

## SYNTHESIS OF A HYPERBRANCHED POLYETHER EPOXY THROUGH ONE-STEP PROTON TRANSFER POLYMERIZATION AND ITS APPLICATION AS A TOUGHENER FOR EPOXY RESIN DGEBA<sup>\*</sup>

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**Abstract** A novel liquid hyperbranched polyether epoxy (HBPEE) based on commercially available hydroquinone (HQ) and 1,1,1-trihydroxymethylpropane triglycidyl ether (TMPGE) was synthesized through an A<sub>2</sub> + B<sub>3</sub> one-step proton transfer polymerization. In order to improve the toughness, the synthesized HBPEE was mixed with diglycidyl ether of bisphenol A (DGEBA) in different ratios to form hybrids and cured with triethylenetetramine (TETA). Thermal and mechanical properties of the cured hybrids were evaluated. Results show that addition of HBPEE can improve the toughness of cured hybrids remarkably at < 20 wt% loading, without compromising the tensile strength. However, the glass transition temperature (*T<sub>g</sub>*) of the cured hybrids decreases with increasing HBPEE content. Fracture surface images from scanning electron microscope show oriented fibrils in hybrids containing HBPEE. The formation and orientation of the fibrils can absorb energy under impact and lead to an improvement of toughness. Furthermore, based on the morphology of fractured surfaces and the single *T<sub>g</sub>* in each hybrid, no sign of phase separation was found in the cured hybrid systems. As a result, the toughening mechanism could be explained by in situ homogeneous toughening mechanism rather than phase separation mechanism.

**Keywords:** Hyperbranched; Epoxy; Polyether; Toughening; Proton transfer polymerization.

### INTRODUCTION

Recently, hyperbranched polymers (HBPs) have attracted lots of interests and have been widely used as processing aids, rheology modifiers and tougheners for conventional thermoplastics and thermosets due to their unique structure, good solubility and high peripheral functionality<sup>[1–3]</sup>. Compared with dendrimers, HBPs can be readily synthesized through a one-pot procedure<sup>[4]</sup> or pseudo one-step procedure<sup>[5]</sup>. Therefore, several hyperbranched polymers are now commercially available.

Hyperbranched epoxy (HBE) combines the unique properties of the hyperbranched inner core with the highly reactive and abundant peripheral epoxy groups, which make it a good additive for epoxy resins<sup>[6]</sup>. In the literatures, HBEs are often used as tougheners for various types of epoxy resins and proved to be effective. Most of the synthesized HBEs are based on polyester because of the availability of various monomers to date. For example, a commercially available hyperbranched epoxy with aliphatic polyester backbone (Boltorn E1) has been widely investigated as a toughener for epoxy in the literature<sup>[7]</sup>. Results showed that the addition of Boltorn

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E1 into diglycidyl ether of bisphenol A (DGEBA) can increase toughness significantly<sup>[8]</sup>. In addition, Zhang and coworkers prepared an aromatic liquid hyperbranched polyester epoxy with low viscosity and used it to toughen DGEBA<sup>[9, 10]</sup>. At 9 wt% loading of the synthesized HBE, the impact strength of the cured hybrid increased from 17.4 kJ/m<sup>2</sup> to 58.2 kJ/m<sup>2</sup>, and the tensile strength also enhanced by about 20%<sup>[10]</sup>.

Aside from the HBEs with polyester backbone, HBEs with polyether backbone could be another kind of reactive tougheners. The polyether structure is chemically more stable than polyester, thus is more desirable in places where high chemical stability is demanded. To our knowledge, there are only a handful of studies which used polyether-based HBEs as tougheners for DGEBA. In 1999, Chang and Fréchet reported a new approach to synthesize polyether-based HBE through “proton transfer polymerization” (PTP) of an AB<sub>2</sub> type diepoxyphenol monomer<sup>[11]</sup>. Later, this methodology was extended to A<sub>2</sub> + B<sub>3</sub> system<sup>[12, 13]</sup>. Compared to the conventional way of preparing epoxidized HBPs, PTP provides a facile way to synthesize HBEs in a one-step procedure. In addition, the A<sub>2</sub> and B<sub>3</sub> monomers used for PTP are usually commercially available or can be easily prepared. Therefore, numerous multifunctional monomers could be used in synthesizing HBEs with polyether backbone. However, reports on the polyether-based HBE from A<sub>2</sub> + B<sub>3</sub> approach are still rare.

In order to further explore new HBEs for application as high performance tougheners, in this study, a novel hyperbranched polyether epoxy (HBPEE) based on two commercially available raw materials, hydroquinone (HQ) (A<sub>2</sub> monomer) and 1,1,1-trihydroxymethylpropane triglycidyl ether (TMPGE) (B<sub>3</sub> monomer), was prepared *via* PTP procedure. Then the synthesized HBPEE was mixed with DGEBA in different ratios to form hybrid epoxy systems, which were then cured with a hexafunctional amine. Mechanical and thermal properties of the cured hybrid materials were investigated. It is found that addition of HBPEE can improve the toughness of the cured epoxy resins remarkably without sacrificing tensile strength. Furthermore, addition of HBPEE has little effect on the thermal stability of the cured hybrids. The increase in toughness is explained by an *in situ* homogeneous toughening mechanism.

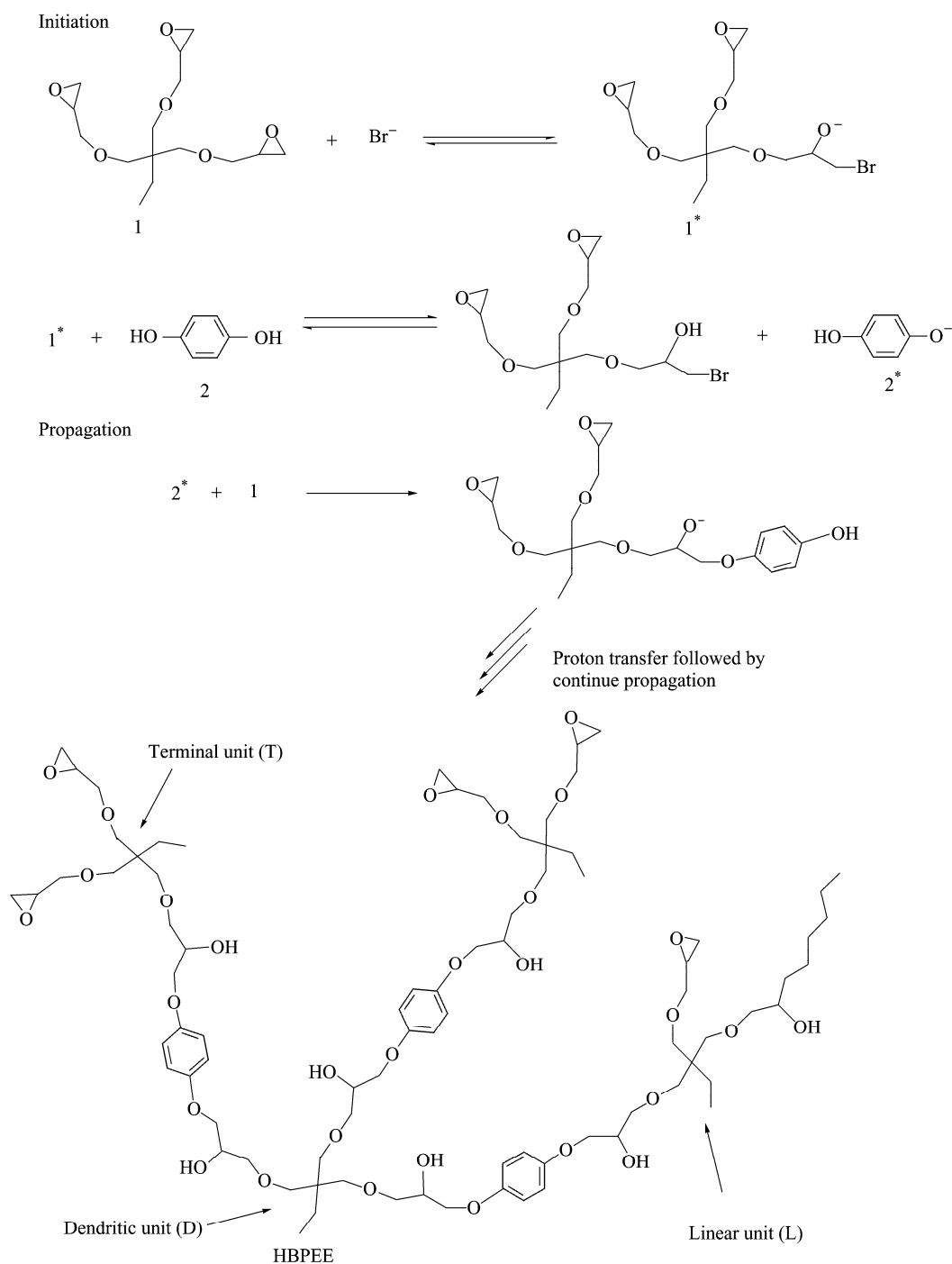
## EXPERIMENTAL

### Materials

Hydroquinone (HQ) (98%) was supplied by Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). 1,1,1-Trihydroxymethylpropane triglycidyl ether (TMPGE) (99%) was purchased from Titanchem Co. Ltd. (Shanghai, China). The catalyst tetrabutyl ammonium bromide (TBAB) (99%) was obtained from Beijing Chemical Works (Beijing, China). Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight (EEW) of 188.7 g/eq was purchased from Yueyang Resin Factory (Yueyang, China). The curing agent triethylenetetramine (TETA) (99%) was supplied by Guangfu Research Institute (Tianjin, China). All other solvents and reagents were obtained from Beijing Chemical Works (Beijing, China) and used without further purification.

### Characterizations

NMR spectrum of the synthesized compound was recorded on a Bruker Fourier Transform AVANCE 600 spectrometer. The molecular weight of the polymer was determined using a Waters gel permeation chromatography (GPC) 515-2410 system with tetrahydrofuran as an eluent at 30°C. Fourier transform infrared spectrum (FT-IR) of HBPEE was analyzed using a Thermo Nicolet Impact 210 spectrometer in the form of KBr pellets at room temperature. Epoxy equivalent weight (EEW) of HBPEE was determined by HCl-acetone titration with a Metrohm (848 Titrino plus) titrator. Thermal transition was detected by a METTLER DSC 1 instrument under nitrogen at a heating rate of 10 K/min and a gas flow 20 mL/min. Thermal stability was measured with a Perkin Elmer TGA 4000 thermogravimetric analyzer at a heating rate of 10 K/min under nitrogen from 50°C to 800°C. Tensile strength of the cured material was characterized by a SANS electronic universal testing machine according to GB/T 2568-2006. Non-notch impact strength of the cured sample was determined by a Ceast Resil impactor according to GB/T 2571-1995. Fracture surface of the cured sample after impact test was sputter coated with gold and characterized using a TESCAN VEGA 3 SBH scanning electron microscope (SEM).



Scheme 1 Synthesis route of HBPEE

**Synthesis of Hyperbranched Polyether Epoxy (HBPEE)**

The synthesis of HBPEE followed a PTP procedure developed by Fréchet and coworkers<sup>[13]</sup>. The synthesis route of HBPEE is presented schematically in Scheme 1. HQ (22 g), TMPGE (181.2 g) and TBAB (9.66 g) were added to a three-necked flask equipped with thermometer and mechanical stirring under N<sub>2</sub> protection. The mixture was heated to 80°C and allowed to react for 6 h. After cooling to room temperature, 100 mL

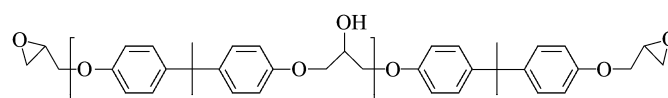
tetrahydrofuran (THF) was added into the flask under stirring until a homogeneous solution was obtained. And the solution was poured into hot water (*ca.* 60°C) under stirring to remove the catalyst TBAB. Then the organic phase was separated and dissolved in 80 mL THF. After the solution was dried by MgSO<sub>4</sub> and filtered, the filtrate was stirred into ether. At last, the organic phase at the bottom was separated and the residual solvents were removed by rotatory evaporating under vacuum to afford a light yellow transparent liquid. Yield: 133 g, 66%.

### Preparation of HBPEE/DGEBA Hybrids and Curing

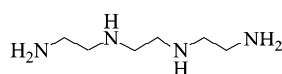
Different proportions (0, 5%, 10%, 15%, and 20 wt%) of HBPEE (entry 7 in Table 1) and 5 mL acetone were dissolved in DGEBA at room temperature through continuously stirring with a glass stick. A stoichiometric amount of TETA was then added into the mixture under continuously stirring to form a homogeneous solution. After degassing, the mixture was poured into silicone rubber molds for curing. The curing schedule was a three-step protocol: cured at room temperature for 24 h, 100°C for 3 h, and a post cure at 200°C for 2 h. After curing, the cured samples were allowed to cool naturally to room temperature. The chemical structures of DGEBA and TETA used in this study are shown in Scheme 2.

**Table 1.** Reaction conditions and results of the polymerization

| Entry | Concentration (mol/L) | A <sub>2</sub> /B <sub>3</sub> (mol ratio) | Temperature (°C) | Time (h) | M <sub>w</sub> | M <sub>n</sub> | PDI  | Yield (%) |
|-------|-----------------------|--------------------------------------------|------------------|----------|----------------|----------------|------|-----------|
| 1     | 1                     | 1/1                                        | 60               | 24       | 831            | 656            | 1.27 | 46        |
| 2     | 1                     | 1/2                                        | 60               | 24       | 827            | 581            | 1.42 | 47        |
| 3     | 1                     | 1/3                                        | 60               | 24       | 838            | 643            | 1.30 | 45        |
| 4     | 0.5                   | 1/2                                        | 60               | 24       | 630            | 502            | 1.25 | 40        |
| 5     | 2                     | 1/2                                        | 60               | 24       | 1384           | 782            | 1.77 | 68        |
| 6     | 3                     | 1/2                                        | 60               | 24       | 1859           | 1076           | 1.73 | 69        |
| 7     | Bulk                  | 1/3                                        | 80               | 6        | 2390           | 1587           | 1.51 | 66        |
| 8     | Bulk                  | 1/3                                        | 80               | 10       | 2548           | 1632           | 1.56 | 70        |
| 9     | Bulk                  | 1/3                                        | 80               | 24       | 4207           | 2771           | 1.52 | 70        |
| 10    | Bulk                  | 1/3                                        | 100              | 24       | 4695           | 3070           | 1.53 | 72        |
| 11    | Bulk                  | 1/2                                        | 80               | 24       | 9764           | 4459           | 2.19 | 75        |
| 12    | Bulk                  | 1/1                                        | 80               | Gelation | —              | —              | —    | —         |



Diglycidyl ether of bisphenol A (DGEBA)



Triethylenetetramine (TETA)

**Scheme 2** Chemical structure of the used materials

## RESULTS AND DISCUSSION

### Synthesis of HBPEE

The mechanism of PTP has been fully investigated by Fréchet and coworkers<sup>[11–13]</sup>. In this study, 5 wt% of Bu<sub>4</sub>NBr (based on TMPGE) is added as the catalyst, because it is more effective than base in controlling the polymerization and avoiding gelation<sup>[13, 14]</sup>. In order to ensure an epoxy ended product, an excess of tri-epoxy monomer was employed in the reaction mixture. The polymerizations of HQ (A<sub>2</sub>) and TMPGE (B<sub>3</sub>) are studied in THF which is superior to other polar or protic solvents<sup>[11]</sup>. In addition, bulk polymerization of the two monomers is also investigated. The different reaction conditions and the results are shown in Table 1.

Based on Flory's theory, during the reaction of  $A_2 + B_3$  polymerizations, gelation can occur before full conversion is reached<sup>[15]</sup>. The gelation point corresponds to the incipient period of forming a three-dimensional crosslinked network which is insoluble and loses its processability. To avoid gelation in the  $A_2 + B_3$  polymerizations, it is usually carried out in a dilute solution to lower the propagation rate. Furthermore, once the product has reached a desired molecular weight, the reaction can be quenched before gelation. As shown in Table 1, no gelation occurred after a 24 h polymerization both in THF and bulk except entry 12. It is found that the polymerization rate is largely dependent upon the monomer concentration and reaction temperature. The polymerizations carried out in THF (entry 1–6) are too slow to be practical due to the lower monomer concentration comparing with bulk polymerization. In the bulk polymerization, excess of  $B_3$  is employed to ensure an epoxy-terminated product. In addition, the excess amount of liquid tri-epoxy, acting as a solvent, can lower the concentration of  $A_2$  monomer to avoid gelation. As a result, no gelation occurred for entry 6–11. However, a higher  $A_2/B_3$  ratio can lead to a very rapid gelation as in entry 12. Therefore, the bulk polymerization carried out at higher temperature serves a better route for synthesizing HBPEE compared with that carried out in THF.

### Characterization of HBPEE

The ideal molecular structure of synthesized HBPEE is shown in Scheme 1. The EEW of HBPEE corresponding to entry 7 in Table 1 is determined to be 322.6 g/eq by titration. FTIR spectrum of HBPEE (entry 7 in Table 1) is shown in Fig. 1. The broad and strong absorption peak at about  $3441\text{ cm}^{-1}$  corresponds to the  $-\text{OH}$  stretching vibration. Peaks at  $2961\text{--}2878\text{ cm}^{-1}$  belong to the aliphatic  $-\text{C}-\text{H}$  stretching vibration. The aromatic rings stretching vibration can be observed at  $1591$  and  $1508\text{ cm}^{-1}$ . Peaks at about  $1232$  and  $1101\text{ cm}^{-1}$  can be assigned to  $\text{Ph}-\text{O}-\text{C}$  and  $\text{C}-\text{O}-\text{C}$  stretching vibration, respectively. The characteristic absorption of epoxy groups can be observed at about  $908$  and  $753\text{ cm}^{-1}$ . The peak at  $827\text{ cm}^{-1}$  corresponds to  $\text{Ph}-\text{H}$  bending vibration, indicating the phenylene structure with two  $p$ -substitution groups. Furthermore, the structure of HBPEE (entry 7 in Table 1) is characterized accurately by  $^1\text{H}$ -NMR spectrum as shown in Fig. 2.

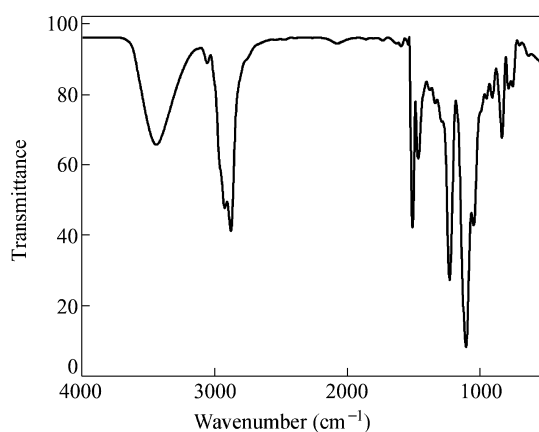


Fig. 1 FTIR spectrum of HBPEE (entry 7 in Table 1)

### Degree of Branching

Degree of branching (DB) is used to characterize the hyperbranched structure, and several ways of quantifying DB have been developed<sup>[16, 17]</sup>. Among them, the most commonly used way is proposed by Fréchet<sup>[1]</sup>:

$$\text{DB} = (N_D + N_T)/(N_D + N_T + N_L) \quad (1)$$

where  $N_D$ ,  $N_L$ , and  $N_T$  represent the fractions of dendritic (D), linear (L), and terminal (T) units in hyperbranched molecules, respectively.

Quantitative  $^{13}\text{C}$ -NMR spectrum of HBPEE (entry 7 in Table 1) can reveal the fine structures of different repeating units. As shown in Fig. 3, signal of the methylene carbons connecting to methyl groups splits into three

peaks due to their different chemical circumstances. Based on the integration results of these three peaks, DB of HBPEE is calculated to be 0.47.

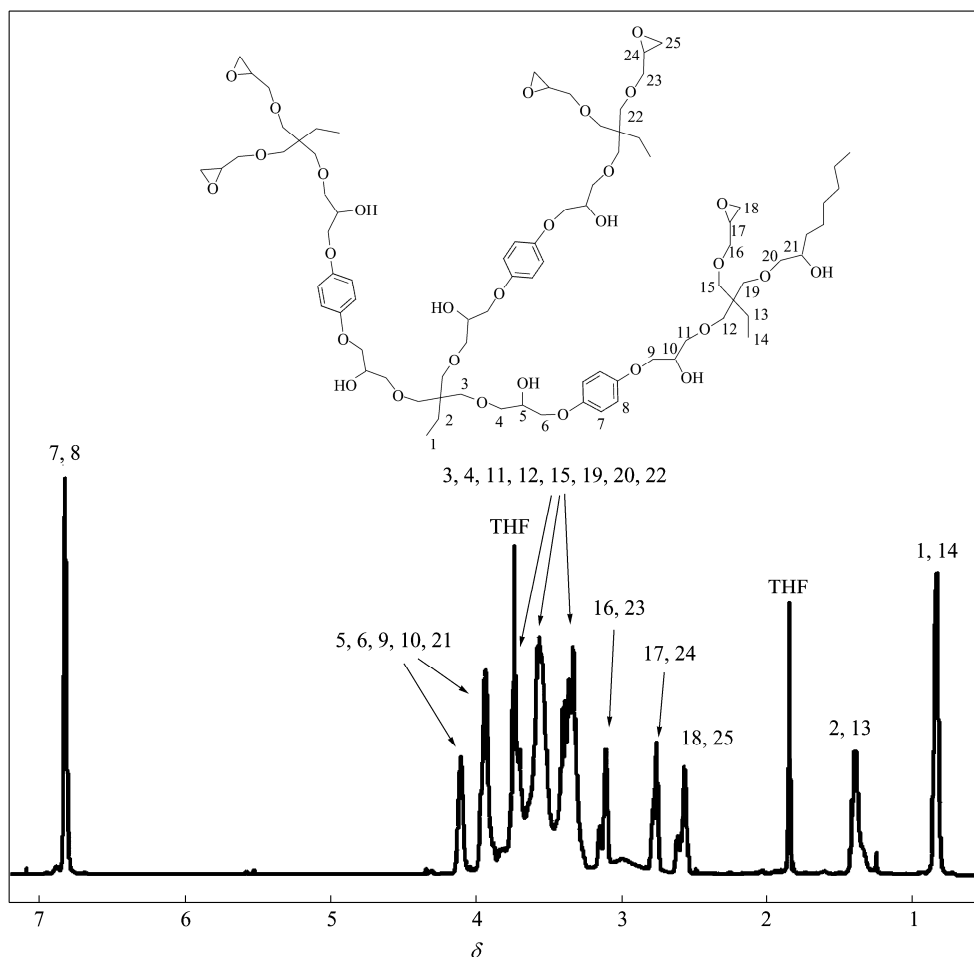


Fig. 2  $^1\text{H}$ -NMR spectrum of HBPEE (in  $\text{CDCl}_3$ )

### Mechanical Properties of the Cured Hybrids

Although cured epoxy materials have lots of desirable properties, they are usually brittle. Thus, a second component, the toughener, is usually added to improve the toughness. However, incorporation of common tougheners, such as liquid carboxyl-terminated butadiene acrylonitrile (CTBN) elastomers<sup>[18]</sup>, thermoplastics<sup>[19]</sup> and core/shell particles<sup>[20]</sup>, often compromises other mechanical properties, especially the tensile strength. As a result, toughening epoxy without compromising other mechanical properties is still a challenge. In the next paragraph, we are going to show how the synthesized aromatic polyether structure of HBPEE can be used to improve the toughness without lowering tensile strength of the cured hybrids. Tensile strength and impact strength of cured hybrids are shown in Fig. 4.

Tensile strength of thermosets is related to the rigidity of chain segments and the crosslinking density of cured networks. Generally speaking, incorporation of linear flexible additives leads to a decrease in tensile properties<sup>[21, 22]</sup>. A series of flexible aliphatic hyperbranched polyesters (e.g. Boltorn H30 and Boltorn E1) have been used to toughen epoxy resins, however the tensile strength is seldom discussed<sup>[23–25]</sup>. Zhang and coworker find that incorporation of hyperbranched polyesters with rigid aromatic rings into DGEBA increases the tensile strength of cured resins to a certain extent<sup>[10]</sup>. Yang and coworkers studied the effects of the length of oxyethylene units in linear epoxy resin and showed that strength and modulus can be maintained if enough

crosslinking sites and rigid aromatic rings exist in the curing system<sup>[26]</sup>. In this study, aromatic rings from A<sub>2</sub> monomer provide rigidity for HBPEE. In addition, the abundant peripheral reactive epoxy groups, which act as potential crosslinking sites, in HBPEE can react with the curing agent. As a result, addition of HBPEE ( $\leq 20$  wt%) does not compromise the tensile strength of cured hybrids if properly cured.

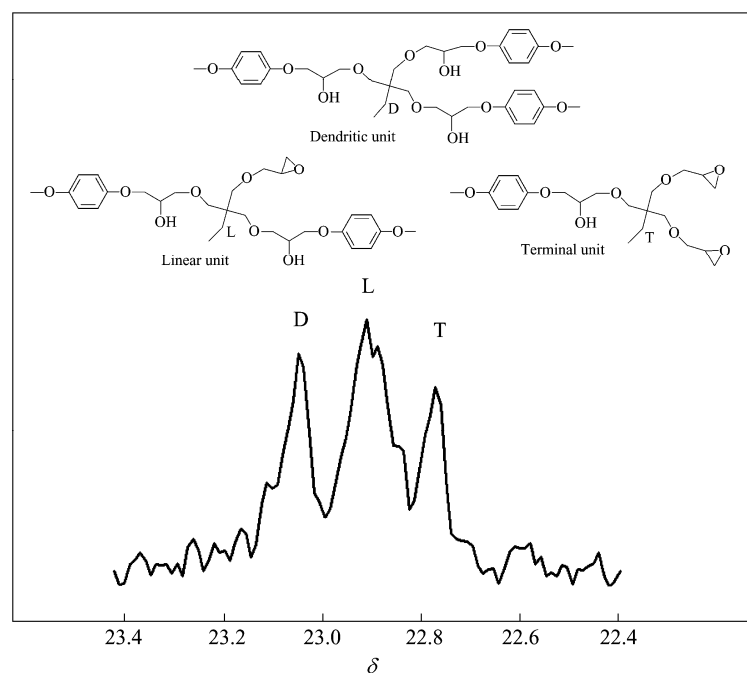


**Fig. 3** The split signal of methylene carbons of quantitative  $^{13}\text{C}$ -NMR spectrum of HBPEE (in  $\text{CDCl}_3$ )

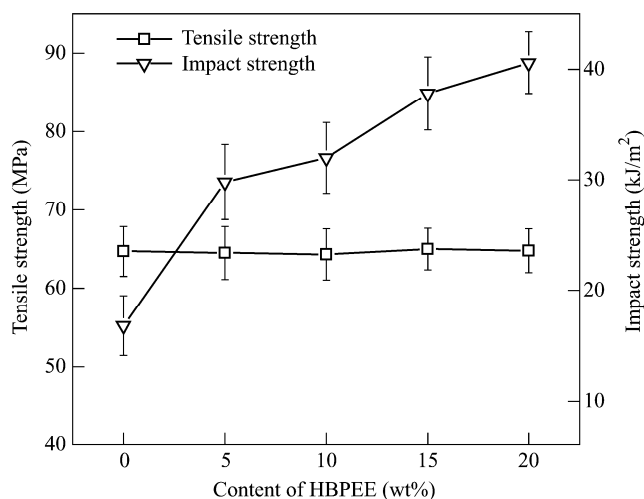


**Fig. 4** Effect of HBPEE content on tensile and impact strength of cured DGEBA/HBPEE hybrids

With the increase in HBPEE content, impact strength of the cured resins increases steadily from 16.8 kJ/m<sup>2</sup> of neat DGEBA to 40.6 kJ/m<sup>2</sup> at 20% loading, indicating that addition of HBPEE can greatly enhance the toughness of DGEBA. On one hand, improvement of toughness can be attributed to the flexible aliphatic units in HBPEE. Yang and coworkers incorporated flexible oxyethylene units into DGEBA to prepare a linear additive

and showed that the impact strength of cured resins is directly proportional to the oxyethylene content<sup>[26]</sup>. As a result, abundant flexible aliphatic units in HBPEE can contribute to the toughness of cured hybrids. On the other hand, similar to the reports which used hyperbranched polyester as toughening agents for epoxy resins<sup>[25, 27]</sup>, the highly branched structure of HBPEE imparts some nanometer sized intra-free volume into cured hybrids<sup>[27, 28]</sup>. Moreover, the additional free volume (or “intermolecular defects”) from crosslinking of the semi-globular hyperbranched epoxy molecules are also created<sup>[29]</sup>. The intra-free volume and “intermolecular defects”, can deform and absorb energy under impact and increase the impact strength<sup>[10]</sup>. Therefore, it can be concluded that hyperbranched polymers with relative rigid aromatic polyether backbones can also toughen epoxy resins. Furthermore, compared with most hyperbranched tougheners which have polyester backbones, HBPEE has better chemical stability due to its relatively inert nature of ether bonds<sup>[13]</sup>.

### Thermal Properties of the Cured Hybrids

The DSC traces of the cured hybrids obtained on 2<sup>nd</sup> heating at a heating rate of 10 K/min are depicted in Fig. 5. The glass transition temperatures ( $T_g$ ) are taken to be the point where the heat capacity change is 50% in the step. In all curves, only one  $T_g$  is found for each cured hybrid, suggesting that HBPEE and DGEBA have good compatibility and do not phase separate after cure due to their similar structures.  $T_g$  of the cured resins decreases continuously as HBPEE content increases.  $T_g$  of the cured epoxy materials is largely determined by structural rigidity and crosslinking density. Thus the lower  $T_g$  of the hybrids could be explained by the following considerations. Compared with DGEBA, HBPEE has more flexible aliphatic chain units, which reduces the rigidity of the chain and leads to a reduction in  $T_g$ . In addition, the pseudo-globular structure of the hyperbranched molecules results in two effects on the cured systems: on one hand, it imposes huge steric hindrance when cured with amine<sup>[30]</sup>; on the other hand, it creates more intramolecular defects (or free volume) in the cured system. Thus, a lower  $T_g$  is obtained.

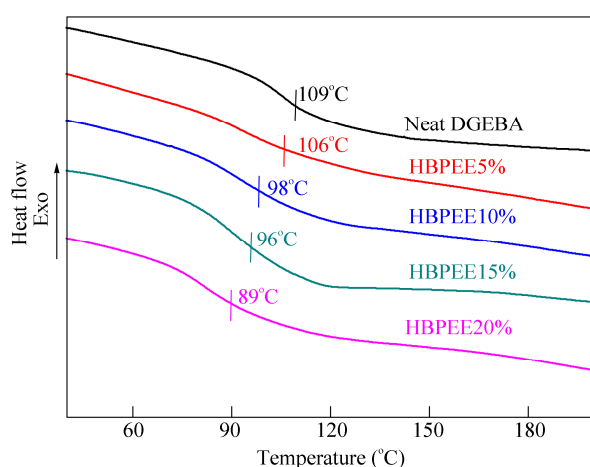


**Fig. 5** DSC curves of the cured DGEBA/HBPEE hybrids

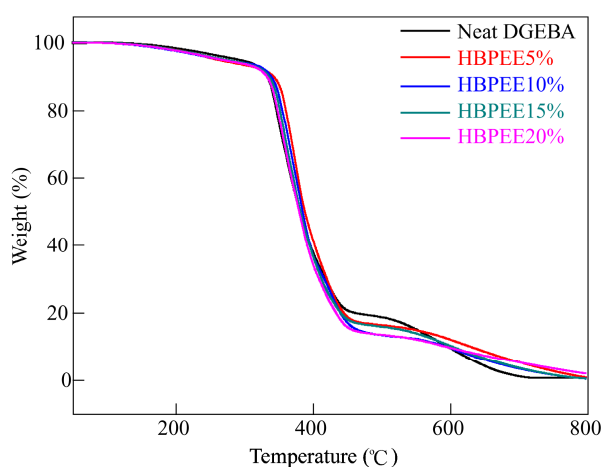


**Fig. 6** TGA curves of the cured DGEBA/HBPEE hybrids

Thermal stability of the cured hybrids is characterized by the temperature corresponding to 5% weight loss ( $T_{d,5\%}$ ). TGA curves of the cured hybrids with different amounts of HBPEE are shown in Fig. 6. It can be seen that addition of HBPEE has little effect on  $T_{d,5\%}$  of the cured hybrids thanks to its polyether backbone.

### Toughening Mechanism

Scanning electron micrographs of the fracture surfaces of the cured neat DGEBA and DGEBA/HBPEE hybrids under impact are shown in Fig. 7. The fracture surface of the cured neat DGEBA is relatively smooth, which is typical for unmodified brittle epoxy. In contrast, fracture surfaces of the cured hybrids with HBPEE inside show a rougher morphology. A lot of oriented “protonema” or “fibrils” are clearly evident, which indicates that the

hybrids undergo more deformation than the neat system. The orientation of fibrils could absorb energy to improve the toughness. What is more, as more HBPEE is added, both the size and density of “protonema” or “fibrils” increase. It has been reported that the unique hyperbranched molecular structure of HBPEE could lead to lots of nanometer sized cavities and defects after curing<sup>[27]</sup>. Under impact, these cavities and defects distort to absorb much energy and form “protonema” or “fibrils” which are also observed by other researchers<sup>[10, 27]</sup>. In addition, no sign of phase separation is evident, indicating adequate compatibility of the HBPEE and DGEBA due to the aromatic polyether structure of HBPEE. Thus, the toughening effect should not be explained by the phase separation mechanism<sup>[31]</sup>. This phenomenon is in good agreement with *in situ* homogeneous toughening mechanism<sup>[32, 33]</sup>.

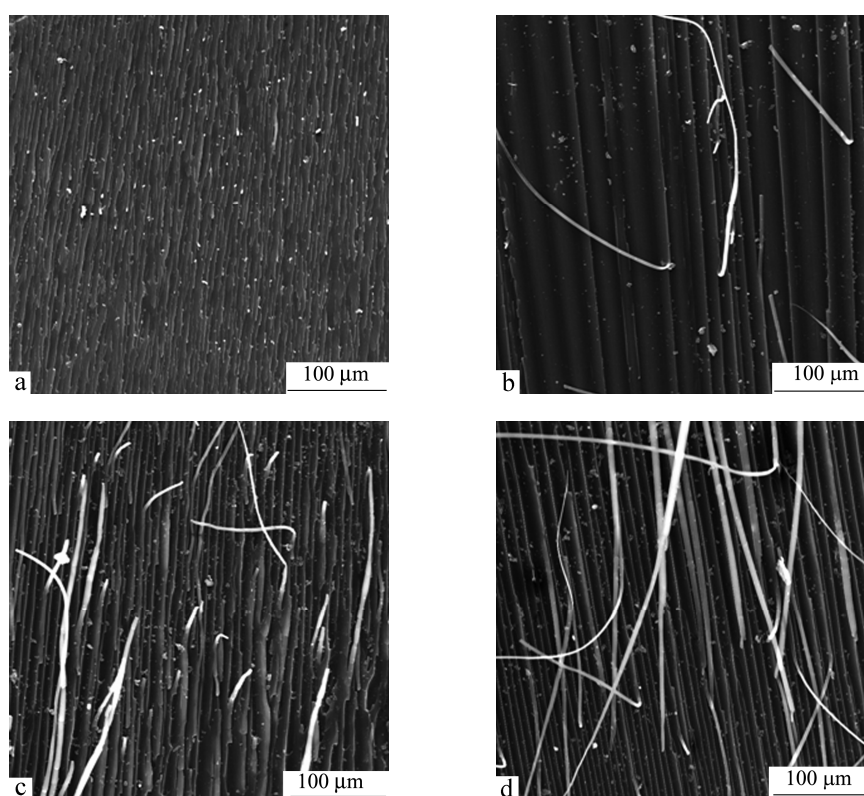


**Fig. 7** SEM of the fracture surface of the cured DGEBA/HBPEE hybrids after impact tests: (a) neat DGEBA, (b) HBPEE5%, (c) HBPEE10% and (d) HBPEE15%

## CONCLUSIONS

A liquid hyperbranched aromatic polyether epoxy (HBPEE) was synthesized through a one-step  $A_2 + B_3$  proton transfer polymerization. The synthesized HBPEE is proven to be an effective toughener for DGEBA in spite of its relatively rigid aromatic polyether structure. Impact strength of cured HBPEE/DGEBA hybrids increases without compromising tensile strength. At 20 wt% loading of HBPEE, the impact strength of cured resins increases from 16.8 kJ/m<sup>2</sup> of cured neat system to 40.6 kJ/m<sup>2</sup>. Toughening mechanism is explained by deformation of nano-sized free volume and formation of oriented fibrils. Although addition of HBPEE leads to a decrease in  $T_g$  of cured hybrids, it has minimal effects on the thermal stability.

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