

# Preparation of Hyperbranched Epoxy Resin Containing Nitrogen Heterocycle and Its Toughened and Reinforced Composites

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**ABSTRACT:** Low-viscosity hyperbranched epoxy resin-containing nitrogen heterocycle (HTPE) is synthesized from epichlorohydrin (ECH), dimethylol propionic acid (DMPA), and tris(2-hydroxyethyl)-isocyanurate. The structure and properties of HTPE are characterized by FTIR, GPC, and molecular simulation. The performance of HTPE/diglycidyl ether of bisphenol-A (DGEBA) composites first increase and then decrease with the increase of the content and molecular weight of HTPE. Compared to those of pure DGEBA, the impact strength, fracture toughness, tensile, and flexural strength of HTPE-2/DGEBA composite can be enhanced by

about 192%, 39%, 18%, and 23%, respectively. The absence of microphase separation and the presence of lots of "proto-nema" on the fracture surface of the composites are explicated by an *in situ* reinforcing and toughening mechanism. The intramolecular cavity of HTPE and the strong interaction between HTPE and DGEBA are two key factors to toughening and reinforcing DGEBA. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3261–3269, 2012

**Key words:** hyperbranched polymers; composites; epoxy resin

## INTRODUCTION

Hyperbranched polymers (HBP) have received considerable attention over the past decade due to their interesting properties, such as large number of end groups, low intrinsic viscosity, and three-dimensional structure<sup>1,2</sup> and have been broadly used as rheology modifiers,<sup>3</sup> toughening components,<sup>4</sup> adhesion,<sup>5</sup> and macroscopic tubes.<sup>6</sup> Some initial studies have reported the toughening of common epoxy resin by HBP.<sup>7–10</sup> Several-fold increase in fracture toughness was obtained for a commercial diglycidyl ether of bisphenol-A (DGEBA) epoxy resin using only 5 wt % hyperbranched epoxy resin,<sup>4,11,12</sup> but the strength, including tensile strength, flexural strength decreased to some extent due to low crosslinking density. Until 2006, the synthesis of low-viscosity liquid epoxidized aromatic hyperbranched polymer with low-epoxy equivalent weight, which could simultaneously toughen and reinforce the common DGEBA,<sup>13,14</sup> was reported<sup>15</sup> by our group.

The toughening effect was attributed to the intramolecular cavity from the noncrosslinking structure of HBP, which can absorb significant amount of energies upon impacting.<sup>4,14</sup>

HBP has many noncrosslinking intramolecular cavities, the incorporation of HBP into DGEBA would predicatively result in lower crosslinking density and lower strength. Nevertheless, why some HBP can increase<sup>14</sup> the strength of DGEBA, whereas other HBP decrease<sup>16</sup> it to some extent? We originally attributed the reinforcing effect of our hyperbranched epoxy resin to the presence of more rigid group than that of Boltorn E1. But, recently, we have prepared a relative flexible hyperbranched epoxy resin, which also demonstrated reinforcing and toughening effect on DGEBA.<sup>17</sup> To understand the underlying causes, a novel low-viscosity hyperbranched epoxy resin (HTPE) containing similar chemical structure with Boltorn E1 was synthesized, and the performance of HTPE/DGEBA composites was studied.

## EXPERIMENTAL

### Materials and instrumentation

Dimethylol propionic acid (DMPA), tris(2-hydroxyethyl) isocyanurate (THEIC), tetrabutyl titanate

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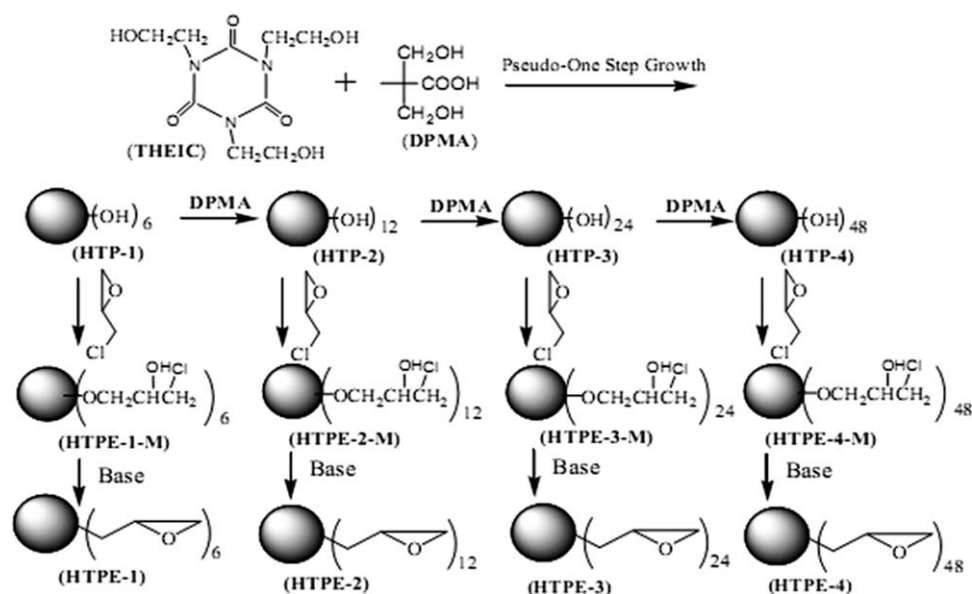


Figure 1 Synthetic scheme of hyperbranched epoxy resin HTPE.

(TBT), epichlorohydrin (ECH), DGEBA containing 5.1 mmol epoxy group per gram of resin, and other organic solvents were commercially purchased. The curing agent DETA-AN was produced by the addition reaction of equal molar acrylonitrile (AN) and diethylene triamine (DETA).

FTIR measurements were performed on a Bruker Vector 33 spectrometer. The viscosity of the resin was measured by a Brookfield DV-II+ Viscometer with RV-S06 spindle at 25°C and 20 rpm. The molecular weight distribution (PDI) and molecular weight were measured by Agilent 1100 Series HPLC, with the Agilent PLgel 5  $\mu\text{m}$  MIXED-C as GPC stationary phase and the tetrahydrofuran (THF) as eluent phase.

Differential scanning calorimetry (DSC) measurement was carried out on the cured samples with a DSC204 F1 (NETZSCH Gerätebau GmbH). Thermal scan at a constant heating rate of 10°C/min was performed in a temperature range 30–100°C for all the cured samples. All TGA analyses were performed on a NETZSCH TG209 (NETZSCH Gerätebau GmbH) instruments. Samples of 10–15 mg were heated to 800°C under nitrogen at a flow rate of 20 mL/min and a heating rate of 10.0°C/min. Dynamic mechanical thermal analysis (DMTA) was performed on the cured materials for attaining  $\tan \delta$  traces with a DMA242 (NETZSCH Gerätebau GmbH) by ramping from –100 to 150°C at a rate of 3°C/min and a frequency of 2 Hz, with a sample dimension 1 mm  $\times$  4 mm  $\times$  20 mm.

No-notch impact strength of the modified epoxy samples were determined by a Zwick-5113 (Zwick-Roell, Germany) digital impact tester according to ASTM D256. Their tensile strength was measured by AG-1 omnipotent electron tensile tester (AG-1 Japan) according to ASTM D638. Their flexural properties

were determined according to ASTM D790 by using an Instron 5500 universal testing machine. Fracture toughness ( $K_{IC}$ ) test was carried out by using the compact tension method according to ASTM D5045-96 using an Instron 5500 universal tester.

A low-voltage scanning electron microscope (SEM) (XL-30FEG, Philip) was used to examine the fracture surface morphology of the samples. A thin section of the fracture surface was cut and mounted on an aluminum stub using a conductive (silver) paint and sputter coated with gold before fractographic examination. SEM photomicrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 10–15 kV.

### Synthesis of HTPE

The synthetic scheme of the novel low-viscosity liquid hyperbranched epoxy resins (HTPE) is shown in Figure 1. About 0.3 mol of  $\text{AB}_2$  monomer (DMPA), 0.1 mol of THEIC, 0.001 mol of TBT, and 100 mL of xylene were added into a four-necked reaction flask equipped with stirrer, cooler, nitrogen inlet, and water-trap (Dean-Stark). The reaction temperature was raised to 140–145°C, stirred for 5 h, and then the solvent was removed under a pressure of 3–5 mm Hg at 140–145°C for 30 min. A yellowish transparent solid was obtained and designated as the first generation of hydroxyl-ended HBP (HTP-1). The HTP-2, HTP-3, and HTP-4 were obtained by a similar pseudo-one step growth according to the scheme in Figure 1.

About 0.1 mol of HTP-1, 1.2 mol of ECH, and 0.01 mol of catalyst tetrabutyl ammonium bromide (TBAB) were added into a three-necked reaction

TABLE I  
Characterization of HTP-n ( $n = 1, 2, 3,$  and  $4$ )

Polymer no.	HTP-1	HTP-2	HTP-3	HTP-4
Theoretical hydroxyl value (mg KOH/g)	552.16	515.30	498.68	490.75
Experimental hydroxyl value (mg KOH/g)	553.42	519.35	499.30	493.66
$p_B$	0.330	0.419	0.465	0.478
$\bar{X}$	1/3	1/9	1/21	1/45
$\bar{X}_n$	2.91	7.76	20.13	32.06
$\bar{X}_w$	3.23	8.71	34.95	101.35
$PDI = \bar{X}_w/\bar{X}_n$	1.11	1.12	1.74	3.16
PDI from GPC	1.20	1.07	1.13	1.17
Molecular weight from GPC	765.00	853.00	1027.00	1214.00
Theoretical molecular weight	609.61	1306.39	2699.95	5487.07
$\bar{M}_n$ from "Recursive Probability Approach"	608.22	1296.24	2696.58	5454.77

flask equipped with stirrer, cooler, and thermometer. The reaction temperature was raised to 115–120°C for 2.5 h, and then the excessive ECH was removed under a pressure of 3–5 mm Hg at 100°C for 10 min. The temperature was lowered to 25°C, and THF was added to completely dissolve the compound. About 80 g of NaOH was then slowly added. The reaction was allowed to continue for 5 h, and the reaction mixture was passed through a pressurized filter to remove precipitated NaCl. Na<sub>2</sub>SO<sub>4</sub> was added to the mixture for removing water after washing the mixture twice by 200 mL water. Thereafter, the remaining solvents were removed under a pressure of 3–5 mm Hg at 100°C. The yellowish low-viscosity transparent liquid thus obtained was designated hyperbranched epoxy resins HTPE-1, HTPE-2, HTPE-3, and HTPE-4 could be obtained from a similar procedure as shown in Figure 1.

### Preparation of HTPE/DGEBA composites

The hyperbranched epoxy resin (HTPE)/diglycidyl ether of bisphenol-A (DGEBA) composites were prepared by mixing the HTPE in the DGEBA at about 40°C through stirring. Then, a stoichiometric amount of DETA-AN was added into the blend by continuously stirring the mixture for 5 min at about 25°C. The mixture was degassed under vacuum for 10 min and then cured in a silicone rubber mold at about 25°C for 5 h and at 80°C for 2 h. The composites containing 0–20 wt % of HTPE-n ( $n = 1, 2, 3,$  and  $4$ ) were so obtained. Afterward, the mechanical performance of the cured system was measured after the samples were cooled gradually to room temperature and placed for 12 h.

## RESULTS AND DISCUSSION

### Characterization of HTP

The molecular weight of HBP is of pivotal importance. According to the polycondensation between hydroxyl group and carboxyl group, the hydroxyl

value of the HTP can be used to calculate the degree of polymerization and further the number-average molecular weight. The precise relationship about theoretical average degree of polymerization and average molecular weight is established in  $AB_f + B_g$  type polymerization by a "Recursive Probability Approach."<sup>18</sup> In such case,  $\bar{X}_w$ ,  $\bar{X}_n$ ,  $\bar{M}_n$ , and  $p_A$  satisfy the following relationships:

$$\bar{X}_w = 1 + \frac{2p_A(f + gx)[f(1 - p_A) + gx] + p_A^2[f(f - 1) + gx(g - 1)]}{(1 + x)[f(1 - p_A) + gx]^2} \quad (1)$$

$$\bar{M}_n = M_0 + 18 + \bar{X}_n(M_{AB_2} - 18) \quad (2)$$

where  $\bar{X}_w$  and  $\bar{X}_n$  refer to the mass-average degree and the number-average degree of polymerization respectively.  $\bar{M}_n$  refers to the number-average molecular weight.  $p_A$  refers to the fraction of A groups that have reacted, and  $x$  refers to the ratio of the core  $B_g$  to  $AB_2$  monomer.  $M_0$  and  $M_{AB_2}$  refer to molar mass of  $B_g$  and  $AB_2$  monomers, respectively.

Hydroxyl value ( $H_v$ ) refers to the number of milligrams of KOH per gram resin. In the system,  $p_B$ ,  $H_v$ , and  $\bar{X}_n$  satisfy the following relationships:

$$H_v = \frac{56100(3 + \bar{X}_n)}{261.12 + 116.13\bar{X}_n} \quad (3)$$

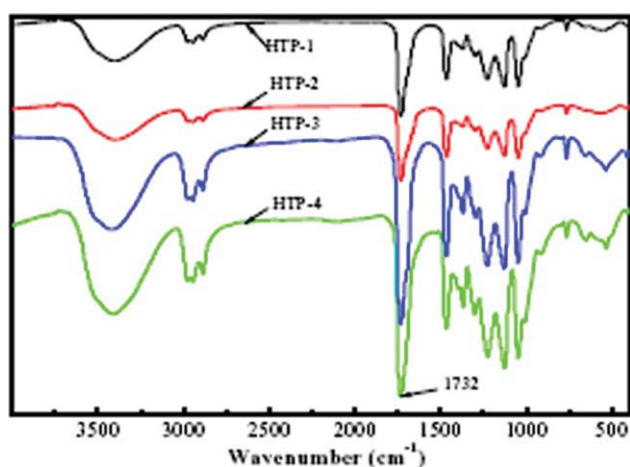
$$p_B = \frac{\bar{X}_n}{2\bar{X}_n + 3} \quad (4)$$

Therefore, the relationship of  $H_v$  and  $p_B$  satisfies the following relationship:

$$p_B = \frac{168300 - 261.12H_v}{168300 - 173.85H_v} \quad (5)$$

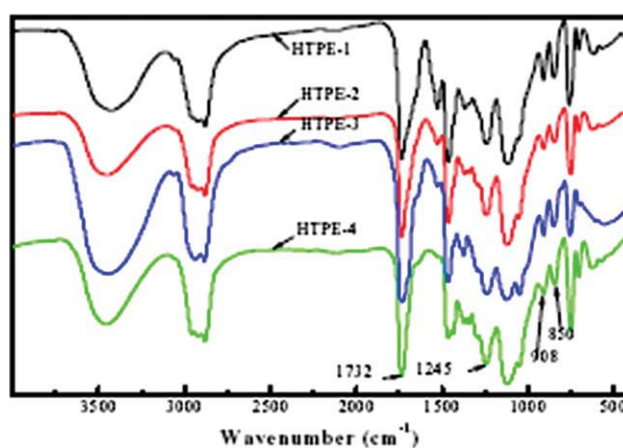
In this system, because  $p_A = f p_B$ ,  $f = 2$ , and  $g = 3$ , and so from the eqs. (1)–(5), the molecular weight may be calculated (Table I). Table I illustrates that





**Figure 2** FTIR spectra of HTP- $n$  ( $n = 1, 2, 3,$  and  $4$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

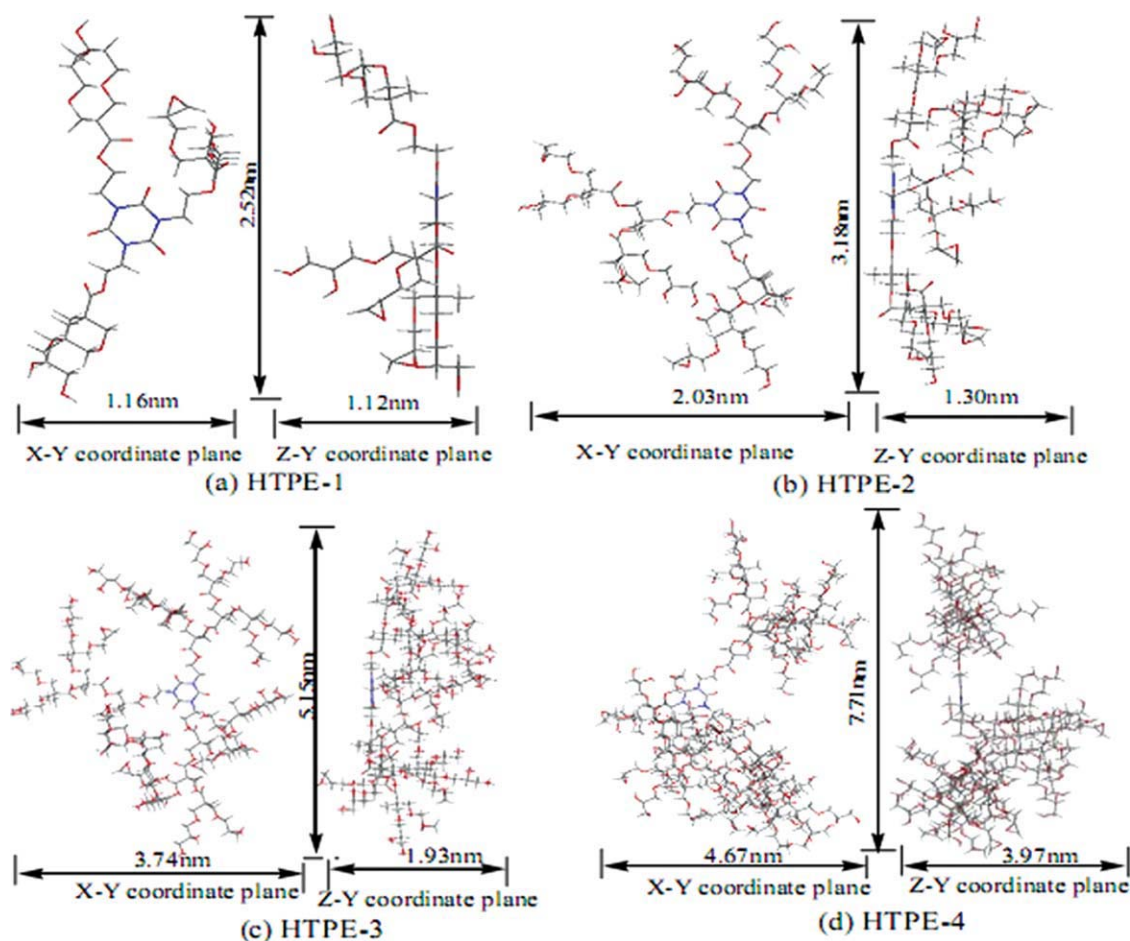
$\overline{M}_n$  of HTP obtained by “Recursive Probability Approach” are almost equal to their theoretical molecular weight. The FTIR spectra (shown in Fig. 2) of HTP- $n$  ( $n = 1, 2, 3, 4$ ) show main peaks at  $3500\text{ cm}^{-1}$  ( $-\text{OH}$ ) and  $1732\text{ cm}^{-1}$  ( $-\text{COO}-$ ).



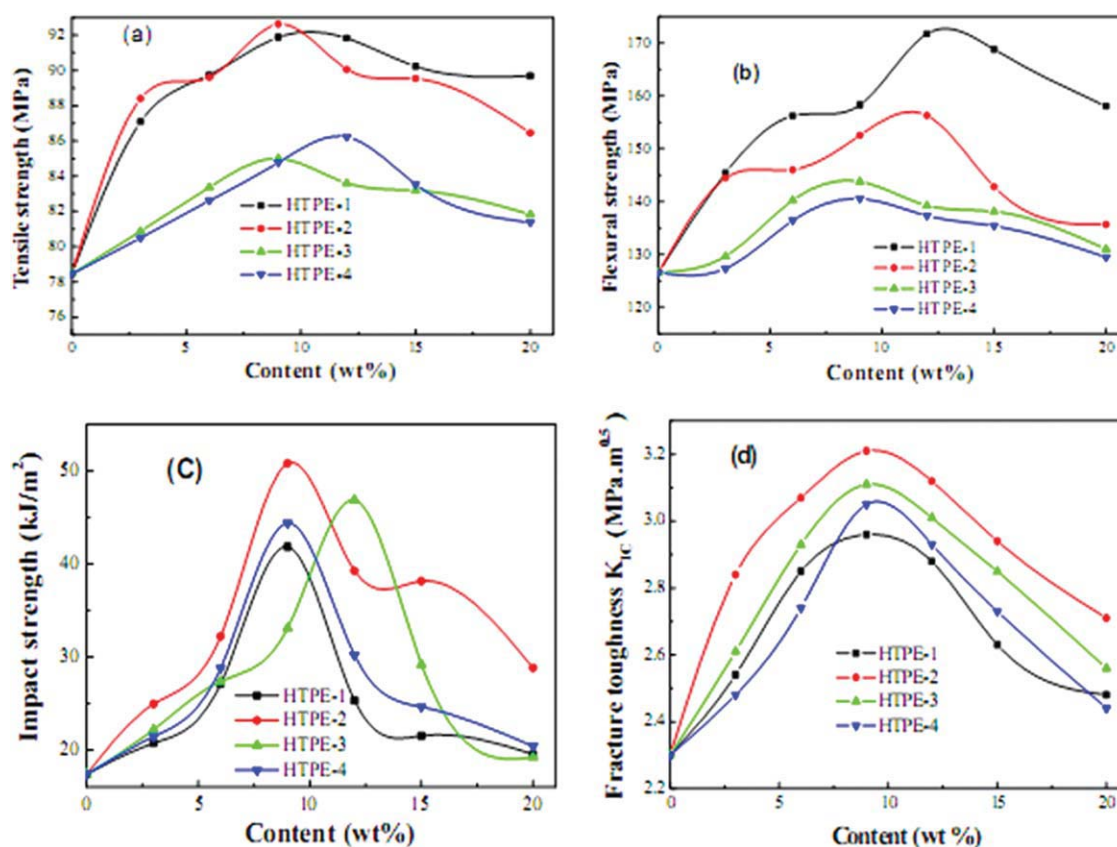
**Figure 3** FTIR spectra of HTPE- $n$  ( $n = 1, 2, 3,$  and  $4$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Characterization of HTPE

The viscosities of hyperbranched epoxy resin (HTPE)-1, HTPE-2, HTPE-3, and HTPE-4 are 17,500, 11,700, 24,300, and 32,600 cp, and their theoretical molecular



**Figure 4** Molecular simulation size and shape of HTPE- $n$  ( $n = 1, 2, 3,$  and  $4$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5** Effect of the content and molecular weight of HTPE on the mechanical strength of the HTPE/DGEBA composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

weights are 945.61, 1978.39, 4043.95, and 8175.07 g/mol, and their epoxy equivalent weight measured by acid titration (ASTM D1652-73) is 318.47, 343.64, 323.62, and 348.43 g/mol, respectively.

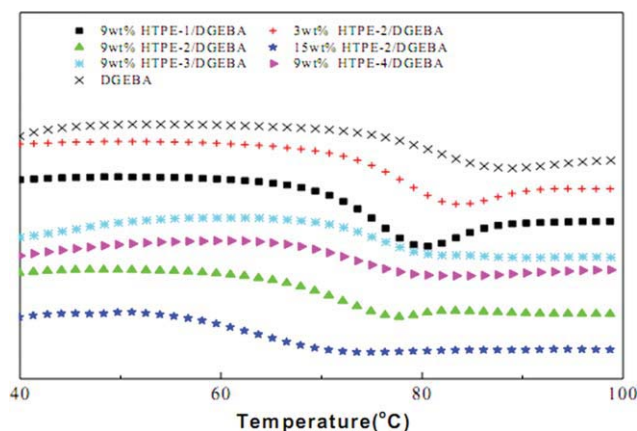
The viscosity of the hyperbranched epoxy resins with nitrogen heterocycle decreases first and then increases with the increase of their molecular weight, and the relationship confirms that the hyperbranched epoxy resins have higher branching degree, and their structure is similar to that of dendrimers.<sup>19,20</sup>

FTIR spectra (shown in Fig. 3) of HTPE: 3050–3690  $\text{cm}^{-1}$  (—OH), the epoxy group at 1244, 909, and 854  $\text{cm}^{-1}$ , 732  $\text{cm}^{-1}$  (—CO—), and 1477  $\text{cm}^{-1}$  (C—N group of THEIC).<sup>21</sup>

Figure 4 shows that the molecular size of HTPE-1, HTPE-2, HTPE-3, and HTPE-4 as obtained by simulation are 1.16 nm  $\times$  1.12 nm  $\times$  2.52 nm, 2.03 nm  $\times$  1.30 nm  $\times$  3.18 nm, 3.74 nm  $\times$  1.93 nm  $\times$  5.15 nm, and 4.67 nm  $\times$  3.97 nm  $\times$  7.71 nm, respectively. The thickness of some section is not more than 4 nm.<sup>22</sup> Moreover, there are many molecular cavities in the HTPE structure. The nanometer size and ellipsoid-like shape of HTPE would result in lower hydromechanical volume and lower viscosity than those of sticklike linear polymers.

### Performance of HTPE/DGEBA composites

Figure 5 shows the effect of the content and molecular weight of hyperbranched epoxy resin (HTPE) on the mechanical performance of the HTPE/diglycidyl ether of bisphenol-A (DGEBA) composites. Tensile, flexural, impact strength, and fracture toughness of the composites increase first and then decrease with the increase of HTPE content, and they decrease with the increase in their molecular weight. The maximum tensile strength of the four kinds of modified HTPE-1/DGEBA, HTPE-2/DGEBA, HTPE-3/DGEBA, and HTPE-4/DGEBA composites are, respectively, 91.89 MPa, 92.63 MPa, 85.01 MPa, and 86.23 MPa, representing an increase by about 17.10%, 18.05%, 8.33%, and 9.89% compared to that of DGEBA (78.47 MPa). Their maximum flexural strength are respectively, 171.79 MPa, 156.31 MPa, 143.82 MPa, and 140.57 MPa, improved by about 35.73%, 23.50%, 13.63%, and 11.06% compared to that of DGEBA (126.57 MPa). Their maximum impact strength are 41.82  $\text{kJ/m}^2$ , 50.79  $\text{kJ/m}^2$ , 46.86  $\text{kJ/m}^2$ , and 44.39  $\text{kJ/m}^2$ , improved, respectively, by about 140.76%, 192.40%, 169.78%, and 155.56% compared to the impact strength (17.37  $\text{kJ/m}^2$ ) of unmodified DGEBA. The maximum fracture

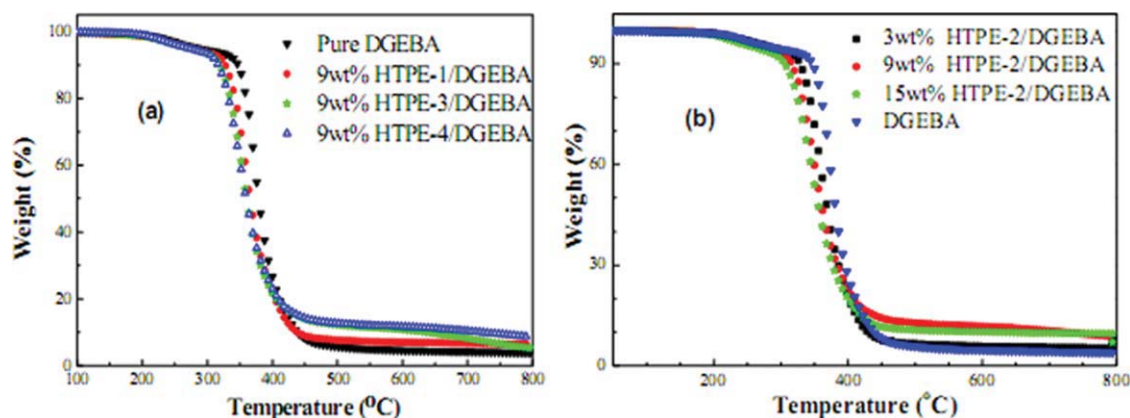


**Figure 6** DSC curves of HTPE/DGEBA composites and DGEBA epoxy resin. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

toughness are 2.96 MPa m<sup>1/2</sup>, 3.21 MPa m<sup>1/2</sup>, 3.11 MPa m<sup>1/2</sup>, and 3.05 MPa m<sup>1/2</sup>, improved, respectively, by about 28.70%, 39.57%, 35.22%, and 32.61% compared to that (2.30 MPa m<sup>1/2</sup>) of unmodified DGEBA.

Figure 6 shows the glass transition temperature ( $T_g$ ) of the composites. The  $T_g$  of 9 wt % HTPE-1/DGEBA, 9 wt % HTPE-2/DGEBA, 9 wt % HTPE-3/DGEBA, 9 wt % HTPE-4/DGEBA, 3 wt % HTPE-2/DGEBA, 15 wt % HTPE-2/DGEBA, and pure DGEBA are, respectively, 75.9°C, 72.0°C, 75.5°C, 73.6°C, 78.8°C, 63.3°C, and 81.6°C. The DSC traces of the composites show the decrease in  $T_g$  with the increase of HTPE-2 content, and the initial decrease and then increase with the increase of the molecular weight of HTPE. The  $T_g$  decrease could be attributed to the decrease of crosslink density and the increase of intramolecular cavities.<sup>17</sup>

The effect of the HTPE content and molecular weight on thermal degradation temperature of the HTPE/DGEBA composites is shown in Figure 7. Relative mass loss is obtained from Figure 7 and



**Figure 7** Effect of HTPE molecular weight and content on TGA of the composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

shown in Table II. With the increase of molecular weight and content of HTPE in the composites system, ring-close degree of the HTPE is lower than that of DGEBA epoxy resin, which results in the increase of hydroxyl content of the composites and lower crosslinking density; therefore, initial thermal degradation temperature (temperature at 5% mass loss) of HTPE/DGEBA composites decreased.

Thermal degradation kinetics data of the HTPE/DGEBA composites also can be calculated by Coats–Redfern model.<sup>23</sup> The plot of  $\ln[g(a)/T^2]$  against  $1/T$  of DGEBA during thermal degradation and its simulation curves can also be obtained. All activation energy data of DGEBA and HTPE/DGEBA composites are obtained and shown in Table II. The thermal degradation reaction under 340.5°C is attributed to dehydration of the hydroxyl groups of epoxy resin owns. The low-temperature reaction activation energy ( $E_{a1}$ ) has little difference with the increase of HTPE content and molecular weight. The thermal degradation reaction is related to chemical bond fracture of epoxy resin at over 340.5°C.<sup>24</sup> With the increase of molecular weight and content of HTPE in the composites, the high-temperature reaction activation energy ( $E_{a2}$ ) of the composites decreases sharply because of high-thermal degradation reaction activity resulting from the multieffects of much more intramolecular cavities, much more flexible chain, higher epoxy equivalent weight of HTPE than those of DGEBA.

## REINFORCING AND TOUGHENING MECHANISM

The impact behavior of the HTPE/DGEBA composites can be explained in terms of morphology observed by SEM. Scanning electron micrographs of the fracture surfaces of pure DGEBA and HTPE/DGEBA composites are presented in Figure 8. The smooth surface and clear crack of pure DGEBA are



TABLE II  
TGA and Kinetics Data of HTPE/DGEBA Blends and DGEBA Epoxy Resin

Typical data	DGEBA	HTPE-1 9 wt %	HTPE-2 3 wt %	HTPE-2 9 wt %	HTPE-2 15 wt %	HTPE-3 9 wt %	HTPE-4 9 wt %
Temp.5% weight loss (°C)	286.7	278.3	286.7	271.0	260.2	275.2	271.9
Temp.10% weight loss (°C)	347.2	327.5	328.8	315.6	305.8	318.4	316.7
Temp. max. Degrad. rate (°C)	368.9	353.9	358.2	351.6	350.3	355.4	355.8
Residual weight at 800°C (%)	3.82	6.47	8.28	8.66	6.85	5.25	8.65
$E_{a1}$ (kJ/mol)	29.14	27.52	30.37	27.79	25.03	28.48	26.31
Regress ( $R_1$ )	-0.991	-0.992	-0.991	-0.993	-0.989	-0.990	-0.991
$E_{a2}$ (kJ/mol)	202.08	153.41	162.39	133.78	115.66	134.47	119.65
Regress ( $R_2$ )	-0.999	-0.999	-0.999	-0.999	-0.999	-0.999	-0.998

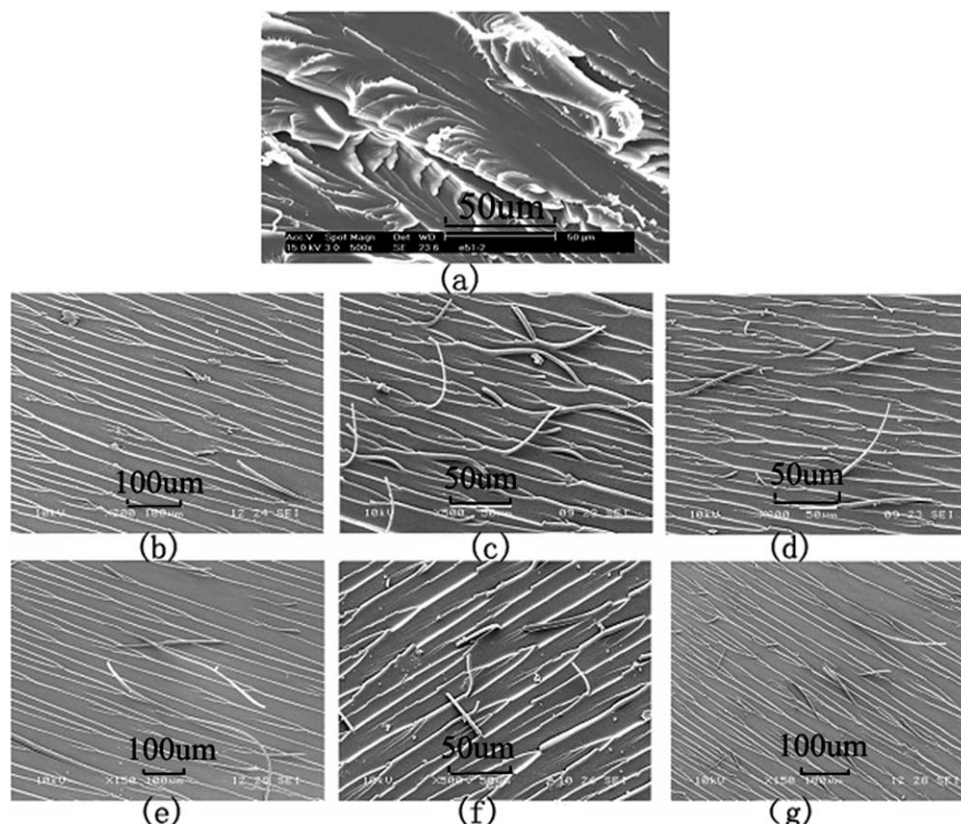
substantial evidence of a brittle material, whereas the appearance of a lot of “protonema” (which refers to filar shape) in Figure 8 confirm high toughness of the HTPE/DGEBA composites. Moreover, the density of “protonema” increases with the increase of HTPE content.

In the HTPE/DGEBA composites system, the similarity of the chemical structure of HTPE and DGEBA and the nanometer molecular size of HTPE (Fig. 4) result in excellent miscibility, and there is no micro-phase separation on the fracture surfaces. Therefore, the toughening mechanism is not the phase separation mechanism, two-phase structure mechanism,<sup>4</sup> or particle cavitation mechanism,<sup>16</sup> but is a new *in*

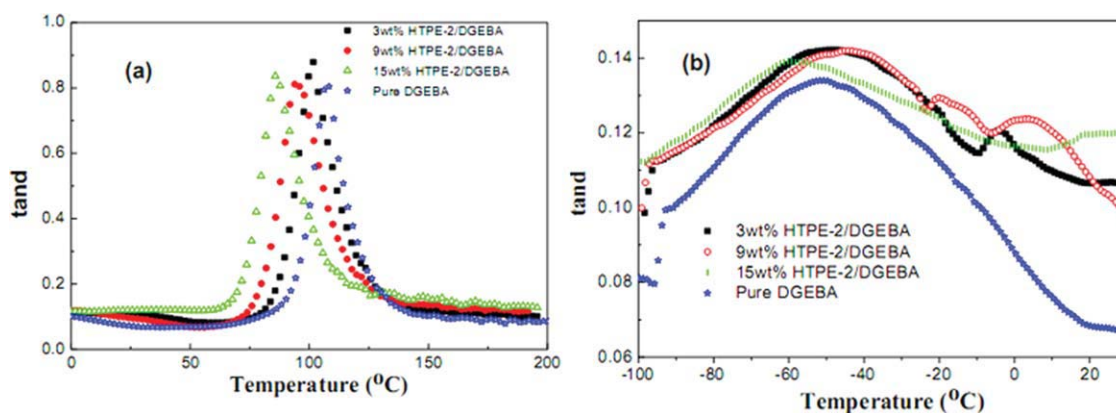
*situ* reinforcing and toughening mechanism.<sup>13,14,17</sup>

Either epoxy group of HTPE or DGEBA reacts with amine group of DETA-AN during curing but the hydroxyl group of HTPE or DGEBA cannot. The external crosslinking reaction of HTPE will inhibit the movement of hydroxyl end-group and intramolecular chain, the intramolecular noncrosslinking structure thus forms intramolecular cavity. These intramolecular cavities will distort and form “protonema” upon impacting, and the shape of the “protonema” is similar to the morphological structure of HTPE by molecular simulation technology.

With the increase of molecular weight and content of HTPE in HTPE/DGEBA composites, the enhancement



**Figure 8** Effect of the content and molecular weight of HTPE on SEM micrographs of impact fracture surface of the composites: (a) pure DGEBA, (b) 3wt % HTPE-2/DGEBA, (c) 9 wt % HTPE-2/DGEBA, (d) 15 wt % HTPE-2/DGEBA, (e) 9 wt % HTPE-1/DGEBA, (f) 9 wt % HTPE-3/DGEBA, (g) 9 wt % HTPE-4/DGEBA.



**Figure 9** DMA curves of HTPE-2/DGEBA composites and DGEBA epoxy resin. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of the mechanical performance of the composites can be explained as follows. The mechanical performance is influenced by the rigidity of the hyperbranched polymer chain, intramolecular cavity density of HBP, interface interaction, and the crosslinking density. The chain rigidity, interface interaction, and crosslinking density have positive effect on the tensile and flexural strength, but the intramolecular cavity density has negative effect.<sup>14,17</sup> On the contrary, the chain rigidity, interface interaction, and crosslinking density have negative effect on the impact strength and fracture toughness, but the intramolecular cavity density has positive effect.<sup>14,17</sup> With the increase in the content and molecular weight of HTPE, the intramolecular cavity density of the composites increases and their crosslinking density decreases resulting from the fact that the epoxy equivalent weight of HTPE (318–349 g/mol) is more than that of DGEBA (196 g/mol).

Moreover, the excellent miscibility between HTPE and DGEBA will decrease the interchain distance and increase the interface interaction; therefore, all the tensile, flexural, and impact strength demonstrate a maximum with the increase of HTPE content and molecular weight. The strong interaction of interface also explains why there is only one  $T_g$  and no microphase separation, and the lower curing shrinkage.<sup>25</sup> Furthermore, the epoxy equivalent weight of HTPE (318–349 g/mol) is lower than that of Boltorn E1<sup>4</sup> (875 g/mol), which results in HTPE/DGEBA composites having higher crosslink density and stronger interaction of interface; therefore, the HTPE can reinforce the DGEBA while Boltorn E1 cannot.

Another toughness analysis is also discussed by the  $\beta$ -relaxation peak of material through DTMA technology.<sup>26,27</sup> The  $\tan \delta$ - $T$  spectra of the cured systems are shown in Figure 9(b). The only  $\tan \delta$  peak or  $\alpha$ -relaxation peak also is a fundamental evidence of no microphase separation in the cured system. It can be seen that there is a constant decrease in  $T_g$  with increasing HTPE-2 content from Figure 9(a).

The appearance of a narrow  $T_g$  ( $\alpha$ -relaxation peak) confirms the good compatibility between HTPE and DGEBA resins. The  $\beta$ -relaxation peak is very prominent in the cured systems, and it shifts toward low temperature with increasing HTPE-2 content. The magnitude and area of the  $\beta$ -relaxation are often quoted to reflect the toughness<sup>27</sup>: the higher the  $\beta$ -relaxation, the greater the toughness.

## CONCLUSIONS

A novel low-viscosity and low-epoxy equivalent weight of the hyperbranched epoxy resins containing nitrogen heterocycle (HTPE) can be successfully synthesized using THEIC, DMPA, and ECH. The HTPE may be used to reinforce and toughen common epoxy resin (DGEBA), and the mechanical performance of HTPE/DGEBA composites increases first and then decreases with the increase of HTPE content and molecular weight. The study of thermal degradation behavior of the composites show that the high-temperature reaction activation energy ( $E_{a2}$ ) of the composites decreases sharply with the increase of the molecular weight and content of HTPE in the composites. The mechanical performance of the composites is explained in terms of an *in situ* reinforcing and toughening mechanism, including the interplay of the rigidity of the hyperbranched polymer chain, intramolecular cavity density of HBP, interface interaction, and the crosslinking density.

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