

# Effect of the Epoxy Molecular Weight on the Properties of a Cyanate Ester/Epoxy Resin System

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**ABSTRACT:** Bisphenol A dicyanate (BADCy) was modified by diglycidyl ether of bisphenol A epoxy resins with different molecular weights [E20 (weight-average molecular weight = 1000) and E51 (weight-average molecular weight = 400)] to investigate the effects of the epoxy molecular weight on the properties of the modified systems. The reactions were monitored with differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy, and the results showed that more pentacyclic oxazolidinone rings were formed in BADCy/E51 than in BADCy/E20 with the

same epoxy resin weight content. DSC showed that BADCy/E20 had a lower curing temperature than BADCy/E51 because of the higher concentration of hydroxyl groups ( $-\text{OH}$ ) in E20. Thermal, moisture absorption, and mechanical testing showed that E51-modified BADCy performed better because of its lower molecular weight. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1744–1750, 2006

**Key words:** copolymerization; mechanical properties; molecular weight distribution/molar mass distribution; resins

## INTRODUCTION

Cyanate ester (CE) resins are widely used in high-signal-speed printed circuit boards, high-performance electromagnetic-wave-penetrated structural components, and aerospace structural composites because of their many excellent properties, such as low dielectric loss, good adhesive and mechanical properties, resistance to hot and wet conditions, and processability.<sup>1–5</sup> CE resins can form highly crosslinked, three-dimensional triazine-linked polycyanurate networks through a polycyclotrimerization reaction (Scheme 1) in the presence of transition metallic salts and/or compounds containing active hydrogen acting as catalysts. However, highly crosslinked cured resins and their fiber-reinforced composites are not suitable for many practical uses because of their inherent brittleness. Many attempts have been made to improve the toughness of this highly crosslinked thermoset network through modification by elastomers,<sup>6</sup> thermoplastics,<sup>7–9</sup> and thermosetting resins.<sup>10–12</sup>

CE can be modified by a thermosetting epoxy resin (EP) because of the reaction between the triazine rings and epoxy groups, which forms oxazolidinone structures. In addition, the moisture resistance of CE is increased, whereas the thermal properties are not obviously sacrificed, when EP is introduced.<sup>10–13</sup> Thus,

blends of EP and CE have been intensively investigated among these modified CE systems. The toughness of a CE/EP system depends on the molar ratio of CE to EP, and many researchers have been engaged in this area. Unfortunately, there are few researchers focusing on the relationship between the weight-average molecular weight ( $M_w$ ) of EP and the properties of CE/EP-modified systems in detail.

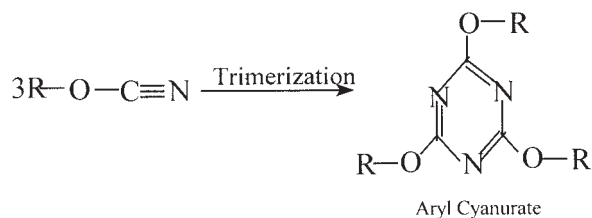
In this study, bisphenol A dicyanate (BADCy) resin was modified by epoxy resins with different molecular weights, E51 ( $M_w = 400$ ) and E20 ( $M_w = 1000$ ), and the effects of the molecular weight of epoxy on the properties of the networks were investigated. The reaction mechanism of the BADCy/EP copolymers was monitored with Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The mechanical properties and the hot/wet performance of the BADCy/E51 and BADCy/E20 systems were also discussed.

## EXPERIMENTAL

### Materials

BADCy was synthesized in our laboratory with a purity greater than 99.5%. Both diglycidyl ether of bisphenol A epoxy resins, E51 ( $M_w = 400$ , hydroxyl group concentration = 0.90 wt %) and E20 ( $M_w = 1000$ , hydroxyl group concentration = 3.95 wt %), were purchased from the Wu Xi Resin Plant (China) and used without further treatment; they were industrial-grade. The structures of the BADCy and epoxy resin are given in Scheme 2.

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**Scheme 1** Cyclotrimerization of CE leading to a triazine ring.

### Preparation of the specimens

The blend of epoxy and BADCy was heated to be less viscous at 100°C. Then, the liquid resin was poured into a mold coated with a release agent that was isothermal at 120°C. After that, the mold, loaded with liquid resin, was degassed *in vacuo* at 90–100°C for 20 min, and this was followed by cure procedures (120°C for 1 h, 150°C for 1 h, and 180°C for 2 h). Then, it was cooled to room temperature before the resin plaque was removed from the mold. The resin plaque underwent a freestanding postcure in a circulating air oven at 200°C for 4 h. After the mold had cooled to room temperature naturally, the resin plaque was cut with a water coolant to a suitable size: 15 mm × 10 mm × 4 mm (type I), 10 mm × 110 mm × 4 mm (type II), or 30 mm × 30 mm × 4 mm (type III). After the cutting, the specimens were immediately placed in an oven at 100°C for 3 h.

### Equipment and testing

#### DSC

DSC measurements were performed with a Perkin-Elmer DSC-7 (Champaign, IL) supported by a PerkinElmer computer for data acquisition; the DSC instrument was calibrated with high-purity indium. Samples (8–10 mg) were weighed into small DSC aluminum pans sealed with holed aluminum lids, and the experiments were conducted under a nitrogen flow of 20 cm<sup>3</sup>/min. All the samples were subjected to a dynamic DSC scan from 50 to 300°C at 10°C/min.

#### FTIR spectroscopy

A resin blend/CHCl<sub>3</sub> solution was coated onto a KBr pellet, and subsequently, the evaporation of the solvent was carried out at room temperature for 3 h. An IBM Instruments WQF-300IR spectrometer (Beijing, China) was used to study the cure reaction. Spectra were obtained in an optical range of 400–4000 cm<sup>-1</sup> by the averaging of six scans at a resolution of 8 cm<sup>-1</sup> to minimize the effects of dynamic scanning.

#### Testing

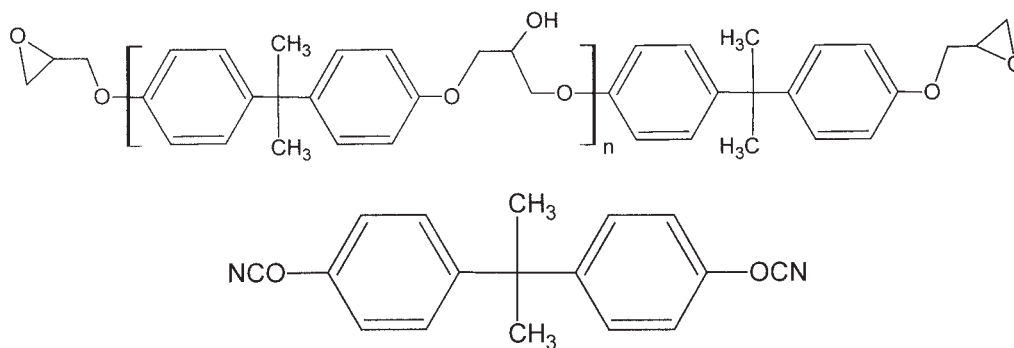
The mechanical properties of the cured resin were obtained with an Instron universal testing apparatus (Darmstadt, Germany). Ten specimens of type I without obvious flaws were tested according to GB2570-1981 to obtain the flexural strength, and another 10 specimens of type I were tested according to GB2571-1981 to obtain the impact strength. Two specimens of type II were tested according to GB1634-1988 to determine the heat deflection temperature (HDT). Three specimens of type III were used for water absorption testing. Before the testing, the specimens were placed at 100°C until their weights reached an asymptotic value ( $W_0$ ). Then, the specimens were placed in boiling water. The weight gain ( $W_t$ ) of each specimen due to moisture absorption was measured on a chemical balance after the removal of the moisture from the specimen surface by soft paper tissue. The moisture content was calculated as follows:

$$\text{Moisture content (\%)} = (W_t - W_0)/W_0 \times 100\%$$

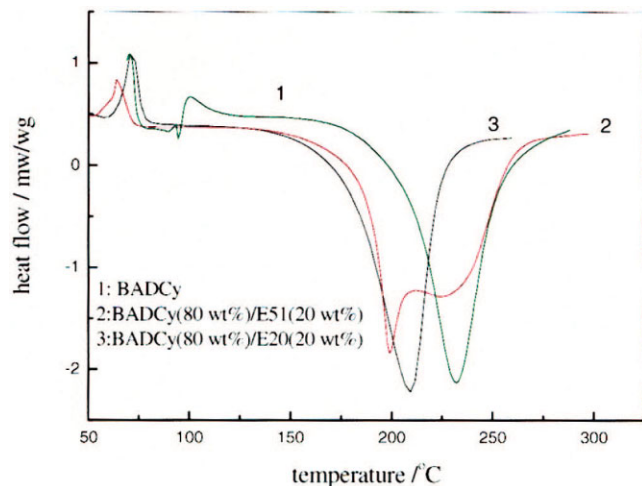
## RESULTS AND DISCUSSION

### Reactivity of the epoxy/BADCy blend

The synthesized CE unavoidably contained a small amount of water and residual monomers, which could act as catalysts for the copolymerization of CE resins, so the industrial-grade CE without any catalyst addition could self-polymerize and form the crosslink net-



**Scheme 2** Structures of BADCy and diglycidyl ether of bisphenol A epoxy resins.

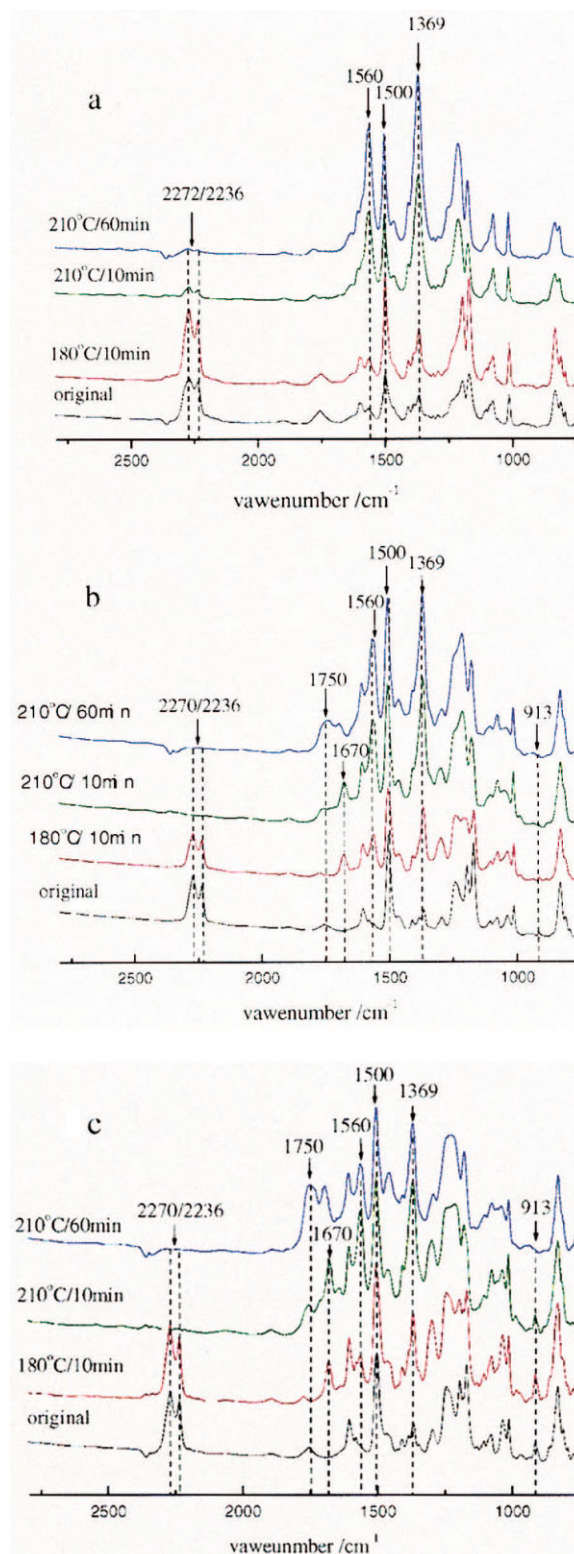


**Figure 1** DSC curves of BADCy and its modified systems: (1) BADCy, (2) BADCy/E51 (80/20 w/w), and (3) BADCy/E20 (80/20 w/w). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

work. The lower its purity degree was, the stronger its reactivity was. The DSC results for BADCy (curve 1) and its modified systems BADCy/E51 (curve 2) and BADCy/E20 (curve 3) are shown in Figure 1. There is only one exothermic peak representing the polymerization of BADCy in DSC curves 1 and 3. The peak temperature of BADCy/E20 (209.4°C) was lower by about 23°C than that of pure BADCy (232°C). This proved that E20 had a strong catalytic effect on the polymerization of BADCy and lowered the peak maximum temperature. The DSC curve of the BADCy/E51-modified system (curve 2) has two observable exothermic peaks, which indicate two exothermic reactions taking place at 198 and 224°C. The latter peak temperature was 14.6°C higher than that of the BADCy/E20-modified system. However, it was lower than that of pure BADCy. This showed that E51 could accelerate the polymerization of BADCy less obviously than E20. The different catalytic effects could be explained by the different contents of hydroxyl groups in the two epoxies, which were effective catalysts for CE polymerization. The higher hydroxyl group content of E20 made BADCy/E20 present a lower peak reaction temperature than that of BADCy/E51.


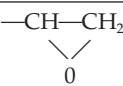
Figure 2 shows the FTIR spectra of BADCy and its modified systems cured at different cure temperatures. The characteristic infrared absorptions of the epoxy-modified CE systems are listed in Table I. The absorbency of the FTIR band is illustrated by the height of the peak versus the height of the absorbent peak of phenyl (1500  $\text{cm}^{-1}$ ) as the internal standard ( $h_{(R)}/h_{(1500\text{cm}^{-1})}$ ).

As can be seen in the FTIR spectra, the —OCN groups (2270  $\text{cm}^{-1}$ ) disappeared when the reaction of pure BADCy went along at 210°C for 1 h, with the



**Figure 2** FTIR spectra of BADCy systems cured at different curing temperatures: (a) BADCy, (b) BADCy/E20 (80/20 w/w), and (c) BADCy/E51 (80/20 w/w). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE I  
Characteristic IR Absorptions of the Epoxy-Modified CE System

Chemical group	$-\text{OCN}$	$>\text{N}-\overset{\text{C}}{\parallel}=\text{O}$	$>\text{C}=\text{N}-$	Triazine ring		$-\text{CH}-\text{CH}_2$ 
Absorption ( $\text{cm}^{-1}$ )	2270	1750	1670	1560, 1369	1500	913

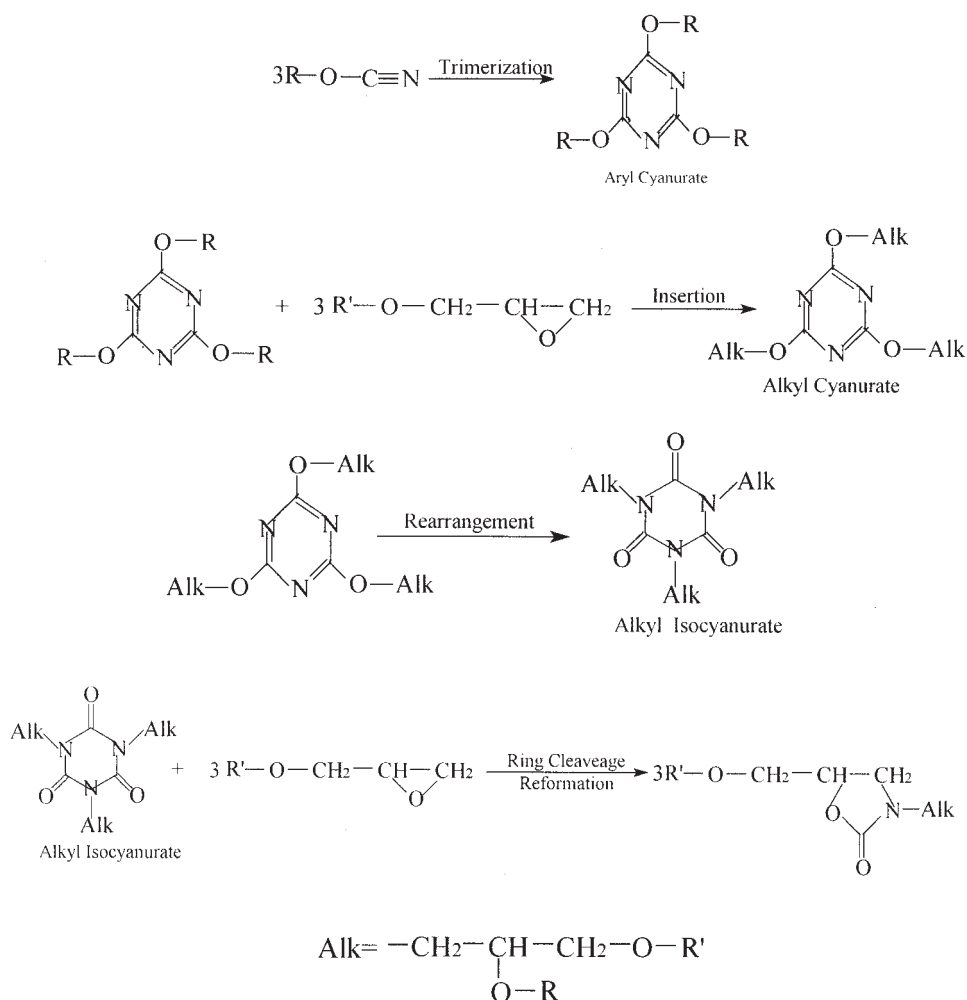
formation of triazine ( $1560$  and  $1369$   $\text{cm}^{-1}$ ). Under the same conditions, it took only 10 min for the  $-\text{OCN}$  groups to react completely when epoxies were introduced into BADCy. As far as the epoxies are concerned, a small decrease in the epoxy groups ( $913$   $\text{cm}^{-1}$ ) was observed when the  $-\text{OCN}$  groups had completely reacted after 10 min at  $210^\circ\text{C}$ . Then, the epoxy group began to decrease and yield a large number of oxazolidinone rings ( $1750$   $\text{cm}^{-1}$ ) when the reaction occurred. For CE modified by the epoxies, the main reaction at lower temperatures was the polyclomerization of  $-\text{OCN}$  groups, whereas the main reaction at higher temperatures was ring-cleavage re-

formation between cyanate and epoxy groups.<sup>13</sup> The main reactions are illustrated in Scheme 3.

The content of oxazolidinone rings in the BADCy/E51 system was obviously higher than that of the BADCy/E20 system because of the different amounts of epoxy groups in the two epoxies.

### Mechanical properties of BADCy modified by epoxy

Figure 3 shows the relationships between the impact strength and flexural strength and the epoxy resin contents in the BADCy/E20- and BADCy/E51-modi-

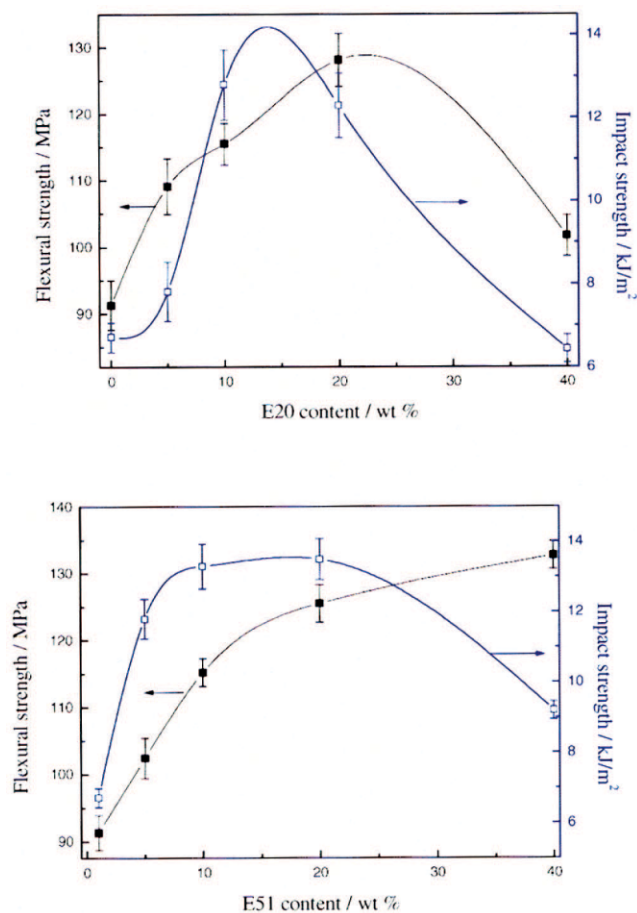


Scheme 3 Main reactions of the BADCy/epoxy system.

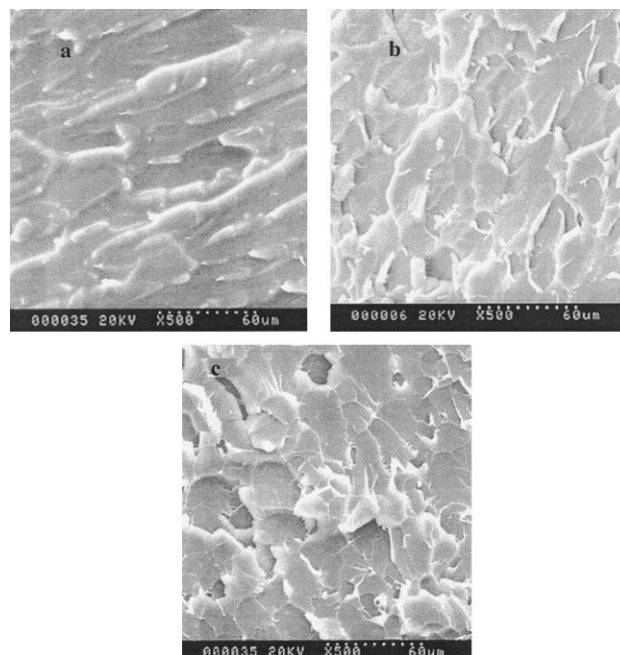


fied systems. When the concentration of E20 was less than 10%, the impact strength of the modified system increased with increasing E20 content and reached its maximum value of 12.8 kJ/m<sup>2</sup>, which was 1.90 times that of unmodified BADCy. Further increasing the E20 concentration (>10 wt %) resulted in a decrease in the impact strength, which almost reached the initial value when 40% E20 was introduced. The changes in the flexural strength were similar to those of the impact strength. The flexural strength increased largely with the concentration of E20 increasing when the concentration of E20 was less than 20 wt % and obtained its maximum value (128 MPa) when the concentration of E20 was 20 wt %. This maximum value was greater than that of unmodified BADCy by a factor of 1.4.

The flexural strength of the BADCy/E51 system increased with the concentration of E51 up to 40 wt % and reached its maximum value of 132.7 MPa, which was greater than that of unmodified BADCy by a factor of 1.45. The best impact strength (13.5 kJ/m<sup>2</sup>) for this modified system was obtained when the con-



**Figure 3** Mechanical properties of modified BADCy versus the epoxy resin content. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** SEM microphotographs of fracture surfaces of BADCy and its modified systems: (a) BADCy, (b) BADCy/E20 (80/20 w/w), and (c) BADCy/E51 (80/20 w/w).

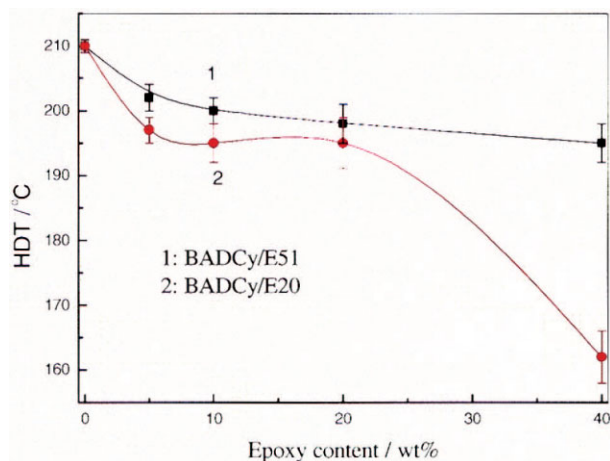
centration of E51 was 20 wt % and almost twice the initial value. A comparison of BADCy/E51 and BADCy/E20 showed that the mechanical properties of the former were slightly higher than those of the latter, and this indicated that E51 might be the better modifier for BADCy. The reason was that E51 had a lower  $M_w$  value, that is, more epoxy groups in the same weight of epoxies. As a result, more oxazolidinone rings instead of stiff triazine rings and more extended molecular chains formed in the cured network.

Scanning electron microscopy (SEM) micrographs of the fracture surfaces of BADCy and its modified systems blended with 20 wt % epoxy resins (BADCy/E20 and BADCy/E51) are shown in Figure 4. The smooth fracture surface of pure BADCy indicated its brittle feature. Abundant tough whorls were observed in the fracture surfaces of both modified systems, suggesting an obvious toughness improvement of BADCy through modification by the epoxy resins, in agreement with the results of mechanical tests in Figure 3.

Because of the different molecular weights of the two epoxies, the E20-modified system had less tough whorls with larger dimensions than E51.

#### Heat and water resistance of the modified BADCy system

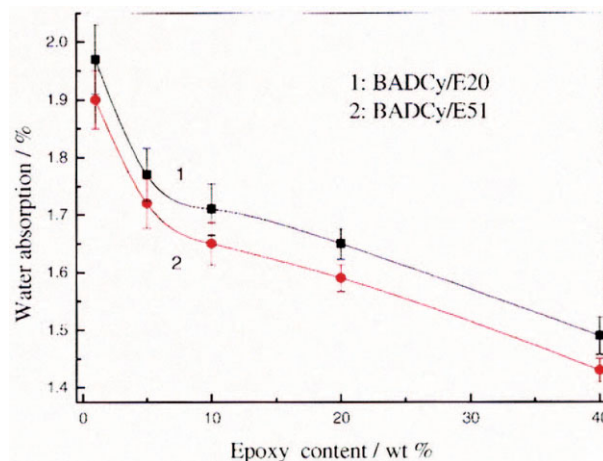
Figure 5 shows curves of HDT versus the epoxy content of the BADCy/E20 and BADCy/E51 systems. The HDTs of these two modified systems decreased with



**Figure 5** HDT of E51/BADCy and E20/BADCy versus the epoxy resin content. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

increasing epoxy content, and the heat resistance of BADCy/E20 was poorer than that of BADCy/E51 at the same weight ratio. Moreover, the HDT value changed differently when the epoxy concentration was higher than 20 wt %. HDT of BADCy/E20 decreased drastically, whereas for the BADCy/E51-modified system, the HDT values decreased slightly. This phenomenon could be explained by the long and flexible chains of E20 introduced into the stiff, crosslinked, cured networks, which led to the decrease in HDT. However, there existed a large number of oxazolidinone rings linked by short chains in the E51-cured system, and this caused HDT to decrease slightly.

Figure 6 shows the relationships between the water absorption and epoxy contents of the two modified systems, BADCy/E20 and BADCy/E51, after boiling for 100 h. The water absorption of the modified systems decreased with the epoxy content increasing. This might be attributed to the different water boiling resistances of triazines and oxazolidinone rings. It is well known that polymerized BADCy displays large free volume because of the structure of the triazinebicyclopentane cage<sup>2</sup> (as shown in Fig. 7). Because of the oxazolidinone rings with smaller free volume in the epoxy-modified BADCy copolymers, the modified system had lower water absorption. Besides, E51-modified BADCy had lower water absorption than the E20-modified system under the same circumstances. This phenomenon was caused by the different structures of the two modified systems. E20 had a higher hydroxyl group concentration (3.95 wt %) than E51 (0.90 wt %), so the cured BADCy/E20 system contained more hydrophilic hydroxyl groups, which were prone to absorb water. In addition, the smaller free volume in the BADCy/E51 system with more penta-

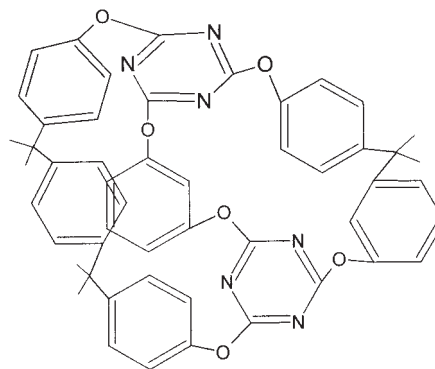


**Figure 6** Water absorption of modified BADCy versus the epoxy resin content. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

cyclic oxazolidinone rings was also responsible for its lower water absorption.

## CONCLUSIONS

Two epoxy resins, E51 and E20, with different  $M_w$  values were used as modifiers for CE resin. DSC and FTIR studies showed that the cure temperature of BADCy was reduced by 23 and 8°C with the introduction of E20 and E51, respectively, and this suggested that the former had stronger catalysis than the latter with the same epoxy weight (20 wt %) incorporation. The modified BADCy systems exhibited good mechanical and hot-wet properties when the E20 concentration ranged from 10 to 20 wt %, whereas the concentration range for E51 was 5–30 wt %; this indicated that the lower  $M_w$  epoxy resin, E51, might be the better modifier for improving the performance of BADCy.



**Figure 7** Structure of the triazinebicyclopentane cage.

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