A Reactive Polymer for Toughening Epoxy Resin

Hsu-Chiang Kuan,[1,2] Jia-Bin Dai,[3] Jun Ma[1]

[1]School of Advanced Manufacturing & Mechanical Engineering and Mawson Institute, Division of Information Technology, Engineering and the Environment, University of South Australia, SA5095, Australia
[2]Department of Computer Application Engineering, Far East University, Tainan 744, Taiwan
[3]Harbin Institute of Technology, Heilongjiang, China

ABSTRACT: Epoxy resins are hardly toughened by low weight content of tougheners. In this study, 5 wt % polyurea was adopted to significantly toughen piperidine-cured epoxy, as fracture toughness improved from 0.78 to 1.98 MPa $m^{1/2}$. We focused on the reactions and morphology evolution of epoxy/polyurea mixture. The polyurea molecular weight was reduced by the exchange reactions of polyurea with epoxy during mixing, as evidenced by gel permeation chromatograph and Fourier transform infrared spectroscopy. As a result, epoxy molecules were chemically bonded with polyurea, improving particle content and interface thickness. Transmission electron microscope observation shows that (a) polyurea *in situ* formed nanoparticles in matrix which subsequently aggregate into micron-sized particles of thick interface with matrix; and (b) the particles became less stainable with increasing the mixing time, because the reactions promoted high levels of crosslink density of the particles which were thus more resistant to the diffusion of staining chemicals. Longer mixing time improved, obviously, the fracture toughness of epoxy/polyurea composite. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3265–3272, 2010

Key words: epoxy; toughening; nanoparticle; interface; polyurea

INTRODUCTION

Epoxy resins are often used as adhesives and coatings, and as matrices for composite laminates and structures. However, they are brittle and vulnerable to the presence of microcracks that are caused by the mismatch of thermal expansion coefficients between epoxy resins and their surrounding environment or bonded parts. Extensive research has thus been conducted to toughen epoxy (see Refs. 1 and 2). A popular toughener is liquid rubber, 15–20 wt % of which improves significantly the fracture toughness but suffers from a large loss of elastic modulus. In a typical preparation procedure, a homogeneous solution is obtained by mechanically mixing epoxy resin with liquid rubber. Upon curing, rubber particles of 1–10 μm in diameter precipitate as a second phase. Compounding 15 wt % rubber with diglycidyl ether of bisphenal A (DGEBA) improved the fracture toughness from 0.75 to 1.48 MPa $m^{1/2}$ but caused 27% modulus loss.[3] To address this disadvantage, rigid thermoplastics have been studied in the last 20 years. However, effective toughness improvement requests a co-continuous structure, which unfortunately results in loss of other desirable properties such as solvent resistance.[1] Noteworthy is that obvious toughness improvement in these conventional composites requests a substantial toughener content 15–20 wt %, which inevitably leads to loss of other properties. An assumption made in this study is that the loss of the other properties can be avoided if epoxy is effectively toughened by low content of tougheners such as 5 wt %.

Recently, two types of new materials were reported to toughen epoxy without or with little modulus loss. One uses nanoparticles such as nanoclay,[4–8] nanorubber,[9] nanosilica,[10–13] and nanotube.[14] As expected, 5–10 wt % high modulus inorganic nanoparticles increase significantly the Young's modulus but not the fracture toughness of epoxies. Another uses block copolymers, not pure rubber, as effective particles to toughen brittle polymers with little loss in stiffness. This strategy was first proposed by Hillmyer et al.,[15] followed by numerous other studies. These block copolymers formed self-organized nanostructures during mixing, which were finally fixed through subsequent curing after hardeners were added. Noteworthy is that Grubbs et al. developed a reactive block copolymer to enhance interface adhesion.[16] However, the high production cost of these copolymers prohibits their application.

The overall elastic modulus of a particle-reinforced epoxy is mainly determined by particle

weight fractions and the elastic moduli of the matrix and the particle. Hence, the modulus loss is unavoidable for rubber-modified epoxy because of the low rubber modulus. A novel method developed by the authors takes advantage of a reactive polymer, being composed of stiff and flexible segments, which increases the particle weight fraction and interface strength via chemical reactions between epoxy and the polymer. Hence, high toughness can be achieved with low content of toughener while maintaining other desirable properties. Thus, a new toughener is designed with the following essential features: (a) it contains 90 wt % elastomeric segments endowing particle cavitation capability; (b) it comprises 10 wt % stiff chain, providing high mechanical strength and modulus; and (c) it provides reaction sites for epoxy molecules. Polyurethane is a widely used polymer with flexible segments for elastic property and stiff segments to provide physical crosslinks for mechanical strength. Polyuea is structurally similar to polyurethane, but its stiff segment (–HNRNH–) is much more polar resulting in higher mechanical strength. In our previous research, polyurea was used to toughen room temperature-cured epoxy. It was found that polyurea formed thick-interface particles, and created an effective toughness improvement—94% increase in fracture toughness.[17] However, it is not clear how the thick-interface particles were formed and more importantly, what is the mechanism behind this. On the other hand, it is unknown whether polyurea toughens other epoxy systems significantly.

In this study, polyurea was used to toughen piperidine-cured epoxy. We studied the chemical reactions of polyurea with epoxy, and unravelled the effect of the reactions on the morphology evolution and toughness improvement of epoxy/polyurea composite.

EXPERIMENTAL WORK

Materials

Epoxy resin, DGEBA (Araldite-F) with an epoxide equivalent weight 182–196 g/equiv, was supplied by Ciba-Geigy (Australia). Isophorone diisocyanate (IPDI) and hardener piperidine were obtained from Aldrich. Polyoxyalkyleneamine (denoted as Jeff-D2000) with M_w 2000 was provided courtesy of Huntsman (Singapore).

Synthesis of epoxy/polyurea composites

Polyurea, synthesized from Jeff-D2000 and IPDI according to our previous procedure,[17] was mechanically mixed with a desired amount of epoxy in a beaker at 80°C for 20 min to evaporate acetone which had been introduced through polyurea. To investigate the effect of reaction time on the morphology and toughness of epoxy/polyurea composite, three batches of the solution had been mixed for 5, 20, and 35 min at 120°C, respectively, before hardener piperidine (5 g for 100 g epoxy) was added. The blend was then degassed, poured into different molds and followed by curing at 120°C for 17.5 h.

Gel permeation chromatography

A Waters chromatograph system with a 510 HPLC pump was used to measure the molecular weight of polyurea, with a mixed-bed Styragel/HT 6E column and high-purity THF (Unichrom) eluent at a flow rate of 0.8 mL/min. Eluted fractions were detected with a R401 differential refractometer. Solutions for gel permeation chromatography (GPC) were also made up in THF (Aldrich).

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra of epoxy and various epoxy/polyurea samples were recorded between 4000 cm^{-1} and 400 cm^{-1} on a Nicolet Avatar 320 FTIR spectrometer, Nicolet Instrument Co., Madison, WI. FTIR samples were prepared by the solution-casting method on the KBr plate. A minimum of 32 scans was signal averaged with a resolution of 2 cm^{-1}.

Fracture toughness tests

The compact-tension (CT) samples were cured in rubber mold and then both sides were polished by emery paper until all visible marks disappeared. An instantly propagated crack was introduced by razor tapping according to our previous procedure.[18] Six specimens were tested for each data set with a crosshead speed of 0.5 mm/min. Fracture toughness K_{1c} and G_{1c} values of CT specimens were calculated using maximum loads and validated according to ISO 13,586.

Electron microscopy analyses

Ultra-thin sections 50–60 nm in thickness were cryogenically microtomed with a diamond knife in liquid nitrogen at –120°C using a Leica Ultracut S microtome. Sections were collected on 400-mesh copper grids and stained by the vapor of 1 wt % ruthenium tetroxide (RuO$_4$) water solution for 8 min to enhance the phase contrast between particle and epoxy. Subsequently, thin sections were examined using a Philips CM 200 transmission electron microscope (TEM) at an accelerating voltage of 200 kV.
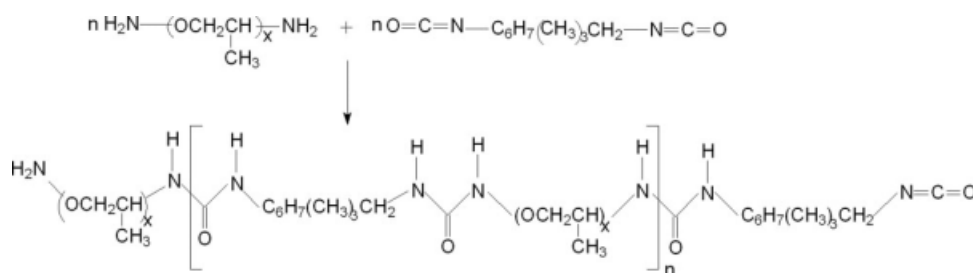
Figure 1 Schematic of diamine oligomer/isophorone diisocyanate reaction.

RESULTS AND DISCUSSION

Characterization of polyurea

As shown in Figure 1, polyurea is prepared by stepwise addition polymerization reaction of diamines and diisocyanates with the migration of a hydrogen atom. Because this polymerization does not involve elimination of small molecules such as water, high molecular weight can be readily achieved by controlling strict equivalence in the proportions of the starting reacting groups.

The molecular weight of polyurea is measured by GPC. Weight-average molecular weight (M_w) and number-average molecular weight (M_n) are 5.1×10^4 g/mol and 3.7×10^4 g/mol, respectively, with molecular weight distribution 1.4. The molecular weight distribution graphically shown in Figure 2 is typical for polycondensation.

Characterization of reactions between epoxy and polyurea

GPC characterization

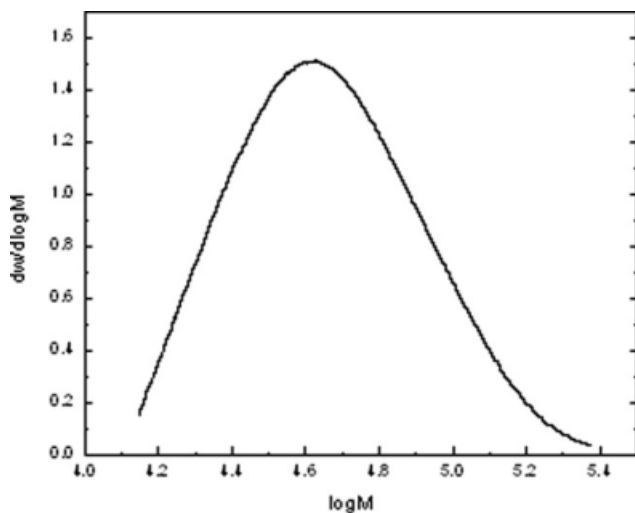During polymerization, the polyurea molecular weight increases continuously with a great number of intermediates formed in independent, individual reactions. These intermediates are oligomeric and polymeric molecules with the same functional end groups (amine and isocyanate) as the starting reactants. Finally, the polymerization reaches a state of dynamic polymerization equilibrium in which the rate of formation and consumption of molecules of a given degree of polymerization are equal. The equilibrium is featured by exchange reactions, which occur between free end groups and junction points in the chain as shown in Figure 3. The exchange reactions alter neither the number of free functional groups nor the number of molecules, nor the number-average degree of polymerization.[19] Upon adding a new reactive component into the reactions, however, the equilibrium breaks and moves toward either higher or lower molecular weight, depending on the molecular weight of the new component.

As described in experimental, the three batches of epoxy solutions containing 5 wt % polyurea were mixed for 5, 20, and 35 min at 120°C, respectively, to investigate the effect of reaction time on the morphology and toughness of the composites. In this case, the polyurea content 5 wt % is low in comparison with the epoxy content 95 wt %; that is, polyurea acts as a solute and epoxy is actually the
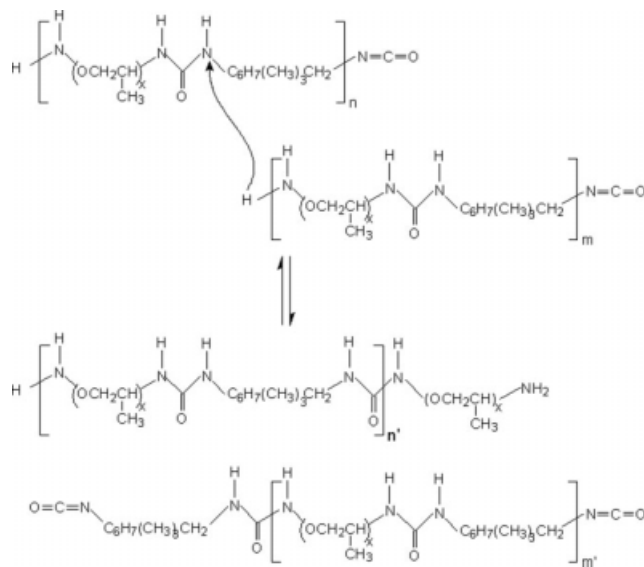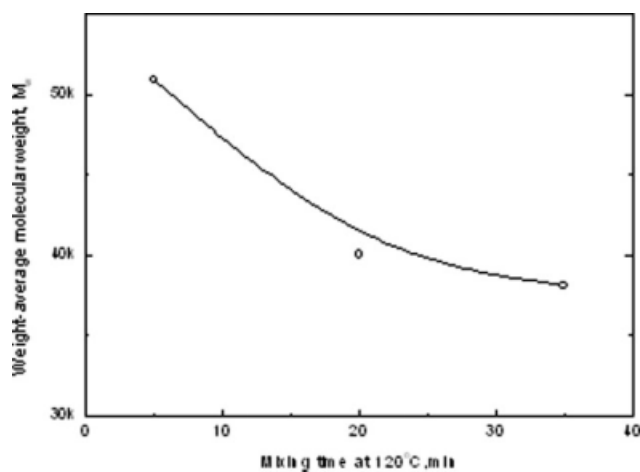

Figure 2 Molecular weight pattern of polyurea.

**Figure 3** Schematic of exchange reaction.

**Figure 4** Dependence of molecular weight on mixing time at 120°C.

solvent. The following chemical reactions may occur during mixing: (a) reaction between the polyurea end group (NH_2) and the epoxide group, and (b) reaction between the polyurea end group (NCO) and the hydroxide group of epoxy. A question to ask is whether these reactions change the molecular weight of polyurea and the morphologies and fracture toughness of the composite. As mentioned earlier, the equilibrium would break and moves as long as a new reactive component is added. The exchange reactions provide the unlimited source of end groups (NH_2 and NCO) of polyurea, which subsequently reacted with epoxy molecules. Because of the excessive quantity 95 wt % of low molecular weight epoxy (~400 g/mol), we expect that upon mixing with epoxy, the polyurea equilibrium would move to low molecular weight because of these reactions. The three batches of the epoxy/polyurea
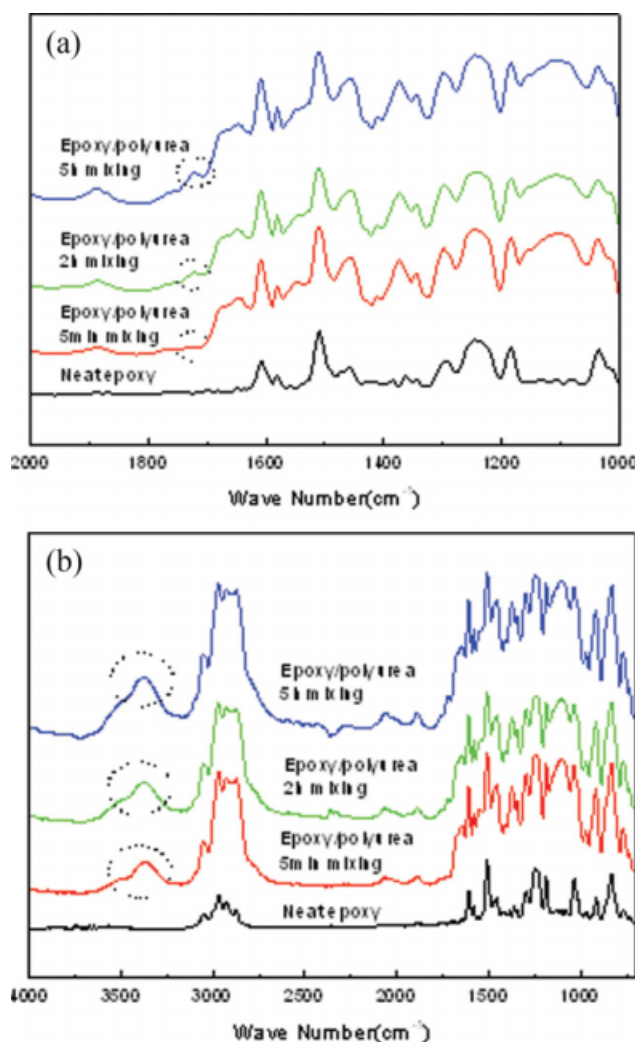
Figure 5 FTIR spectra of neat epoxy and epoxy solutions containing 5 wt % polyurea. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
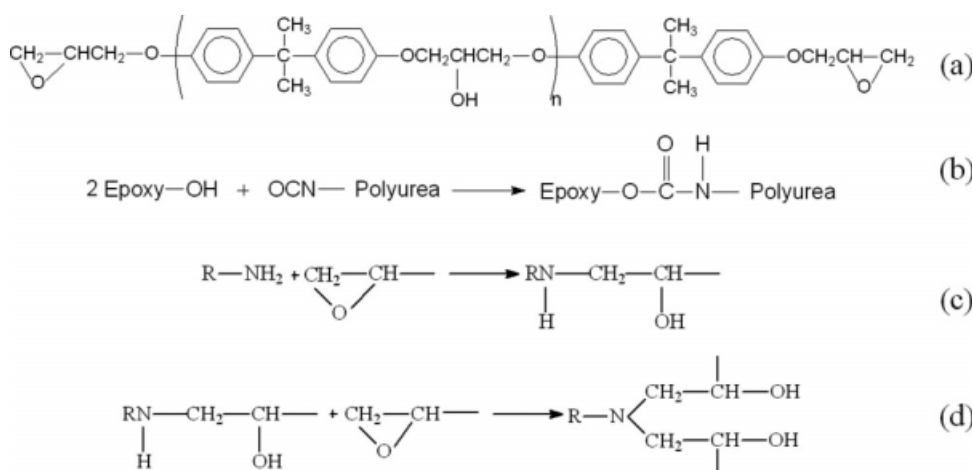
Figure 6 Schematic reactions: (a) Epoxy molecules; (b) reaction of hydroxide with NCO group; (c) and (d) reactions of amine with epoxide group.
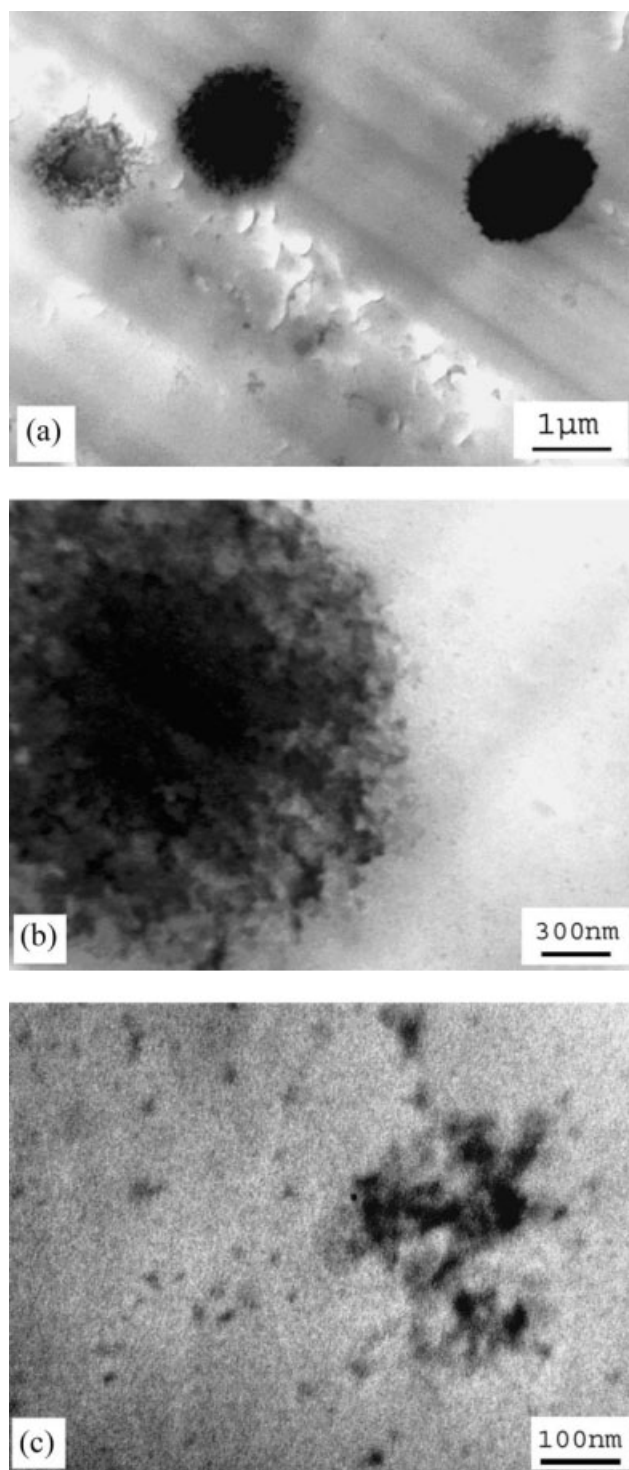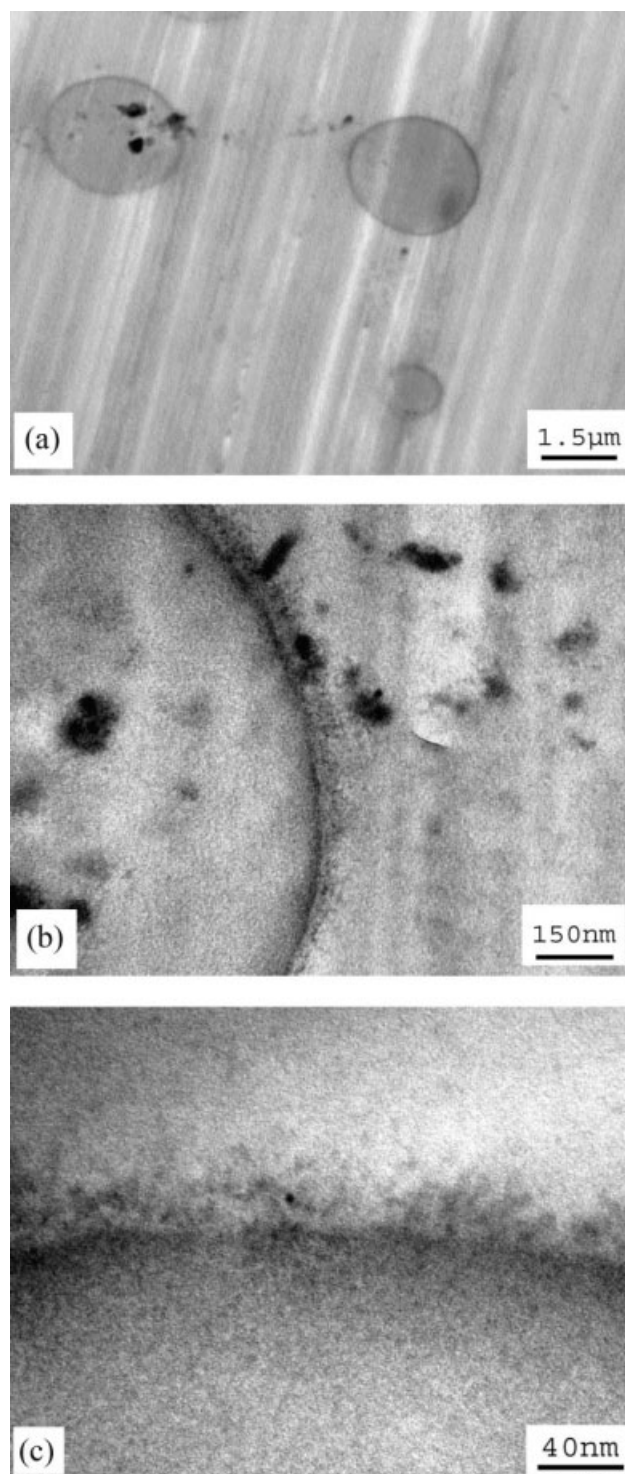
Figure 7 TEM microphotographs of epoxy/polyurea composite (5 wt %) mixed for 5 min at 120°C.

mixed for various time, as described in "Synthesis of epoxy/polyurea composites" section, were measured by GPC. In Figure 4, M_w decreases from 5.1×10^4 to 3.7×10^4 with prolonging mixing for 30 min, and this indicates that epoxy reacted with polyurea, causing the reduction of the molecular weight.

Fourier transform infrared spectroscopy

The aforementioned chemical reactions were to be supported by FTIR characterization of neat epoxy and epoxy/polyurea solutions mixed for different time. Upon reaction, new or more intensive absorption peaks would appear. In Figure 5(a), absorption

Figure 8 TEM microphotographs of epoxy/polyurea composite (5 wt %) mixed for 20 min at 120°C.
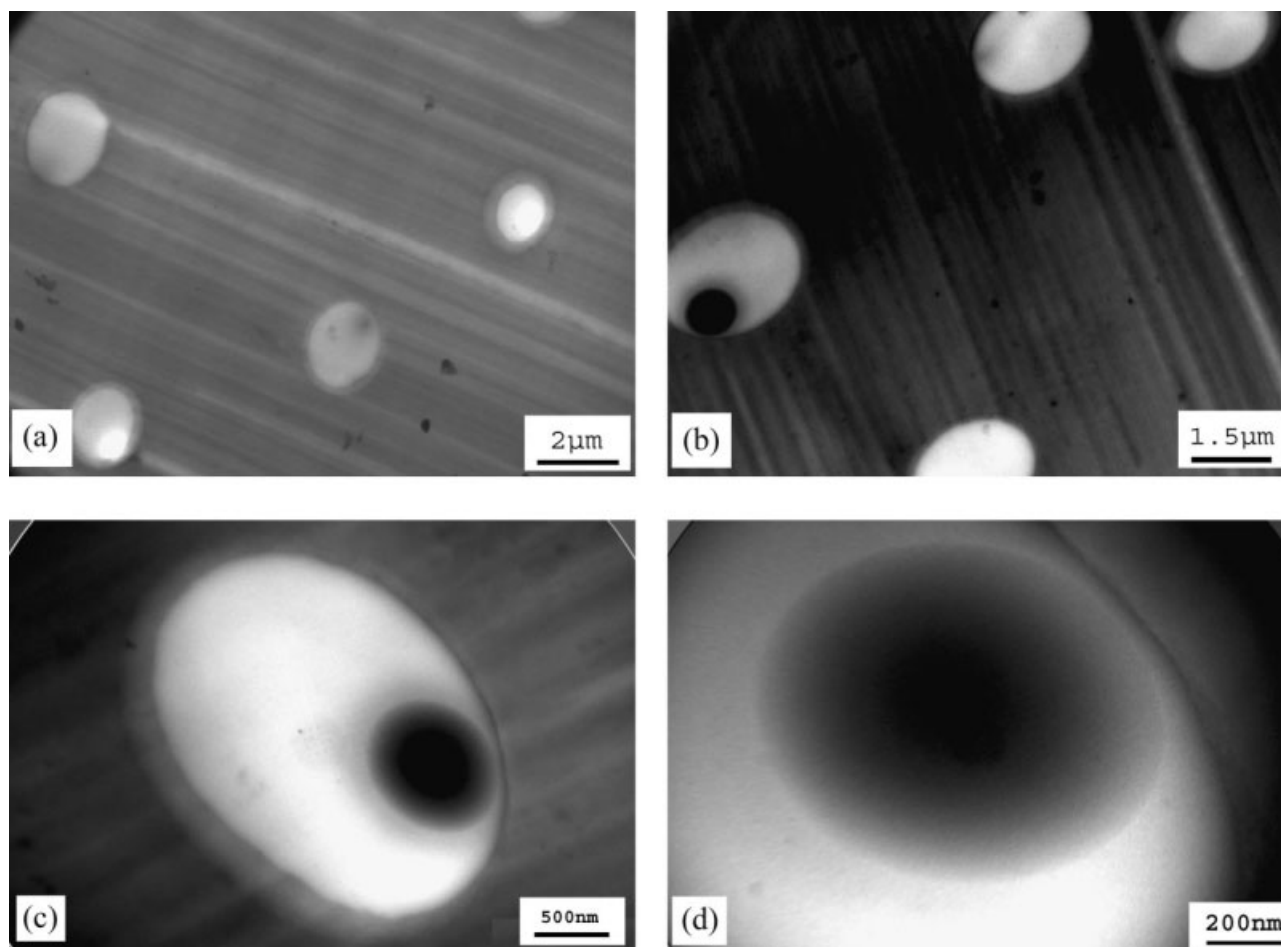
Figure 9 TEM microphotographs of epoxy/polyurea composite (5 wt %) mixed for 35 min at 120°C.

at 1725 cm^{-1} increases significantly with mixing time, and it is caused by the formation of C=O due to the reaction between the polyurea end group (NCO) and the hydroxide group of epoxy. In Figure 5(b), absorption at 3380 cm^{-1} increases significantly with the mixing time, caused by the formation of NH due to the reaction between the polyurea end group (NH$_2$) and the epoxide group. Both reactions are shown in Figure 6. Noteworthy is that the reaction between NCO and OH is a valuable method for modification of tougheners, as illustrated in the work of Soares et al.[20]

The reacted molecules play a critical role in this system for the following functions: (a) it increases the particle weight fraction, which thus improves the toughness; and (b) it acts as a compatibilizer, improving the interfacial adhesion. Because of phase separation in curing, the reacted epoxy/polyurea molecules form nanoparticles. As discussed later, these nanoparticles are either dispersed in the matrix, or located at the interface of dispersed particles, or anchored into the particles.

Morphology evolution with reaction time

TEM was used to study the effect of mixing time on the morphology of the cured epoxy/polyurea composites. All cryosections were stained by the same procedure as described in "Electron microscopy analyses" section. The polyurea consists of flexible

TABLE I
Mechanical Properties and Toughness of Epoxy/Polyurea Composites (5 wt %)

Materials	Neat epoxy	Epoxy/polyurea (5 min)	Epoxy/polyurea (20 min)	Epoxy/polyurea (35 min)
Fracture toughness, K_{1c} (MPa m$^{1/2}$)	0.78 ± 0.02	1.39 ± 0.03	1.75 ± 0.02	1.98 ± 0.02
Young's modulus (GPa)	2.89 ± 0.13	2.84 ± 0.09	2.91 ± 0.14	2.86 ± 0.11

Jeffamine and stiff diisocyanate segments. The flexible Jeffamine segments are more readily stained and thus appear darker under TEM.

Figure 7(a–c) shows TEM microphotographs of the composite mixed at 120°C for 5 min before curing. Particles of 1–2 μm in diameter are shown in Figure 7(a); the contrast between particles and matrix is strong; each particle has a blurred interface with the matrix. At a high magnification in Figure 7(b), it is seen that each particle is actually an aggregate of many nanoparticles. In Figure 7(c), a few nanoparticles form a cluster, whereas others are evenly dispersed in the matrix. The parallel lines in these images are caused by microtoming.

Figure 8(a–c) shows TEM microphotographs of the composite with 20 min of mixing time. When compared with Figure 7(a), these particles have lower contrast; some particles are only partially stained. At a higher magnification in Figure 8(b), some nanoparticles are found inside the microparticles, at the interface and within the matrix. The interface of a typical microparticle, magnified in Figure 8(c), is composed of many nanoparticles.

Figure 9 shows TEM microphotographs with 35 min mixing time. Figure 9(a,b) belong to different sections, which show that the particle color is even lighter than epoxy, as opposed to Figure 7(a). This indicates that the susceptibility of the particles to staining is reduced with increasing the mixing time. The quantity of nanoparticles dispersed in the matrix is also decreased. Many microparticles have multilayered structure. Figure 9(c) shows a particle with a three-layer structure: a dark core, a large white shell, and a gray outer shell of 100–200 nm. The dark core magnified in Figure 9(d) appears to be graded.

The effect of the mixing time on the morphology of epoxy/polyurea composite is generalized as that, with increasing the mixing time, the particles become less stainable, the interface thickness increases, and the amount of nanoparticles dispersed in the matrix reduces. This is due to the reactions occurred between epoxy and polyurea during the mixing at 120°C. As the matrix was cured during crosslinking, the reacted polyurea/epoxy molecules aggregated to form particles which inevitably embedded an amount of epoxy molecules. The exchange reactions of polyurea continued to proceed within particles and provided epoxy molecules with reactive end groups including NCO and NH$_2$. Thus, the reactions of polyurea with epoxy led to high crosslink density of the particles and thick interface. The longer polyurea/epoxy mixed before curing, the higher degree the crosslink density, corresponding to higher resistance to the staining agent. As a result, the particles of longer mixing time were less stainable.

Effect of reaction time on fracture toughness

Fracture toughness is the most important material property for brittle resins, upon which the mixing time has an obvious effect in this study. With increasing the mixing time, in Table I, the toughness increases from 1.39 to 1.98 MPa m$^{1/2}$ without loss of Young's modulus, demonstrating the advantage of the reaction between a toughener and matrix. Given the deviation values, the mixing time has no effect on Modulus. The obvious toughening effect was causes by the reactions between epoxy and polyurea, which increased the particle weight fraction and the particle/matrix interface strength. Detailed analysis of toughening mechanisms will be reported in another article.

CONCLUSION

In this research, piperidine-cured epoxy was significantly toughened by a reactive polymer—polyurea. As elaborated by FTIR, the reactions combined epoxy molecules with polyurea, leading to higher particle concentration and thicker interface and thus higher toughness. GPC measurement shows that the reactions reduced the molecular weight of polyurea. TEM observation demonstrates thick interface of the particles due to these reactions, which strengthened load transfer and thus contributed to high fracture toughness. It was found that the particles became less stainable with prolonging the mixing time, as longer time produced more reaction sites for crosslinking. When the mixing time prolonged from 5 to 35 min, the fracture toughness improved from 1.39 to 1.98 MPa m$^{1/2}$.

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