

## Novel Epoxidized Hyperbranched Poly(phenylene oxide): Synthesis and Application as a Modifier for Diglycidyl Ether of Bisphenol A

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**ABSTRACT:** A novel epoxidized hyperbranched poly(phenylene oxide) (EHPPPO) is designed and synthesized successfully. The structure of EHPPPO is characterized by Fourier transform infrared spectra- and quantitative <sup>13</sup>C nuclear magnetic resonance spectrum. The synthesized EHPPPO is added into diglycidyl ether of bisphenol A as a modifier in different ratios to form hybrids and cured by an anhydride curing agent. Effects of EHPPPO addition on the properties of the cured hybrids are investigated. Thermal mechanical analysis results suggest that addition of EHPPPO can increase the free volume of the cured hybrid materials. Dynamic mechanical analysis characterizations show that the crosslinking density increases with the increase in EHPPPO content. Furthermore, addition of EHPPPO results in an improvement in thermal and mechanical properties. The toughening mechanism is also discussed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** dendrimers; hyperbranched polymers and macrocycles; properties and characterization; thermosets; mechanical properties; thermal properties

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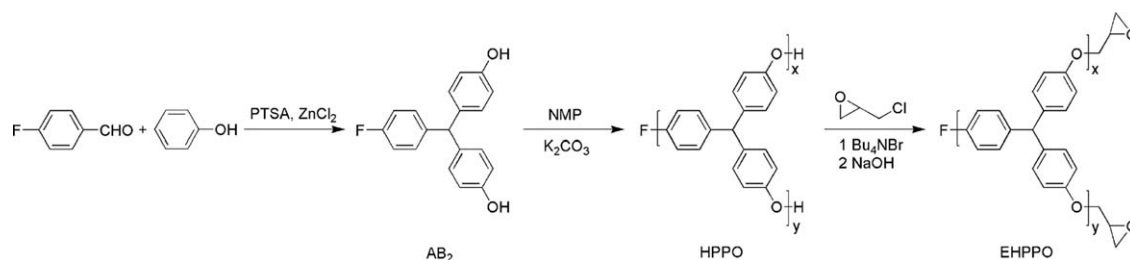
### INTRODUCTION

Epoxy resins have many attractive properties and have been widely used as matrix resins for coatings, adhesives, composites, electrical, and electronic materials.<sup>1–3</sup> However, those applications are often limited by their brittleness.<sup>1</sup> In order to improve the toughness of epoxy materials, various modifiers have been developed in the past, including liquid carboxyl-terminated butadiene acrylonitrile elastomers, thermoplastics, core/shell particles, interpenetrating polymer networks, and hyperbranched polymers (HBPs).<sup>4–10</sup> Unfortunately, introduction of a second component often causes phase separation and lower the thermal and certain mechanical properties, especially the tensile strength.

Recently, HBPs have attracted more attentions due to their unique structure, high peripheral functionality, and good solubility.<sup>11–14</sup> Compared with dendrimers, HBPs can be synthesized more readily through a one-pot procedure or pseudo-one step procedure.<sup>15,16</sup> Therefore, several hyperbranched polymers are now commercially available and have been used as processing aids, rheology modifiers, and tougheners for conventional thermoplastics and thermosets.<sup>9,17</sup> Since 1990s, two commercialized

hyperbranched polyesters based on dimethylolpropionic acid known as Boltorn H30 and Boltorn E1 have been extensively studied as tougheners for epoxy resins.<sup>14,18,19</sup> The incorporation of those hyperbranched polymers, which have aliphatic polyester backbones, into diglycidyl ether of bisphenol A (DGEBA) results in a significant increase in toughness.<sup>14</sup> And all blends showed a phase separation with particulate morphology.<sup>19</sup> Unfortunately, other mechanical properties and glass transition temperature ( $T_g$ ) are compromised to some extent.<sup>20</sup> However, it is worth noting that some aromatic hyperbranched epoxies are able to improve the toughness and strength simultaneously. For example, Zhang and Jia synthesized a hyperbranched poly(trimellitic anhydride-diethylene glycol) ester epoxy resin (HTDE) and used it to toughen DGEBA.<sup>21,22</sup> They found that the impact strength of the cured hybrid epoxy increased from 17.4 kJ·m<sup>-2</sup> to 58.2 kJ·m<sup>-2</sup>, and the tensile strength also increased by about 20% at 9 wt % loading.<sup>22</sup> However, the addition of HTDE decreased  $T_g$  of the cured epoxy because of the flexible polyester backbone and reduction of crosslinking density.

For improving the thermal properties of epoxy, the application of polymers with high temperature resistant backbones could be effective. Jin and Park<sup>23</sup> prepared an amine-terminated hyperbranched



**Scheme 1.** Synthesis route of EHPPO.

polyimide (HBPI) and investigated the thermal properties of DGEBA/HBPI hybrids. They found that the thermal stability of the DGEBA/HBPI hybrids was not affected by the addition of HBPI appreciably. Besides, the glass transition temperature ( $T_g$ ) of the cured DGEBA/HBPI hybrids increased as the HBPI content increased. Poly(phenylene oxide) is also a heat-resisting polymer (high glass transition temperature and high thermal stability) and has excellent mechanical properties. Linear poly(phenylene oxide)s (LPPOs) have been proved to be effective to improve thermal properties when blended with various types of epoxy resins in many open literatures.<sup>24–27</sup>

Based on the former techniques that using hyperbranched polymers as a toughener and using LPPO as a modifier for improving thermal properties, a novel epoxidized hyperbranched poly(phenylene oxide) (EHPPO) was designed and synthesized in order to improve toughness without compromising the thermal property and tensile strength. In addition, compared with the abundant literature involving aliphatic hyperbranched epoxy modifiers, the use of stiff hyperbranched polymers to toughen epoxies has rarely been reported.<sup>18,23</sup> In this study, we first design and synthesis an  $AB_2$  type monomer 4-fluoro-4',4''-dihydroxy triphenyl methane. Through the homopolymerization of the monomer, hyperbranched poly(phenylene oxide) (HPPO) with terminal phenolic groups is obtained. Subsequently, the terminal groups are readily epoxidized by epichlorohydrin (ECH) to afford EHPPO. Then DGEBA/EHPPO hybrids with varying ratios are prepared and cured. Effects of EHPPO on thermal and mechanical properties are investigated.

## EXPERIMENTAL

### Materials

Phenol (99%), ECH (99%), and tetrabutyl ammonium bromide (TBAB) (99%) were purchased from Tianjin Fuchen Reagent Company (Tianjin, China). *p*-fluorobenzaldehyde (98%) was obtained from Zhong Sheng Hua Teng Reagent Company (Beijing, China). *p*-toluenesulfonic acid (PTSA) (99%) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). *N,N*-dimethylbenzylamine (NDMA) (99%) was purchased from J&K Scientific Ltd. (Beijing, China). Methyl nadic anhydride (MNA) (99.8%) was supplied by POLYNT Chemical (Italy). DGEBA (EEW = 188.68 g·eq<sup>-1</sup>) was purchased from Yueyang Resin Factory (Yueyang, China). All other solvents and reagents were obtained from Beijing Chemical Works (Beijing, China) and used without further purification.

### Characterizations

Nuclear magnetic resonance (NMR) spectra of the synthesized compounds were recorded on Bruker Fourier transform NMR

spectrometer AVANCE 600 (Switzerland). The molecular weight of the polymer was determined with a Waters gel permeation chromatography (GPC) 515-2410 system using tetrahydrofuran as an eluent at 30°C. Fourier transform infrared spectra (FTIR) of HPPO and EHPPO were analyzed using Thermo Nicolet Impact 210 spectrometer with KBr pellets at room temperature. Epoxy equivalent weight (EEW) of EHPPO was determined by HCl-acetone titration with Metrohm 848 Titrino plus titrator (Switzerland). Differential scanning calorimetry (DSC) was performed using a METTLER DSC 1 (Switzerland) under nitrogen (20 mL·min<sup>-1</sup>) at a heating rate of 10°C·min<sup>-1</sup>. Thermogravimetric analysis (TGA) was carried out with a Perkin Elmer TGA 4000 under nitrogen at a heating rate of 10°C·min<sup>-1</sup>. Coefficients of linear thermal expansion of cured hybrids were measured using a METTLER-TOLEDO thermal mechanical analysis (TMA)/SDTA841e instrument (Switzerland) in the range of 220°C to 40°C at a cooling rate of 2°C·min<sup>-1</sup>. Dynamic mechanical measurements of samples (60 mm × 12.8 mm × 3.2 mm) were performed using a TA Q800 dynamic mechanical analyzer (DMA) from 40°C to 200°C under the dual cantilever mode at a frequency of 1 Hz and a heating rate of 3°C·min<sup>-1</sup>. Tensile strengths of the cured products were characterized using a SANS universal testing machine (China) at room temperature according to National standard of the People's Republic of China GB/T 2568-1995.<sup>28</sup> The dumbbell sample size was 200 mm × 10 mm × 4 mm, and the tensile rate was 2 mm·min<sup>-1</sup>. Unnotched impact strengths were determined by a Ceast Resil impactor (Italy) at room temperature according to National standard of the People's Republic of China GB/T 2571-1995, and the sample size was 80 mm × 10 mm × 4 mm.<sup>29</sup> For each composition, at least 10 specimens were tested. The most reproducible five results were averaged and reported. Fracture surfaces of the samples after impact tests were sputter coated with gold and were characterized using a TESCAN VEGA 3 SBH scanning electron microscope (SEM) (Czech).

### Synthesis and Curing

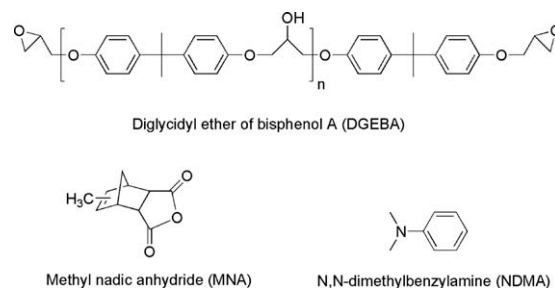
**4-Fluoro-4',4''-Dihydroxy Triphenyl Methane ( $AB_2$ ).** The synthesis route of  $AB_2$  monomer, HPPO, and EHPPO is shown in scheme 1. A three-necked flask charged with phenol (5 mol, 470 g),  $ZnCl_2$  (0.1 mol, 13.6 g), and PTSA (0.1 mol, 19 g) was heated to 45°C under mechanical stirring. Then, *p*-fluorobenzaldehyde (1 mol, 124 g) was added dropwise to avoid high reacting temperature. The reaction mixture was kept at 45°C for 24 h, and then poured into 2 L hot water (~70°C). Organic phase was separated and 1 L toluene was added. After the mixture was cooled by ice water, the precipitate was isolated by

filtration, washed with toluene thoroughly, and recrystallized from toluene. At last, the obtained compound was dried in a vacuum oven at 80°C thoroughly to give orange AB<sub>2</sub> monomer. Yield: 198 g, 67%. <sup>1</sup>H NMR (600 MHz, acetone-d<sub>6</sub>, δ): 5.44 (s, 1H; CH), 6.77 (d, 4H; C<sub>6</sub>H<sub>4</sub>O), 6.93 (d, 4H; C<sub>6</sub>H<sub>4</sub>O), 7.05 (t, 2H; C<sub>6</sub>H<sub>4</sub>F), 7.14 (q, 2H; C<sub>6</sub>H<sub>4</sub>F), 8.21 (s, 2H; OH).

**Hyperbranched Poly(phenylene oxide) (HPPO).** A mixture of AB<sub>2</sub> (29.5 g, 0.1 mol), anhydrous K<sub>2</sub>CO<sub>3</sub> (33.12 g, 0.24 mol), *N*-methylpyrrolidinone (500 mL), and toluene (100 mL) was heated in a four-necked flask under stirring and nitrogen atmosphere. The water in the reaction mixture was removed by azeotropic distillation of toluene. Then the reaction mixture was heated to 190°C and maintained for 24 h. After that time the reaction mixture was allowed to cool to room temperature naturally and acidified with hydrochloric acid. Then the reaction mixture was filtered and the filtrate was precipitated into large amount of water. The precipitate was isolated and dried at 80°C *in vacuo*. Then the crude product was dissolved in THF, and the solution was filtered to remove any insoluble materials. Next, the filtrate was added dropwise into petroleum ether with vigorous stirring over several hours. The precipitate was collected, washed with petroleum ether, and dried thoroughly under vacuum at 60°C to give brick red HPPO. Yield: 23 g, 85%. <sup>13</sup>C NMR (600 MHz, DMSO-d<sub>6</sub>, δ): 53.96 (CH), 115.50 (C<sub>6</sub>H<sub>4</sub>OH), 118.76 (C<sub>6</sub>H<sub>4</sub>O), 130.24 (C<sub>6</sub>H<sub>4</sub>O), 130.78 (C<sub>6</sub>H<sub>4</sub>O), 131.06 (C<sub>6</sub>H<sub>4</sub>F), 134.98 (C<sub>6</sub>H<sub>4</sub>O), 141.13 (C<sub>6</sub>H<sub>4</sub>O), 156.01 (C<sub>6</sub>H<sub>4</sub>O), 160.27 (C<sub>6</sub>H<sub>4</sub>F), 161.87 (C<sub>6</sub>H<sub>4</sub>F).

**Epoxidized Hyperbranched Poly(phenylene oxide) (EHPPPO).** To a four-necked flask, HPPO (30 g), ECH (333 g, 3.6 mol), and TBAB (3.864 g, 0.012 mol) were charged. The mixture was heated to 80°C and stirred for 3 h under N<sub>2</sub> atmosphere. Then NaOH aqueous solution (6 g NaOH in 9 ml water) was added dropwise during 3 h and the mixture was allowed to react for another 1 h. After cooled down to room temperature, the reaction mixture was filtered. The filtrate was precipitated into ethanol and the precipitate was dried under vacuum at 70°C. The crude product was dissolved in THF, and the solution was filtered to remove any unwanted insoluble materials. Next, the solution was precipitated into ethanol. After filtration and washed with ethanol, the precipitate was dried *in vacuo* at 70°C to give light yellow EHPPPO. Yield: 24 g, 65%. <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>, δ): 44.71, 50.15, 54.14, 68.78, 111.78, 114.48, 115.02, 118.61, 130.45, 136.54, 138.78, 140.01, 154.44, 155.64, 157.02, 160.67, 162.20.

**Preparation of DGEBA/EHPPPO Hybrids and Curing.** Different proportions (0, 5%, 10%, 15%, and 20 wt %) of EHPPPO and stoichiometric amount of MNA were dissolved in DGEBA at 70°C under magnetic stirring to form a homogeneous solution. A 0.5 wt % NDMA was then added to the solution. After degassing, the mixtures were poured into a preheated silicone rubber mold and cured in oven using a three-step curing schedule, namely 100°C/2 h, 150°C/3 h, and 180°C/2 h. Samples were allowed to cool naturally to room temperature. Chemical structures of DGEBA, MNA, and NDMA are shown in scheme 2.



Scheme 2. Chemical structures of the materials used in this study.

## RESULTS AND DISCUSSION

### Synthesis of Monomer

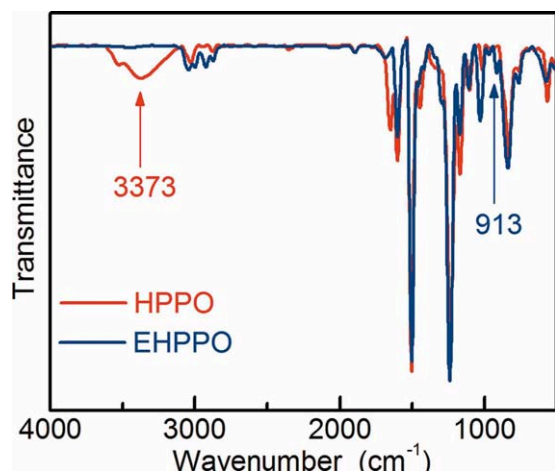
In our previous work, we reported the synthesis and characterization of an AB<sub>2</sub> type monomer, 4-bromo-4',4''-dihydroxytriphenylmethane, which was prepared in a acetic acid/sulfuric acid mixture; however, the yield is a low (45%).<sup>30</sup> In the old strategy, large amount of liquid acid was used as both the catalyst and the solvent. In this study, a Lewis acid ZnCl<sub>2</sub>/PTSA is chosen as harmless catalyst<sup>31</sup> and excess low-cost phenol is used as solvent which also ensure thorough reaction of *p*-fluorobenzaldehyde. In addition, this new strategy results in a much higher yield (67%).

### Polymerization of Monomer

In our previous work, HPPO was prepared from 4-bromo-4',4''-dihydroxytriphenylmethane using a modified Ullmann reaction with the catalysis of CuCl.<sup>30</sup> Ullmann reaction is a variation on nucleophilic aromatic substitution (S<sub>N</sub>Ar). Compared with aryl fluorine groups, the aryl bromine group has a higher reactivity which makes bromine compound a favored reactant for Ullmann reaction. However, this reaction has two major disadvantages: poor reproducibility and difficulty in removing the copper salt. As a result, we do not use the copper analyst in this study. The absence of the copper salt also changes the reaction mechanism to S<sub>N</sub>Ar mechanism. For S<sub>N</sub>Ar reaction, fluorine group has a much higher reactivity than bromine in spite of the strength of carbon-fluorine bond.<sup>32</sup> That is why we replace the aryl bromine with aryl fluorine in the old monomer. And results showed that S<sub>N</sub>Ar polymerization of 4-fluoro-4',4''-dihydroxytriphenylmethane turns out to be a superior strategy for HPPO synthesis and purification.

### Characterization of Polymers

GPC analysis shows that molecular weight and molecular weight distribution of EHPPPO are  $M_w = 2898$  and PDI = 1.82, respectively. EEW of EHPPPO is determined to be 285.71 g·eq<sup>-1</sup> by titration. The low molar mass and terminal epoxy groups of EHPPPO ensure its good miscibility with DGEBA. FTIR spectra of HPPO and EHPPPO are shown in Figure 1. Both the spectra show characteristic absorptions at about 1244 and 829 cm<sup>-1</sup> which is corresponding to Ph-O-Ph stretching and Ph-H distorting, respectively, indicating that the polymers maintain a phenylene structure with two *p*-substitution groups. The spectrum of HPPO also shows an absorption peak of phenolic hydroxyl groups at 3373 cm<sup>-1</sup>. After epoxidation, the absorption peak of phenolic hydroxyl disappears and that of epoxy is observed at 913 cm<sup>-1</sup>.

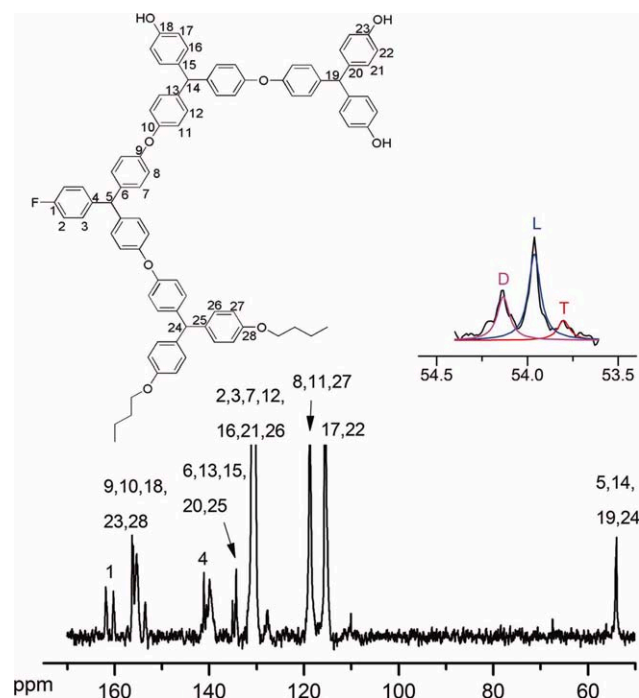


**Figure 1.** FTIR spectra of HPPO and EHPPO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

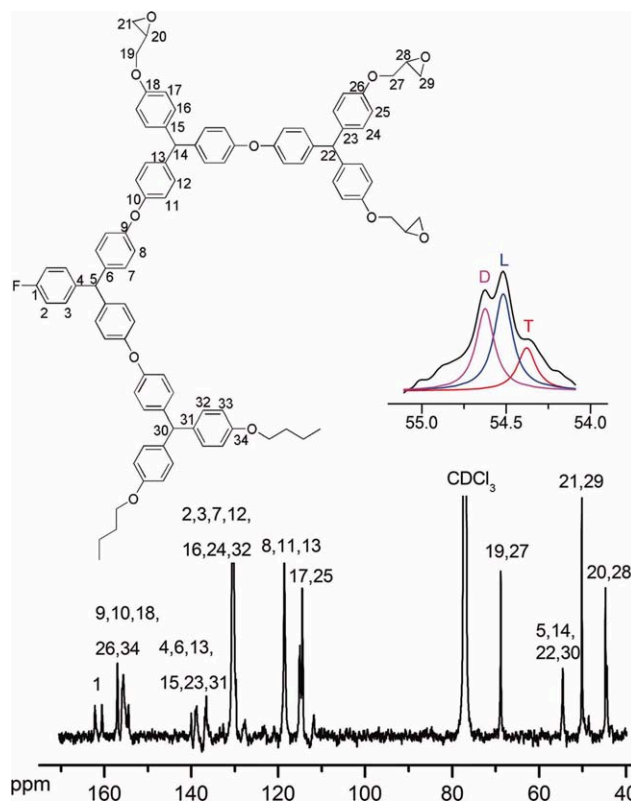
Quantitative  $^{13}\text{C}$  NMR spectra of HPPO in  $\text{DMSO-}d_6$  and EHPPO in  $\text{CDCl}_3$  are shown in Figures 2 and 3, respectively. It can be seen that the signal of carbons connected to fluorine groups of Ph-F splits to two peaks because of the presence of fluorine group. The signal of methylidyne carbon is observed at about 54 ppm and splits into several peaks, which may be attributed to their different chemical circumstances.

#### Degree of Branching of HPPO and EHPPO

Degree of branching (DB) is a typical characteristic frequently used to evaluate the irregularity of the structure of hyperbranched polymers. In principle, condensation polymerization



**Figure 2.** Quantitative  $^{13}\text{C}$  NMR spectrum of HPPO (in  $\text{DMSO-}d_6$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



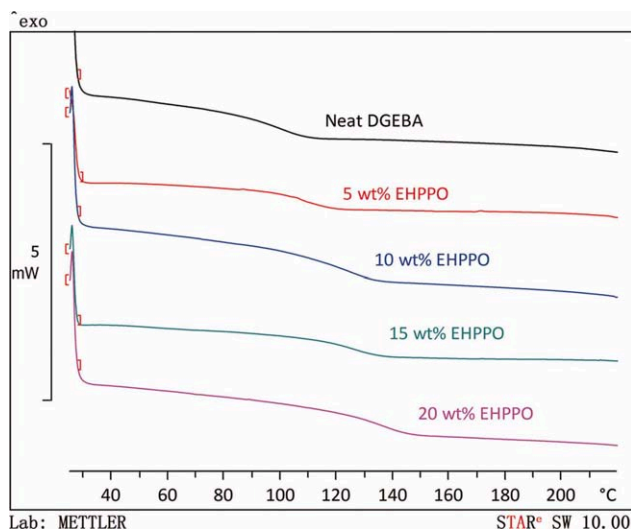
**Figure 3.** Quantitative  $^{13}\text{C}$  NMR spectrum of EHPPO (in  $\text{CDCl}_3$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of an  $\text{AB}_2$  monomer can give rise to dendritic (D), linear (L), and terminal (T) units. According to the definition of DB given by Fréchet, the DB is calculated by the equation  $\text{DB} = (N_D + N_T)/(N_D + N_T + N_L)$ , where  $N_D$ ,  $N_L$ , and  $N_T$  represent the fractions of D, L, and T units in hyperbranched molecules, respectively.<sup>33</sup>

Quantitative  $^{13}\text{C}$  NMR spectra of HPPO and EHPPO reveal the fine structure attributed to the different types of repeat units. As shown in Figure 2, the methylidyne carbons of HPPO at about 54 ppm split into three peaks and the DB is calculated to be 0.43. In Figure 3, similar phenomenon is observed for EHPPO. But the peaks could not be used directly for integration due to overlapping. Therefore, a curve-fitting procedure was adopted to extract the information of each individual peak, and the DB value of EHPPO could be calculated to be 0.56. The higher DB of EHPPO than HPPO can be explained by the reduction of small molecules during the purification of EHPPO.

#### Thermal Properties of Cured Epoxy Hybrids

The synthesized EHPPO was designed to possess sufficient aromatic character to maintain high glass transition temperature ( $T_g$ ). DSC results of the cured epoxy hybrids are shown in Figure 4. As can be seen, there is only one  $T_g$  in each hybrid, which suggests that EHPPO and DGEBA have good compatibility after curing because of their similar aromatic structures. In addition,  $T_g$  of the hybrids increases with the increase in



**Figure 4.** DSC curves of cured systems. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

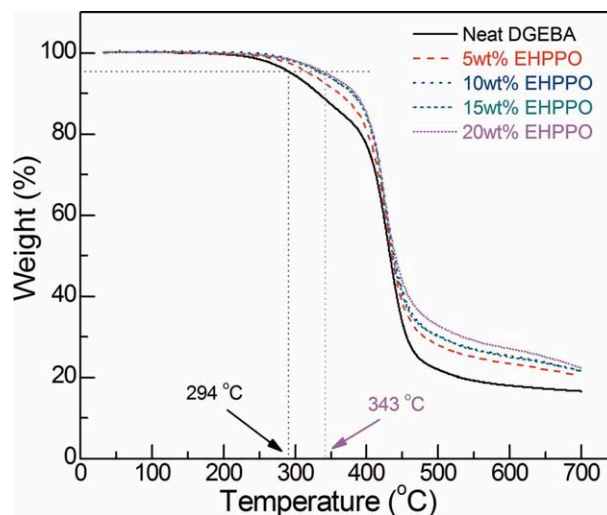
EHPPO content. When 20 wt % EHPPO is added,  $T_g$  increases from 99°C of neat DGEBA to 134°C.

We note that some reports have shown that application of hyperbranched polyester epoxies as modifiers for DGEBA could bring down  $T_g$  of the hybrids.<sup>22,34</sup> The decrease of  $T_g$  could be attributed to flexible aliphatic or polyester backbone of the hyperbranched epoxy. Another possible reason may be that in their curing systems, i.e., epoxy-functionalized hyperbranched polyesters/amine system, the epoxy groups on hyperbranched polyesters have lower reactivity compared to DGEBA<sup>34</sup>, which leads to a lower crosslinking density and  $T_g$ . In this study, an aromatic hyperbranched poly(phenylene oxide) epoxy is designed, and methyl nadic anhydride is chosen as a curing agent. A network with increasing crosslinking density is obtained, which can be confirmed by the following DMA measurements. Thus the increase in crosslinking density may result from high reactivity of epoxy end groups of EHPPO with anhydride. Consequently,  $T_g$  of the cured system increases due to the contribution of high aromatic ring density of EHPPO and high crosslinking density of the cured network.

Thermal stability of the cured hybrids was studied by comparing the 5% weight loss degradation temperature ( $T_{d5\%}$ ) and char yield at 700°C. TGA results of cured epoxy hybrids under nitrogen are shown in Figure 5. With the increase of the amount of EHPPO,  $T_{d5\%}$  of the cured epoxy resins rises from 294°C to 343°C. This is because poly(phenylene oxide) structure has a property of high temperature resistance. Furthermore, char yield of the hybrids at 700°C also increased. This is another evidence to prove that the poly(phenylene oxide) backbone is beneficial to the enhancement of thermostability of the hybrids. In addition, higher crosslinking density also contributes to the improved thermal stability.

#### DMA Characterization of Cured Hybrids

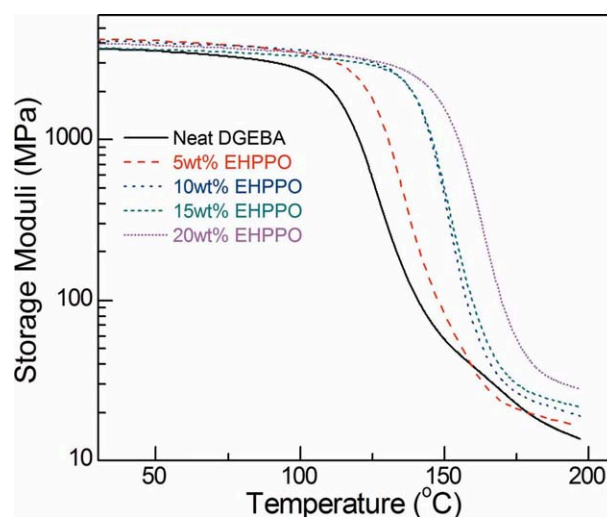
Morphology, miscibility, and crosslinking density of the cured DGEBA/EHPPO hybrids are characterized by DMA tests. Based



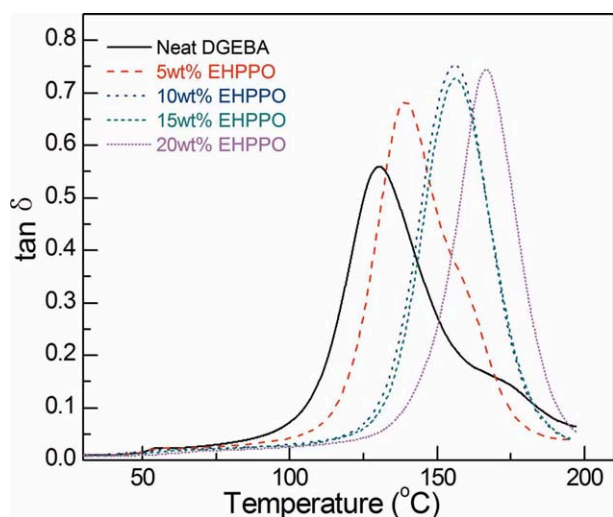
**Figure 5.** TGA curves of cured systems. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

on rubber elasticity theory, the crosslinking density of cured epoxies can be estimated from rubbery plateau modulus.<sup>35</sup> Storage moduli of the cured hybrids as a function of temperature is shown in Figure 6. The increase of the rubbery plateau moduli suggests that the crosslinking density increases with increasing EHPPO content. This could be explained by the high functionality and high reactivity of EHPPO which lead to a more densely crosslinked network.  $T_g$  as defined by the extrapolated onset temperature corresponding to the drop in the storage modulus increases with EHPPO addition due to the increasing crosslinking density and the stiff structure of EHPPO, which is coincident with the DSC result.

The loss tangent ( $\tan \delta$ ) of the different cured hybrids as a function of temperature is shown in Figure 7. All curves show one major peak. For the sample of neat DGEBA, an obvious



**Figure 6.** Logarithmic storage moduli curve versus temperature of cured systems. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Relaxation peaks ( $\tan \delta$ ) of cured systems. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

shoulder appears at about  $160^{\circ}\text{C}$ , indicating a heterogeneous network. This may be explained by the complicated curing reactions in the epoxy/anhydride curing system. When 5 wt % EHPPO is added, the crosslinking density increases and  $\tan \delta$  peak moves to higher temperature and begins to overlap with the shoulder peak. Further addition ( $>10$  wt %) results in a complete merging with the shoulder peak, thus only one peak is evident, indicating a more homogeneous network. The reason for this could be complicated by several factors, including the possible change in mechanisms, the difference in reactivity between EHPPO and DGEBA as well as other factors (such as curing conditions) which may contribute to the network formation. Further detailed investigations are needed to elucidate the exact reasons. In addition, the structural similarity (abundant aromatic rings in the both resins) ensures good compatibility during curing, thus no sign of phase separation is evident judging from loss tangent peaks. This is different from other systems which used aliphatic polyester hyperbranched epoxy as modifier and lead to a phase-separated network.<sup>34</sup>

### Thermal Mechanical Analysis Characterization of Cured Hybrids

According to classical free volume theory, the difference in the coefficients of thermal expansion (CTE) in the rubbery and glassy state could be treated as the CTE of free volume. The TMA was used to measure the difference in free volumes of different cured hybrids. The linear CTEs in the rubbery state ( $\alpha_r$ ) and in the glassy state ( $\alpha_g$ ) as well as the difference between them ( $\Delta\alpha$ ) are listed in Table I. It is clear that  $\alpha_r$  increase systematically with increasing EHPPO content. In contrast,  $\alpha_g$  decreases with increasing EHPPO content. As a result,  $\Delta\alpha$  which represents the expansion of free volume increases systematically with increasing EHPPO content, suggesting a higher free volume at higher EHPPO loading. This result is coincident with the result from positron annihilation lifetime spectroscopy (PALS) in the literature.<sup>36</sup> And this could be explained by the added free volume (or inter free volume) exist between EHPPO

**Table I.** Coefficient of Linear Thermal Expansion of Different Cured Hybrids

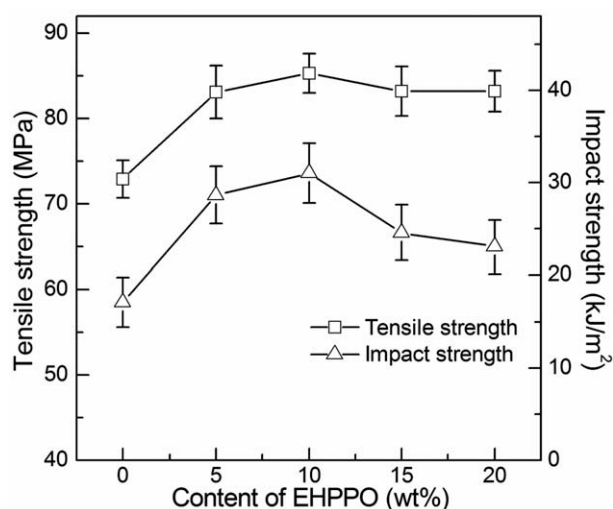
Samples	$\alpha_g$ ( $\times 10^{-6}\text{K}^{-1}$ )	$\alpha_r$ ( $\times 10^{-6}\text{K}^{-1}$ )	$\Delta\alpha = \alpha_r - \alpha_g$ ( $\times 10^{-6}\text{K}^{-1}$ )
Neat DGEBA	71.3	167.8	96.5
5 wt % EHPPO	68.2	174.5	106.3
10 wt % EHPPO	67.2	177.4	110.2
15 wt % EHPPO	62.2	178.6	116.4
20 wt % EHPPO	62.8	183.5	120.7

molecules and possible inherent free volumes (or cavities) inside EHPPO.

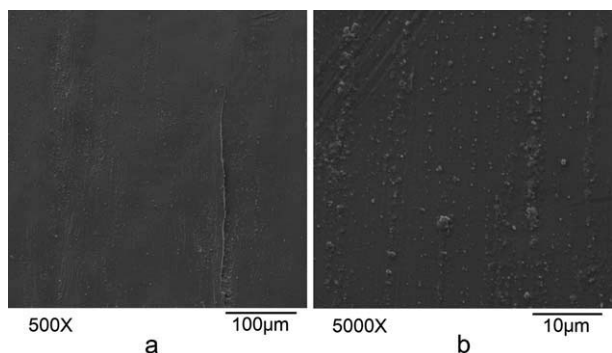
### Mechanical Properties of Cured Hybrids

As we know, the biggest deficiency of DGEBA is brittleness. Several ways for improving impact strength without compromising tensile strength of the resins have been studied so far. In this contribution, the effects of EHPPO content on tensile strength and impact strength are investigated. As shown in Figure 8, addition of EHPPO improves both the tensile strength and impact strength. However, both properties go through a maximum at 10 wt % EHPPO loading, and then decrease with further addition.

Tensile strength of thermosets can be related to the rigidity of the chain segments and crosslinking density of the cured network. During curing, both EHPPO and DGEBA are reactively incorporated into the hybrid network. Addition of EHPPO not only introduces aromatic poly(phenylene oxide) structure into the network but also increases the crosslinking density of the cured hybrids as demonstrated by the rubbery plateau. Consequently, the tensile strength is improved. However, the addition of EHPPO also introduces nanometer sized free volume into the cured network because of its highly branched structure. Excessive cavities could result in unfavorable effect on the tensile strength.<sup>37</sup> However, those cavities could be advantageous for toughness. At 10 wt % EHPPO loading, the impact strength of



**Figure 8.** Effects of EHPPO content on tensile and impact strength.



**Figure 9.** SEM photographs of the fracture surface of cured DGEBA: (a) 500×; (b) 5000×.

the cured materials increases from  $17.1 \text{ kJ}\cdot\text{m}^{-2}$  to  $31.0 \text{ kJ}\cdot\text{m}^{-2}$ . In cured hybrids, the cavities and intramolecular defects, acting as internal plasticizers, can absorb much energy during impacting.<sup>38</sup> In addition, internal frictions due to the dangling chains might also contribute to the increase in toughness. The overall toughness, among other things, is mainly determined by the chain stiffness, crosslink density, and the defects. Further increase in EHPPPO content leads to big increases of the chain stiffness and crosslinking density, and overrides the effects of cavities. Thus, the overall toughness passes a maximum at approximately 10 wt % EHPPPO loading.

#### Toughening Mechanisms

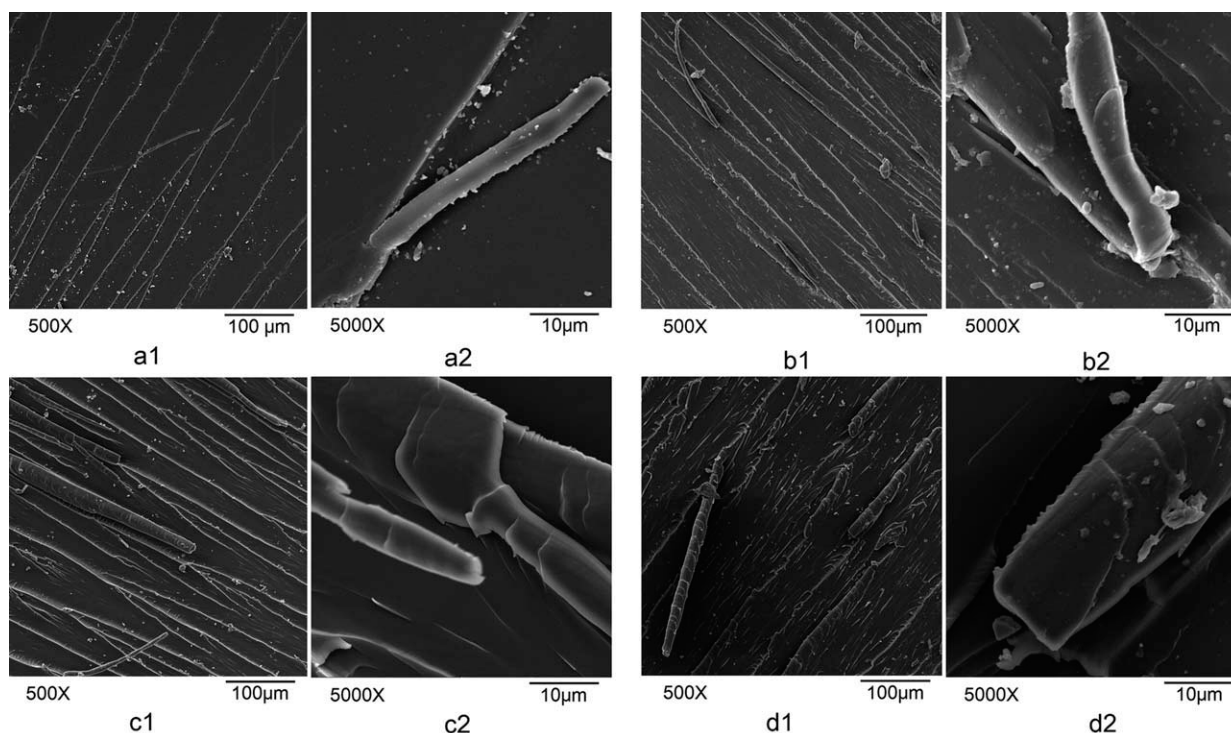
SEM photographs of the fracture surface of cured neat DGEBA are shown in Figure 9. The smooth, glassy fracture surface of

neat DGEBA indicates a brittle material and no deformation, which accounts for its poor impact strength.

SEM photographs of the fracture surface of cured hybrids with different EHPPPO content are shown in Figure 10. When EHPPPO is added, the fracture surface becomes rough and a lot of “protonema” or “fibrils” are observed, which is similar with other reports.<sup>22,38</sup> And there is no evidence of phase separation, which is in accordance with the results of DSC and DMA. In this cured system, with the increase in EHPPPO content, the “protonema” increases both in size and density. As shown above, addition of EHPPPO into epoxy resins incorporates a large amount of nanometer sized cavities and intramolecular defects due to its hyperbranched structure. During curing, the terminal epoxy groups react with curing agent to form a homogeneous crosslinking network, therefore the cavities and defects are maintained inside. The more EHPPPO is added, the more cavities and defects are incorporated into the cured network. During impacting, these cavities act as inside plasticizers will distort and form protonemas to absorb much energy.<sup>22,38</sup> Since no phase separation occurred in the cured materials, the toughening mechanism cannot be explained by phase separation mechanism.<sup>13</sup> The phenomenon is in good agreement with former reports and should be explained by *in situ* homogeneous reinforcing and toughening mechanism.<sup>22,38,39</sup>

#### CONCLUSIONS

A novel AB<sub>2</sub> monomer 4-Fluoro-4',4''-dihydroxy triphenyl methane is designed and synthesized. Through the homopolymerization of the AB<sub>2</sub> monomer, a novel hyperbranched



**Figure 10.** SEM photographs of the fracture surfaces of hybrids with different EHPPPO content: (a1) 5 wt %, 500×; (a2) 5 wt %, 5000×; (b1) 10 wt %, 500×; (b2) 10 wt %, 5000×; (c1) 15 wt %, 500×; (c2) 15 wt %, 5000×; (d1) 20 wt %, 500×; (d2) 20 wt %, 5000×.

poly(phenylene oxide) (HPPO) with terminal phenolic groups is obtained. Then the polymer is epoxidized by ECH to afford epoxidized hyperbranched poly(phenylene oxide) (EHPPPO). As a modifier, EHPPPO is added into DGEBA in different ratios and cured with methyl nadic anhydride to form hybrids. Results show that incorporation of EHPPPO can improve the thermal and mechanical properties of the resin. When 20 wt % EHPPPO is added,  $T_g$  and  $T_{d5\%}$  increase from 99°C and 294°C of the neat DGEBA to 134°C and 343°C, respectively. Besides, the strength and toughness of the cured epoxy are improved simultaneously. At 10 wt % EHPPPO loading, the increase of tensile strength and impact strength is 17% and 81%, respectively. Furthermore, the free volume and crosslinking density of the cured system increase with the addition of EHPPPO and no phase separation occurs. The improvement in strength and toughness can be explained by *in situ* reinforcing and toughening mechanism.

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