile strength of toughened epoxy resins at room temperature is the main purpose of this article.

In this work, a new flexible curing agent based on poly(oxypropylene) diamines was prepared in this article, which had urea functionality in molecule chain. Studies showed that the introduction of urea bond had significant effect on improving the reactivity, toughness, and mechanical properties of epoxy resins.

EXPERIMENTAL SECTION

Materials

The epoxy resin (E44), a low molecular weight liquid DGEBA with epoxide number of 0.44, was supplied by Wuxi Lanxing Co. of China. Jeffamine D-230 and D-2000, purchased from Huntsman Polyureas Co. of
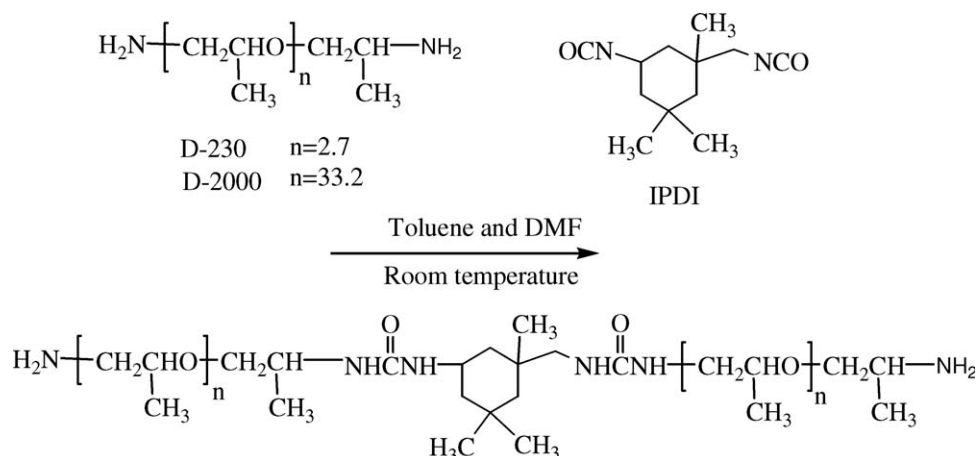
Scheme 1 Synthesis of modified poly(oxypropylene) diamines.

China, were dehydrated at 105°C under vacuum for 2 h before use. Isophorone diisocyanate (IPDI), supplied by CREN-DVA Spezialchemie of Germany, was used as received. N-N-dimethylformamide (DMF) and toluene were dehydrated by molecular sieve for 24 h before use.

Synthesis

The modified poly(oxypropylene) diamines were synthesized according to the following procedure: a mixture of D-2000 and D-230 was solved in a 1 : 1 mixture (v/v) of DMF and toluene, and a solution of IPDI in toluene was dropped into the above mixture under stirring at room temperature for 4 h. Then, the solvent was distillated to produce prepolymer as a colorless viscid liquid.

The toughened epoxy resins were prepared at the stoichiometric ratio of epoxy/amine. The curing agent and epoxy resin were completely mixed by a mechanical stirrer and degassed by a Siemens DAC 150FV high-speed mixer by 3000 r/min (Produced by Hauschild, Herrliberg, Germany). Then, the bubble-free mixtures were poured onto a nylon film with a mold of PTFE and kept at different temperature according to the demand of measurement.

Measurement and characterization

The viscosity of samples was measured on a NDJ-1 Rotational Viscometer (produced by Jinan Sumspring Lab Instrument Co., China). The FTIR spectra were obtained using a Nexus 870 FTIR spectrophotometer. The samples were smeared on KBr discs.

The mechanical properties of samples were measured on an Instron 4466 Universal Materials Testing Machine (produced by Instron Co., Norwood, MA, USA) with a speed of 50 mm/min at 23°C. The cured film in 2 mm thickness was cut into dumb-

bell-shaped specimens. Each result was obtained by the test repetition with three specimens.

The cure of epoxy resin with amine was evaluated by dielectric analysis (DEA) at a DEA 230/1 Cure Monitor (produced by NETZSCH-Geratebau GmbH, Selb/Bavaria, Germany) controlled by a microcomputer connected to a planar wafer-thin sensor inserted into the reactor. The sensor was inert and has 2 cm × 1 cm in area and 1 mm thick. The electrode configuration was set in the reactor so as to be swept by the axial flow generated by the propeller.

All dynamic mechanical thermal analysis (DMA, tension mode) was carried out using a DMA+450 (Produced by 01 dB- Metravib Co., France). The dimensions of the samples were 20 mm × 18 mm × 1 mm. The frequency was fixed at 10 Hz. The samples were heated at a nominal rate of 3°C/min from −100°C to + 150°C.

The TGA data were achieved on an Yris 1 TGA (Perkin Elmer) in a Pt crucible in nitrogen at a heating rate of 20°C/min.

The fracture surface was observed by a scanning electronic microscope on a SEM LEO1530VP Germany. The fracture surface was coated with a thin layer of gold to improve conductivity.

RESULTS AND DISCUSSION

Synthesis of modified poly(oxypropylene) diamines

The synthetic procedure of modified poly(oxypropylene) diamines is shown in Scheme 1. Because of high reactivity of isocyanate group (NCO) with amine group (NH_2), the reaction system had to be proceeded at lower temperature. The mole ratio of NCO/NH_2 was fixed as 1 : 2 in this work. The higher ratio of NCO/NH_2 would result in very viscous prepolymer. The formulations, viscosity and amine functions of poly(oxypropylene) diamines

TABLE I
The Formulations, Viscosity and Amine Functions of Poly(oxypropylene) diamines
Before and After Modification

poly(oxypropylene) diamines	D-2000/g	D-230/g	IPDI/g	Brookfield Viscosity at 23°C/cP	Amine function mmol/g
D	3.50	0.70	0	258	2.29
C	3.50	2.50	1.14	16600	2.29

before and after modification are outlined in Table I. Here, sample C is modified poly(oxyprolene) diamines with urea group in chain, whereas sample D is simply the mixture of D-2000 and D-230 as a control. After addition of IPDI, the viscosity of the poly(oxypropylene) diamines increases apparently due to an increase in the overall molecular weight and hydrogen bond function in the urea structure.

Infrared absorption spectra of poly(oxypropylene) diamines before and after modification are shown in Figure 1. After modification, an absence of NCO peak at 2270 cm^{-1} in the spectrum of sample C indicates that the reaction between isocyanate and amine was complete. The formation of urea linkage is conformed by the bands around 3200–3500 cm^{-1} (urea N—H stretching). Another major band is centered at about 1640 cm^{-1}, attributed to hydrogen bond C=O urea, and a weak shoulder at 1690 cm^{-1} is ascribed to free C=O urea[14] (shown in inset spectrum). The result reveals that there is strong hydrogen bond function in the modified poly(oxypropylene) diamines, which brings strong effect on the properties of toughened epoxy resins.

Reactivity of the curing system

The toughened epoxy resins were prepared at the stoichiometric ratio of amine and epoxy group. The modified system (sample M) is prepared from the epoxy resin and modified polyether amines (prepolymer C) with the weight ratio of 100 : 106, and the unmodified system (sample R) is based on the epoxy resin and unmodified polyether amines (prepolymer D) with the same ratio.

In this work, DEA is used for evaluating the reactivity of epoxy resins with poly(oxypropylene) diamines. DEA is based on the study of the electrical response of a polymer, and dielectric cure monitoring is sensitive to the mobility of ions and the rotational mobility of dipole on the polymer molecule in the presence of an electric field. The important information that can be obtained by DEA includes relative viscosity change, cure rate, cure state, and the end of cure.[15,16]

Referring to literature,[17] the dielectric loss factor can be used to determine the degree of cure, α as a function of curing time (*t*):
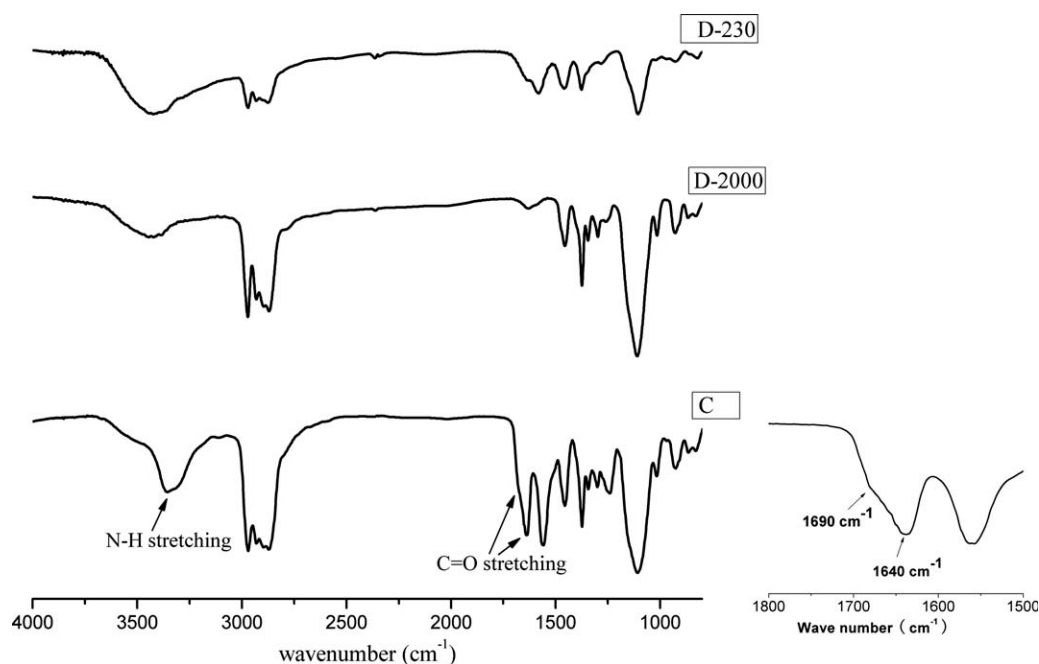

Figure 1 Infrared absorption spectra of modified poly(oxypropylene) diamines.

TABLE II
Tensile Strength of Sample M and R with Different Cure Temperature and Time

Sample	Cure at 70 °C		Cure at 90 °C	
	Cure time	Tensile strength (MPa)	Cure time	Tensile strength (MPa)
M	6 h	7.8 ± 0.5	3 h	10.3 ± 0.4
	12 h	10.1 ± 0.6	4 h	12.6 ± 0.5
	16 h	11.4 ± 0.6	5 h	13.3 ± 0.5
	17 h	15.2 ± 0.5	6 h	14.4 ± 0.4
	18 h	15.4 ± 0.5	7 h	14.3 ± 0.5
R	7 h	1.6 ± 0.2	5 h	2.0 ± 0.2
	12 h	2.2 ± 0.2	7 h	3.9 ± 0.3
	20 h	4.6 ± 0.3	8 h	5.0 ± 0.3
	24 h	5.9 ± 0.4	9 h	6.6 ± 0.4
	26 h	6.2 ± 0.4	10 h	6.7 ± 0.3
	28 h	6.4 ± 0.3		

Figure 6 Storage modulus curves of sample M and R in DMA analysis.

is 18 h for sample M and 28 h for sample R at 70 °C, respectively. Similar results are obtained when samples are cured at 90 °C. These results validate DEA tests that the urea structure improved reactivity of epoxy and amine group in the modified system.

Dynamic mechanical thermal analysis

The results of DMA analysis for sample M and R are displayed in Figures 5 and 6. Figure 5 shows that there is only one broad T_g peak between 0 °C and 100 °C. This is due to better compatibility of hard segment (epoxy resin) and soft segment (polyether). The introduction of flexible polyether curing agent lowers the T_g of cured epoxy resins. Figure 5 also shows that the T_g of modified system (sample M) is 30 °C higher than that of unmodified system (sample R) with the same amine functions in curing agent. The reason lies in that there is strong intersegmental hydrogen bonding in modified polyether
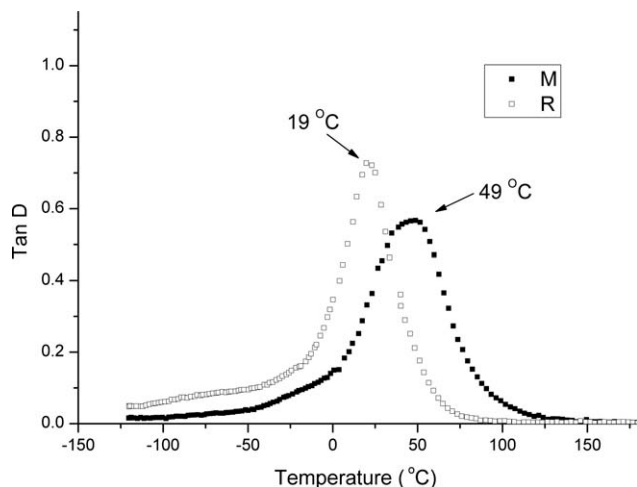
amine (revealed by IR), which reduces the compatibility of polyether with the epoxy resin. Consequentially, sample M has higher T_g than sample R. On the other hand, epoxy-based materials with higher ultimate elongation usually require more additive of flexible polyether amine in the formulation. Usually, more polyether amine added, lower T_g obtained. As a result, improved ultimate elongation will sacrifice the storage modulus of cured epoxy resins. However, in this modified system, sample M still has enough storage modulus due to the existence of urea bond at room temperature (shown in Fig. 6). This is consistent with the results of later mechanical property test.

Mechanical properties

The stress–strain curves (23 °C) for the samples are shown in Figure 7, and the results are summarized in Table III. The samples were cured at 50 °C for
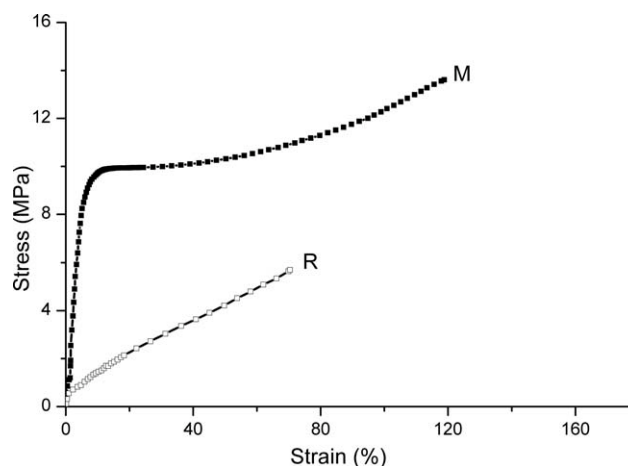

Figure 5 Loss factor curves for sample M and R in DMA analysis.

Figure 7 Stress–strain behavior of sample M and R at 23 °C.

TABLE III
Tensile Strength of Sample M and R at 5°C, 23°C, or 50°C

Sample	Measured at 5 °C		Measured at 23 °C		Measured at 50 °C	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
M	23.9	111	15.8	118	4.1	133
R	13.1	98	6.0	73	1.4	42

48 h, and then 100 °C for 4 h. Comparison between sample R and M shows a substantially difference in mechanical properties. The tensile strength of sample M is 2.5 times as much as that of sample R. Apparently, it was the introduction of the urea bond into poly(oxyprolene) diamines that resulted in the remarkable increase in both the tensile strength and ultimate elongation of the cured epoxy resin, for the urea bond are strongly polar groups, and the action of hydrogen bonds played an important part in the increasing of tensile strength.[20]

The tensile properties of samples studied at 5 °C or 50 °C are also listed in Table III. It can be concluded from Table III that the modified system (sample M) has better mechanical properties than the unmodified system (sample R) both at 5 °C and 50 °C. This is probably due to the enhanced phase separation in modified system because of the introduction of urea bond (revealed by DMA and morphology of the fracture surface analysis later). Microstructure phase separation between flexible curing agents with epoxy resins helps to maintain better tensile strength and elongation of cured epoxy resins simultaneously at 50 °C.

Thermal stabilities

The thermal studies were carried out by thermogravimetric analysis. Figure 8 indicates the thermal degradation of toughened epoxy resins before and after modification. General speaking, liquid rubber additives can significantly improve the toughness of cured epoxy resins. However, these rubbers lack heat resistance because of the double bond,[21] and thus, the modification with these rubbers usually leads to low thermal stability. By making use of poly(oxypropylene) diamines as flexible curing agents instead of liquid rubber additives, one of main advantages is their thermally stable.[7–10] Figure 8 shows that sample R exhibits indeed excellent thermal stability with 5% weight loss at temperature over 380 °C. Although sample M is ratherish unstable compared to the unmodified system, its 5% weight loss temperature is around 310 °C. This is

due to presence of urea bond, which have relatively lower decomposition temperature.

Morphology of the fracture surface

The surfaces of impact samples were investigated by SEM. The toughening mechanism can be explained in terms of the morphological behavior because the morphological examination can give the interesting information microstructure of the cured systems. Figure 9 shows the fracture surface comparison between the modified system M and the unmodified system R. It can be seen that the morphology of the modified system is quite different from the unmodified system. Clearly, the unmodified system exhibits typical brittle fracture. While in the fracture surface of sample M, there is a great deal of granule. The scale of these granule is about 10–1000 nm. The fractured surface looks like most of the rubber-toughened epoxy systems, which have a rigid continuous epoxy matrix with a dispersed rubbery phase as isolated particles.[3,22,23] The results indicate that introduction of urea bond has a significant toughening effect on the epoxy resin system. The noted increase in the fracture toughness possibly is a result of two
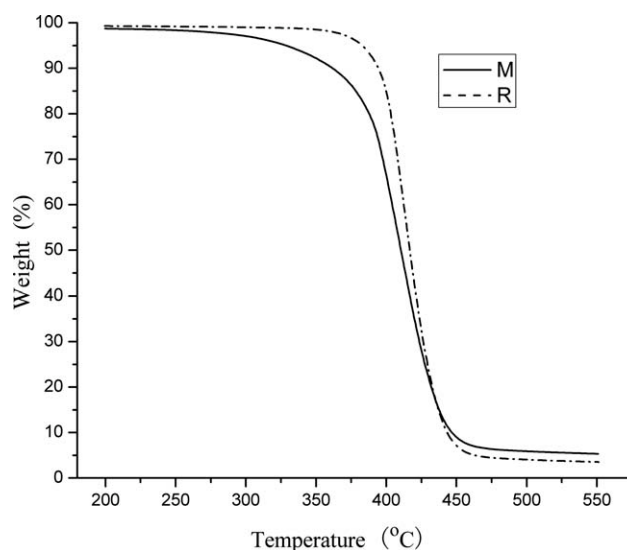

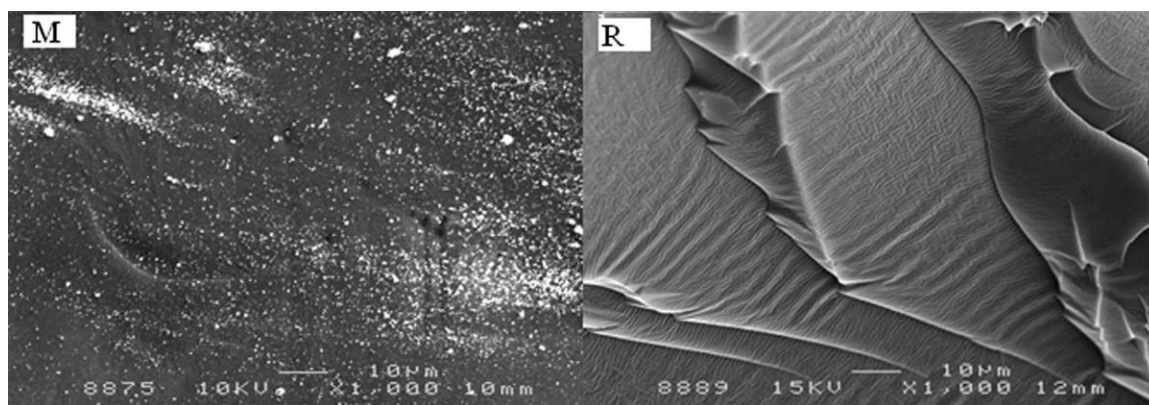**Figure 8** TGA curves of sample M and R.

Figure 9 Comparison of the fracture surface between sample M and R.

factors[24]: phase separation occurring in the modified system and an increase in the overall molecular weight between crosslinks, which leads to a higher deformability of the mixtures but maintains and even increases its rigidity. This is in very good agreement with the tensile strength of the modified system.

CONCLUSIONS

Modified amino-terminated polyether was synthesized and used as a new flexible curing agent for epoxy resins. On the basis of DEA, stress–strain, DMA, and SEM analysis results, the introduction of urea bond into polyether chain has significant effect on improving the curing activity, toughness and mechanical properties of toughened epoxy resins: The urea bond can accelerate the curing reaction between epoxy resins and amine-terminated polyether. Furthermore, the existence of urea bond results in increased T_g and storage modulus of the modified system, which helps to maintain high ultimate elongation without sacrificing tensile strength of the toughened epoxy resin. Finally, the analysis for the morphology of the fracture surface reveals that the modification system has tough fracture, whereas the unmodified system exhibits typical brittle fracture. Our work gives a simple method to prepare toughened epoxy resin with higher tensile strength.

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