

An Epoxy-ended Hyperbranched Polymer as a New Modifier for Toughening and Reinforcing in Epoxy Resin

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ABSTRACT: A new epoxy-ended hyperbranched polyether (HBPEE) with aromatic skeletons was synthesized through one-step proton transfer polymerization. The structure of HBPEE was confirmed by Fourier transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) measurements. It was proved to be one high efficient modifier in toughening and reinforcing epoxy matrix. In particular, unlike most other hyperbranched modifiers, the glass transition temperature (T_g) was also increased. Compared with the neat DGEBA, the hybrid curing systems showed excellent balanced mechanical properties at 5 wt % HBPEE loading. The great improvements were attributed to the increased cross-linking density, rigid skeletons, and the molecule-scale cavities brought by the reactive HBPEE, which were confirmed by dynamical mechanical analysis (DMA) and thermal mechanical analysis (TMA). Furthermore, because of the reactivity of HBPEE, the hybrids inclined to form a homogenous system after the curing. DMA and scanning electron microscopy (SEM) results revealed that no phase separation occurred in the DGEBA/HBPEE hybrids after the introduction of reactive HBPEE. SEM also confirmed that the addition of HBPEE could enhance the toughness of epoxy materials as evident from fibril formation. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

As one of the most important thermosetting materials, epoxy materials are widely used in coatings, adhesives, electrical laminates, and structural components because of their versatility, low cure shrinkage, good solvent and chemical resistance, excellent adhesion and mechanical properties. However, the application of epoxy materials is often limited by their intrinsic brittleness.^{1,2} The toughening of epoxy materials is very important and has long been the focus of many research investigations^{3–7}. Toughening of epoxy can be achieved by addition of organic or inorganic fillers, such as liquid carboxyl-terminated copolymer of butadiene acrylonitrile (CTBN),^{8–11} high performance engineering thermoplastic,^{12–15} inorganic particles,^{16–19} and hyperbranched polymers (HBPs).^{20–23} Among the various fillers, hyperbranched polymers are considered as a new category of promising fillers which can improve the toughness and other mechanical properties simultaneously.²⁴

Both hyperbranched polymers (HBPs) and dendritic macromolecules have highly compacted semi-spherical shape, ample

terminal groups, and internal molecule-scale cavities, which lead to good solubility, processability, and compatibility. Hyperbranched polymers can be synthesized through the one-pot or pseudo-one step procedure, and thus are cheaper and easier to produce in large quantities compared with dendrimers. Since the 1990s, HBPs, which had hydroxyl and epoxy terminal groups, had been used to modify the epoxy resins and other thermosets.^{25,26} Among those HBPs, two typical commercialized hyperbranched polyesters, Boltorn H30 and Boltorn E1, had been extensively studied.^{21,25,27,28} The results revealed that those hyperbranched polyesters could greatly increase the toughness of epoxy materials. However, other mechanical properties such as flexural strength, tensile strength, and the T_g were somewhat compromised. In addition, those hybrids often showed phase-separated morphology, which may complicate the processing process, especially in applications when fibers or other reinforcements have to be added. Recently, Zhang and co-workers^{29,30} showed that both the toughness and the tensile strength of epoxy materials could be improved by adding

compatible HBPs and did not lead to phase separation; however, the glass transition temperature (T_g) was reduced, which lower its usage temperature. Thus, achieving balanced improvements in mechanical properties without sacrificing the T_g still remains a challenge.

In our previous study, it was found that two HBPs with ether groups in the backbones had better chemical stability and comparable flexibility compared with those with ester groups in the backbones.^{31–33} When those HBPs with ether groups in the backbones were added into diglycidyl ether of bisphenol-A (DGEBA) epoxy to form hybrids, the cured hybrids materials did not show improvements in the tensile strength and T_g , because a significant amount of soft segments were presented in those HBPs. In this study, in order to improve both mechanical and thermal properties, a novel epoxy-ended hyperbranched polymer (HBPEE), whose skeletons were comprised of more aromatic rings, was synthesized by one-pot approach. By virtue of its dendritic-like molecular structures, ample reactive sites of the terminal groups, rigid macromolecular backbones, and its inherent molecule-scale cavities or free volumes, the novel HBPEE was expected to be one outstanding modifier in toughening and reinforcing epoxy materials. In the meanwhile, as-modified epoxy materials maintain high T_g s and excellent thermal stabilities. The synthesis of HBPEE with rigid backbones and the preparation of DGEBA/HBPEE cured hybrids were discussed in the following sections. In order to study the influences of HBPEE macromolecules on DGEBA/HBPEE hybrids, macroscopic mechanical performance, thermal stability, and phase morphology of the hybrids were investigated in details. Moreover, high performance DGEBA/HBPEE hybrids with low HBPEE content were successfully obtained by incorporation of reactive HBPEE macromolecules.

EXPERIMENTAL

Materials

Phenol (98%), 4-hydroxybenzaldehyde (PHBA, 98%), and *p*-toluenesulfonic acid (TSA, 99%) were purchased from Tianjin Chemical Reagents Factory. Diglycidyl ether of bisphenol A (DGEBA) was purchased from Yueyang Resin Factory (epoxy equivalent weight EEW = 186.2 g/eq). Methyl hexahydrophthalic anhydride (MeHHPA, 99%) and 2-ethyl-4-methylimidazole (2E4MZ, 99%) were obtained from Acros Organics. Tetrabutyl ammonium bromide (TAB, 99%) and other solvents were purchased from Beijing Chemical Works. All the reagents and solvents were used as received without further purification.

Synthesis of B_3 Monomer: 4,4',4''-Trihydroxytriphenylmethane (THTPM)

Phenol (470 g, 5 mol) and PHBA (122 g, 1 mol) were added into a three-necked flask equipped with a mechanical stirring. After stirring at 45°C, a homogeneous solution was formed. ZnCl₂ (13.6 g, 0.1 mol) and TSA (19 g, 0.1 mol) were then charged into the solution. After 1 h, an orange red suspension was obtained. It was kept at 45°C for another 8 h and was then filtered and washed twice with both dichloromethane and hot water (80°C). The obtained orange products were dried under

vacuum at 80°C for 12 h (75% yield). ¹H-NMR (600 MHz, acetone-*d*₆, δ): 5.33 (s, 1H, CH), 6.76 (d, 6H, C₆H₄O-), 6.94 (d, 6H, C₆H₄O-), 8.15 (s, 3H, -OH); ¹³C-NMR (600 MHz, acetone-*d*₆, δ): 54.32, 114.75, 130.06, 136.04, 155.50.

Synthesis of Hyperbranched Polyether Epoxy (HBPEE)

The HBPEE was synthesized by Proton Transfer Polymerization^{34–36} (PTP) using the A₂ + B₃ approach. Under mechanical stirring, 78.84 g of THTPM (B₃ monomer), 220.00 g of DGEBA (A₂), 13.04 g of TAB, and 135 mL of dioxane were charged into a three-necked flask with a reflux condenser under N₂ protection. After refluxing for 72 h, the solution was cooled to room temperature and poured into methanol with vigorous stirring in order to get rid of the catalyst TAB and the remaining DGEBA. The obtained solid was redissolved in THF and quickly poured into methanol. The resultant light yellow solid was dried under vacuum at 60°C, and the final yield is 72%. The values of epoxide equivalent weight (EEW) and hydroxyl equivalent weight (HEW) determined by chemical titration are 781 and 314 g/eq, respectively. The chemical structure of the HBPEE was determined by ¹H- and ¹³C-NMR measurements, which are shown in Figure 1(a,b), respectively.

¹H-NMR (600 MHz, CDCl₃, δ): 1.63 (*m*, C₆H₅C(CH₃)₂-), 2.60 (broad; -OH), 2.74 (s, -CH₂-, epoxy ring), 2.89 (s, -OCH₂-,

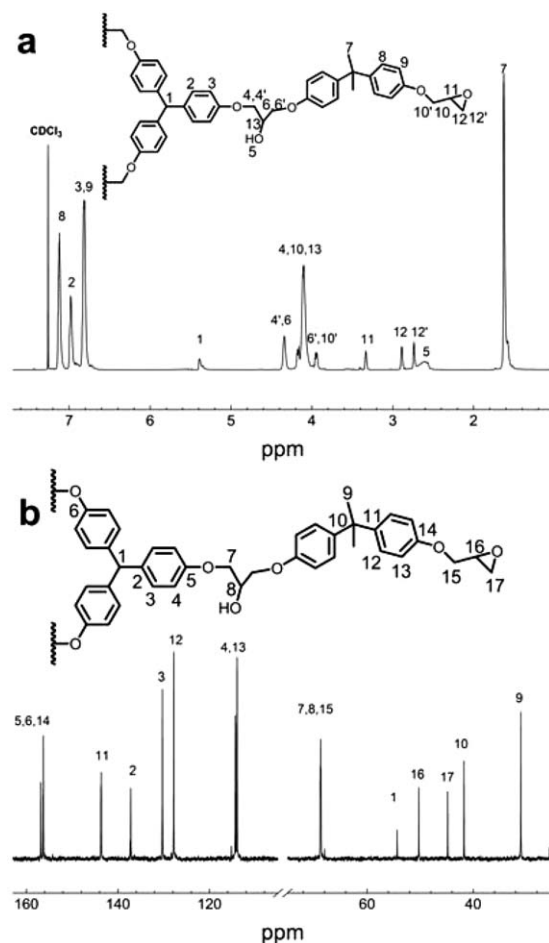


Figure 1. (a) ¹H- and (b) ¹³C-NMR spectra of HBPEE.

glycidyl), 3.33 (*s*, $-\text{OCH}-$, epoxy), 3.94 ~ 4.34 (*m*, $-\text{OCH}_2-$, $-\text{CH}(\text{OH})-$), 5.39 (*t*, $-\text{CH}(\text{C}_6\text{H}_5)_3$), 6.81 ~ 7.12 (*m*, $-\text{C}_6\text{H}_5$).

^{13}C -NMR (600 MHz, CDCl_3 , δ): 30.86, 41.49, 44.81, 50.24, 54.32, 68.65, 68.72, 68.79, 97.45, 114.33, 127.78, 130.09, 137.34, 143.68, 156.13.

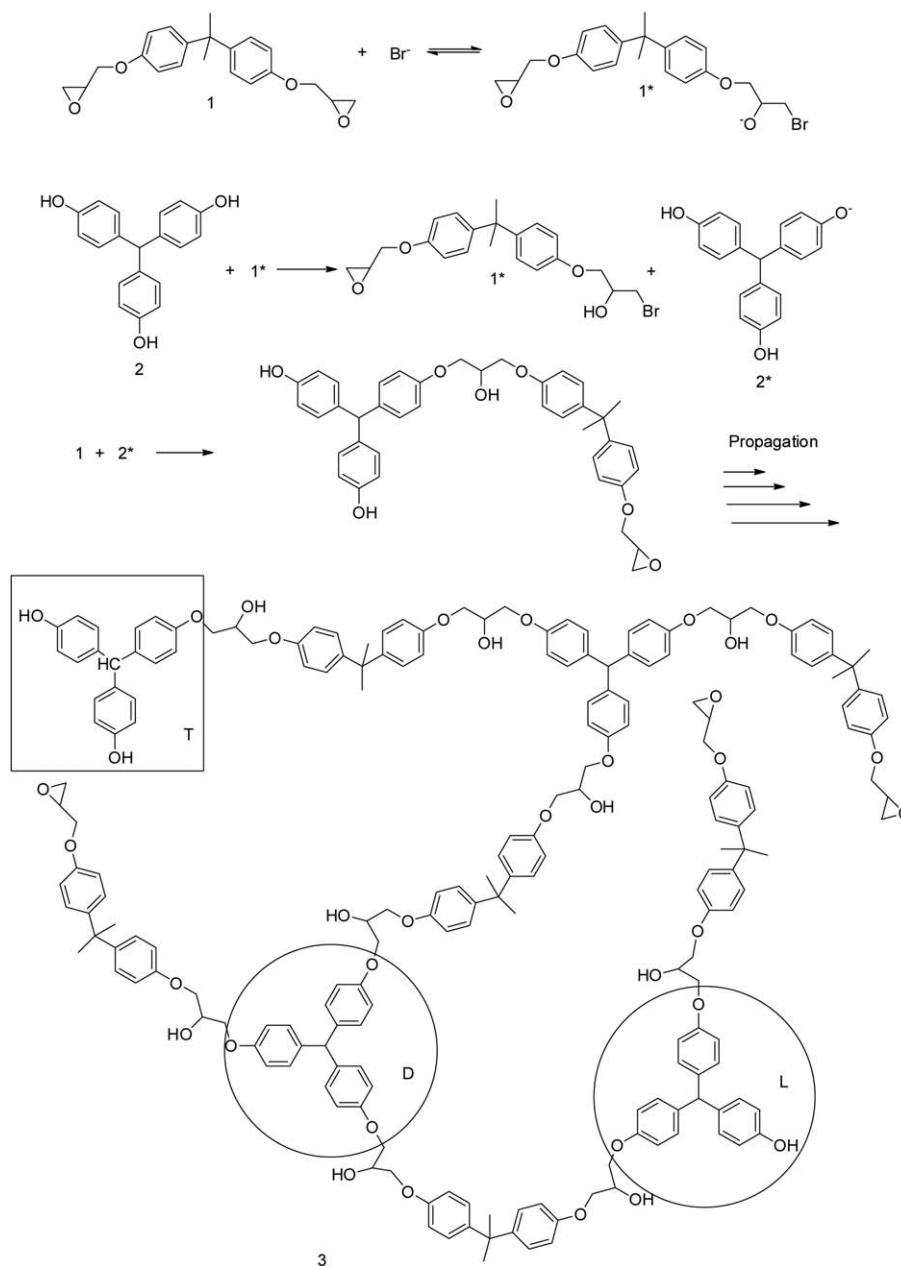
Preparation of DGEBA/HBPEE Hybrid Epoxy Curing Systems

The hybrid epoxy systems containing different amounts, i.e., 3, 5, 10, and 20 total wt %, of epoxy-ended hyperbranched polymers (HBPEE) and DGEBA epoxy resins were prepared by mechanical mixing. Stoichiometric amounts of MeHHPA, the curing agent, were added in the hybrid epoxies under continuously stirring at 80°C . For the different HBPEE loadings, the anhydride values of MeHHPA keep the equivalent

stoichiometric relationships with the sum of both the hydroxyl values and epoxy values of the mixtures of DGEBA and HBPEE, in which one anhydride reacts either with an epoxide or with two hydroxyl groups. The accelerator, 2E4MZ (1 wt % of the total weight of the hybrid epoxy) was then added under vigorous stirring to form a homogeneous mixture (the final curing system). The mixture were degassed and cured in silicone rubber molds to form samples in desirable shapes. The cure schedule was a three-step procedure, i.e., 100°C for 2 h, 150°C for 6 h, and 200°C for 2 h.

Characterizations

All ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were collected using a Bruker Fourier Transform AVANCE 600



Scheme 1. Synthesis of HyperBranched PolyEther Epoxy (HBPEE).

spectrometer, and the solvents are acetone- d_6 or $CDCl_3$. The Infrared spectra of samples in the form of KBr pallets were recorded on a Bruker Tensor 37 spectrometer at room temperature. The molecular weight and its distribution were determined by a Waters Gel Permeation Chromatography (GPC) 515–2410 system with THF as the eluent at 30°C. The epoxy equivalent weight (EEW) and hydroxyl equivalent weight (HEW) of HBPEE were determined by titration methods which have been described elsewhere.^{37,38}

The T_g s of the cured hybrid curing systems were determined by a METTLER DSC1 differential scanning calorimetry on second heating runs at 10 K/min under nitrogen. Thermal stability was measured using a Perkin Elmer Pyris1 thermogravimetric analyzer (TGA) from 50 to 750°C at a heating rate of 10 K/min under nitrogen. Coefficients of thermal expansion (CTE) were measured using a Mettler-Toledo TMA/SDTA841e Thermal Mechanical Analyzer in the range of 25 to 220°C during cooling at 2 K/min and were calculated as

$$\alpha = \frac{1}{L_0} \frac{dL}{dT} = \frac{1}{L_0} \frac{dL/dt}{dT/dt} \quad (1)$$

where L_0 is the initial length of samples, L the length of the sample at temperature T , t the time, and T the temperature.

The dynamic mechanical properties of the cure hybrids at 1 Hz were measured by a TA Q800 Dynamic Mechanical Analyzer (DMA) using the single cantilever mode. The size of the specimen is 35.0 mm × 12.8 mm × 3.2 mm. The temperature range is from 50 to 220 °C, and the heating rate is 3°C/min.

The tensile strength and elongation at break of cured hybrids were characterized by an Instron 1185 test machine according to ISO 527:1993. The flexural strength of the cured hybrids was measured by an Instron 1185 test machine according to ISO 178:1993. Unnotched impact strength tests were performed on a Ceast Resil impact tester according to ISO 179:1982. For each composition, at least five samples were measured.

After impact testing, the fracture surfaces of samples, which were coated with platinum, were observed by a JEOL JSM-6700

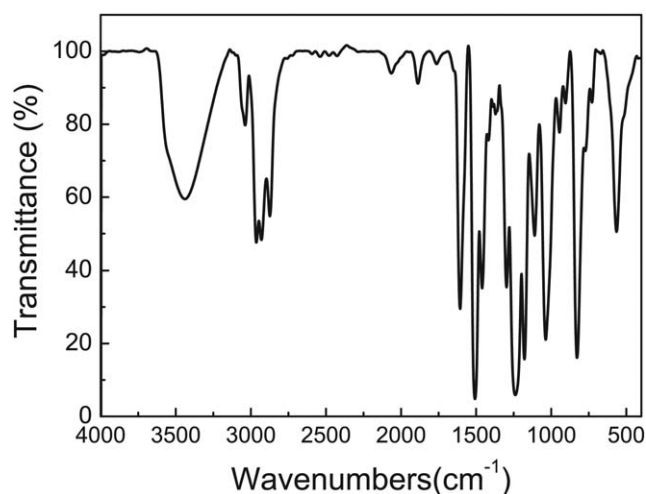


Figure 2. The FTIR spectrum of HBPEE.

Scanning Electron Microscopy (SEM) at an accelerating voltage of 5 kV.

RESULTS AND DISCUSSION

Synthesis and Characterization of Epoxy-ended Hyperbranched Polymer

Herein, a new hyperbranched polyether epoxy with mass aromatic skeletons based on DGEBA (A_2) and THTPM (B_3) was synthesized by an $A_2 + B_3$ one-step proton transfer polymerization. HPBEE macromolecules can be easily obtained from the two starting accessible monomers with vigorous stirring under reflux and N_2 atmosphere. Because of the versatile and low-cost raw material and easy operations, it is considered as a facile approach to obtain such a reactive epoxy-ended hyperbranched polymer compared with the previous studies about the synthesis of hyperbranched polymers, where the synthesis of HBPs required two steps at least^{20,30,39–41}. In order to ensure that the terminal groups can be successfully converted to epoxide groups, excessive DGEBA were added. Due to the mass aromatic

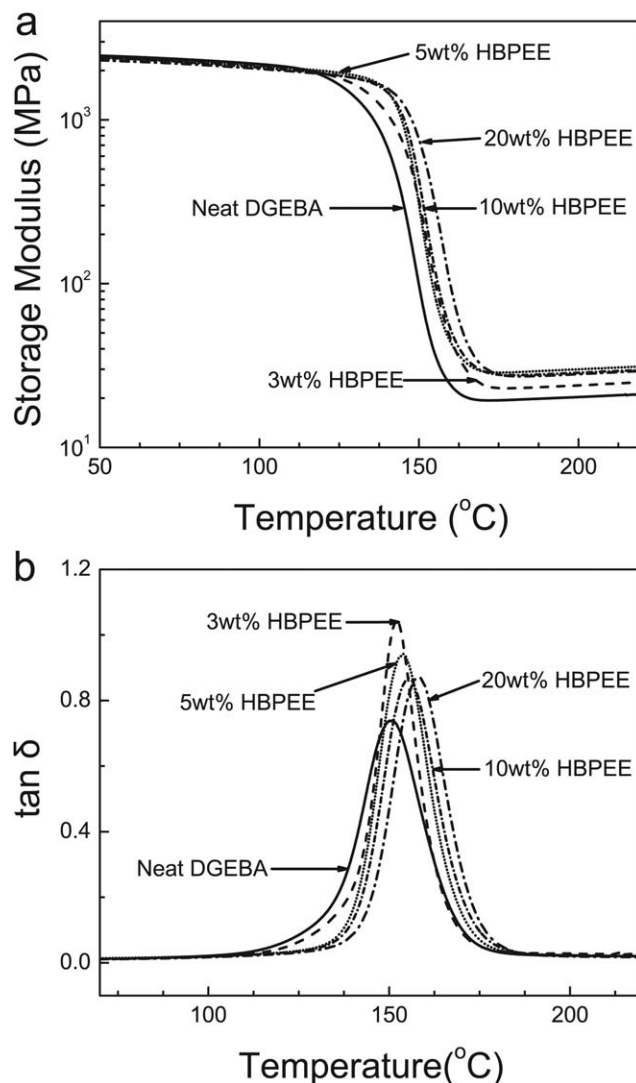


Figure 3. DMA analysis of DGEBA/HBPEE hybrids with different HBPEE loadings. (a) storage modulus changes of DGEBA/HBPEE hybrids; (b) plots of loss tangent ($\tan \delta$) of DGEBA/HBPEE hybrids.

Table I. Thermal Properties of DGEBA/HBPEE Hybrids

Samples	T_g (°C) (DSC)	T_g (°C) (DMA)	T_{d5}^a (°C)	T_{d10}^b (°C)	T_{max}^c (°C)	v_e (mol/dm ³) ^d	Char yield at 700°C (wt %)
Neat DGEBA	133.6	150.1	359	380	426	1719.9	4.40
3 wt % HBPEE	133.8	152.2	333	374	423	2027.5	4.62
5 wt % HBPEE	134.8	154.1	336	370	412	2422.5	4.75
10 wt % HBPEE	135.5	156.9	330	368	413	2386.1	4.80
20 wt % HBPEE	136.4	158.3	322	365	418	2373.4	5.15

^aThe temperature at 5 wt % decomposition.

^bThe temperature at 10 wt % decomposition.

^cThe temperature of the maximum decomposition rate

^dCalculation from DMA and indication of the cross-linking densities to a certain extent.

structures in the backbones of HBPEE, the hyperbranched molecule has a rigid skeleton and good heat resistance. Meanwhile, HBPEE macromolecule with ether groups in the backbones has better chemical stability and comparable flexibility compared with those with ester groups in the backbones.^{31–33} Moreover, the mass reactive groups in the terminal increase the miscibility with the matrices and provide the chemical cross-linking points in the curing reactions.

The synthesis route and the ideal chemical structure of HBPEE are shown in Scheme 1. The trisubstituted, disubstituted, and monosubstituted B₃ are represented by the dendritic (D), linear (L), and terminal (T) structures, respectively. A reactive primary alkoxide is generated by proton exchange between “2” and the secondary alkoxide formed by the addition of bromide ion to “1”. Continued propagation and proton transfer lead to the hyperbranched polyether, as shown schematically in “3,” where the B₃ subunits are distributed throughout the hyperbranched molecule.^{34–36}

The structure of HBPEE is determined by ¹H-NMR and ¹³C-NMR spectra as shown in Figure 1. The weight-average molecular weight and molecular weight distribution are 7696 and 2.5, respectively. The values of EEW and HEW determined by chemical titration are 781 and 314 g/equiv, respectively. The peaks corresponding to different structures are labeled by different numbers. The FTIR spectrum of HBPEE is shown in Figure 2. The broad and strong band at about 3438 cm⁻¹ corresponds to the –OH stretching vibration. The characteristic peaks of epoxy

groups are observed at about 945, 905, and 729 cm⁻¹. The bands at 1239 and 1178 cm⁻¹ can be assigned to the Ph–O–C and C–O–C stretching vibrations, respectively. The bands at 1606 and 1507 cm⁻¹ correspond to the stretching vibrations of aromatic rings. In summary, the spectra of FTIR and NMR confirm that the epoxy-ended hyperbranched macromolecule is successfully synthesized.

DMA Characterization

The storage modulus (E') and $\tan \delta$ of the cured neat epoxy and cured hybrids containing 3, 5, 10, and 20 wt % HBPEE, as a function of temperature are shown in Figure 3(a,b), respectively. Each curve shows a clear glass transition with a well-defined rubbery plateau modulus (E_r). It is well-known that the rubbery plateau modulus increases with increasing cross-linking density, which is primarily observed in the elastomeric modulus from DMA.⁴² In DMA test, as the temperature increases, the moduli pass through the glass transition region reaching the elastomeric region, where more segments in the chains are moving in a cooperative way. Above T_g , network chains have sufficient thermal energy to undergo fast conformational changes by cooperative segmental motions, but cross-linking structures prevent any long range flow⁴³. As described in Ref. 43, it is possible to calculate the average cross-linking densities for DGEBA/HBPEE system. As can be noted in Figure 3(a), the storage modulus in rubbery region varies linearly with temperature. Based on the rubber elasticity theory, the cross-linking density

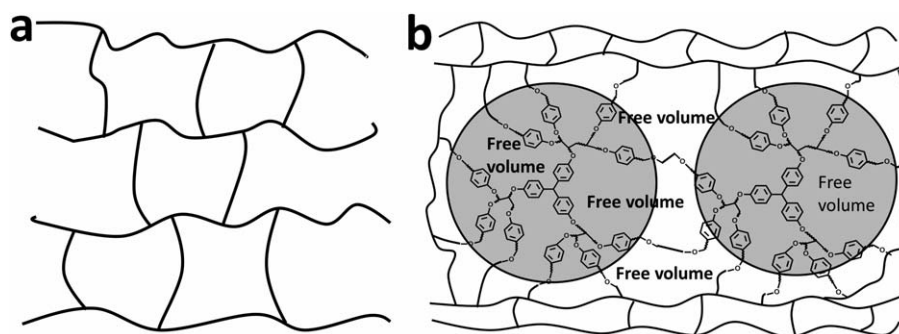


Figure 4. Schematic illustration of (a) neat epoxy networks and (b) free volumes in cured networks of DGEBA/HBPEE hybrids.

Table II. Coefficient of Thermal Expansion from TMA Measurement

Sample	α_g ($\times 10^{-6} \cdot K^{-1}$)	α_r ($\times 10^{-6} \cdot K^{-1}$)	$\Delta\alpha = \alpha_r - \alpha_g$ ($\times 10^{-6} \cdot K^{-1}$)
Neat DGEBA	66.12	188.98	122.86
3 wt % HBPEE	65.40	189.04	123.64
5 wt % HBPEE	65.21	189.16	123.95
10 wt % HBPEE	64.90	189.74	124.84
20 wt % HBPEE	63.93	190.53	126.60

α_g : The linear coefficients of thermal expansion in the glass state.

α_r : The linear coefficients of thermal expansion in the rubbery state.

of cured epoxy resins can be estimated from rubbery plateau modulus^{42,44}:

$$E_r = 3\phi v_e RT \quad (2)$$

where v_e is the concentration of elastic chains between crosslinks which can be used to quantify the cross-linking density, R the gas constant, T the absolute temperature, and ϕ a constant which is usually taken to be unity. The cross-linking densities (estimated from E_r at 200°C) of different curing systems are calculated and tabulated in Table I. As the HBPEE loading increases, the cross-linking density increases and then levels off. At 5wt% loading, the cross-linking density increase by 18% compared with that of the neat DGEBA. The increase in cross-linking density is due to the ample terminal reactive groups in HBPEE including epoxy groups and hydroxyl groups, which can easily participate into the cross-linking networks as chemical cross-linking points, as shown in Figure 4.

In addition, the shape and width of $\tan \delta$ peak can reveal detailed microscopic information such as the miscibility and homogeneity. In Figure 3(b), the curves of cured hybrids are similar to that of cured neat epoxy and show only one distinct peak. This suggests that no phase separation is evident in the cured hybrids and that HBPEE molecules were chemically incorporated into the epoxy networks as chemical cross-linking points because of its reactivity, leading to a homogeneous system. In contrast, in several other systems using non-reactive or aliphatic polyester hyperbranched epoxy as modifiers,^{21,25,45} phase-separated networks are observed. The peak position of $\tan \delta$, which is one way to define T_g , shifts to higher temperatures with the increasing HBPEE contents, and reaches 158.3°C at 20 wt % loading. This trend is consistent with that determined from DSC measurements and could be attributed to the higher cross-linking density due to the reactivity and more rigidity in skeletons of HBPEE macromolecules at higher loadings. Thus, based on the chemical and physical cooperative effects, reactive HBPEE shows big advantages in preparing high cross-linking density and homogeneous epoxy hybrids.

TMA Characterization

The coefficients of thermal expansion (CTE) of epoxy materials are important parameters and minimizing the CTE of cured

epoxy (especially in the glassy state) is favorable. The higher cross-linking density and more aromatic rings due to addition of HBPEE lead to a low CTE in the glassy state.⁴⁶

The CTEs in the rubbery state and in the glassy state as well as $\Delta\alpha$ are listed in Table II. As HBPEE content increases, α_g shows a systematic decrease, which may be related to the increase in cross-linking densities. The increase in α_g is beneficial for the reduction of residual stress developed during cooling. On the other hand, α_r shows systematic increases with increasing HBPEE content, which also lead to a systematic increase in $\Delta\alpha$ ($\Delta\alpha = \alpha_r - \alpha_g$). Based on the classical free volume theory,^{47–50} the difference in CTEs between the rubbery state (α_r) and the glassy state (α_g), is considered as the CTE of the free volume. This assertion has been confirmed by the Positron Annihilation Lifetime Spectroscopy measurements.⁵¹ In Table II, the free volume of hybrids increases with increasing HBPEE contents. The free volumes or molecule-scale cavities (Figure 4) inside hyperbranched HBPEE molecules have a big influence on promoting the toughness of DGEBA/HBPEE hybrids. The increase in free volume could be beneficial for the improvement of toughness of DGEBA/HBPEE hybrids, which will be discussed as follows.

Thermal Properties of DGEBA/HBPEE Hybrids

The DSC curves of cured samples with different amounts of HBPEE are presented in Figure 5. All samples show only one glass transition (T_g). The values of T_g increase with increasing HBPEE loading, which is consistent with the DMA measurements (Table I). This trend is different from other reported results,^{29,30,39} where the introduction of HBPs always induced a decrease in T_g s. The increase in T_g can be explained by the higher cross-linking density and the rigid backbones of HBPEE macromolecules. The thermal stabilities of the different hybrids are shown in Figure 6. The 5% weight loss temperature (T_{d5}), which corresponds to the temperature when 5% of the initial weight are lost, decreases with increasing HBPEE loading, as shown in Table I. However, the decrease is not significant. The shapes of the derivative TGA curves [Figure 6(b)] for all the samples were unimodal, indicating that the structures in hybrids are not significant different from that of the neat DGEBA resin

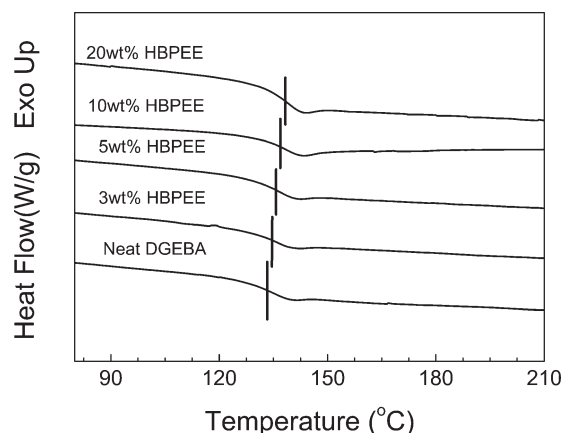


Figure 5. DSC curves of DGEBA/HBPEE hybrids with different HBPEE loading.

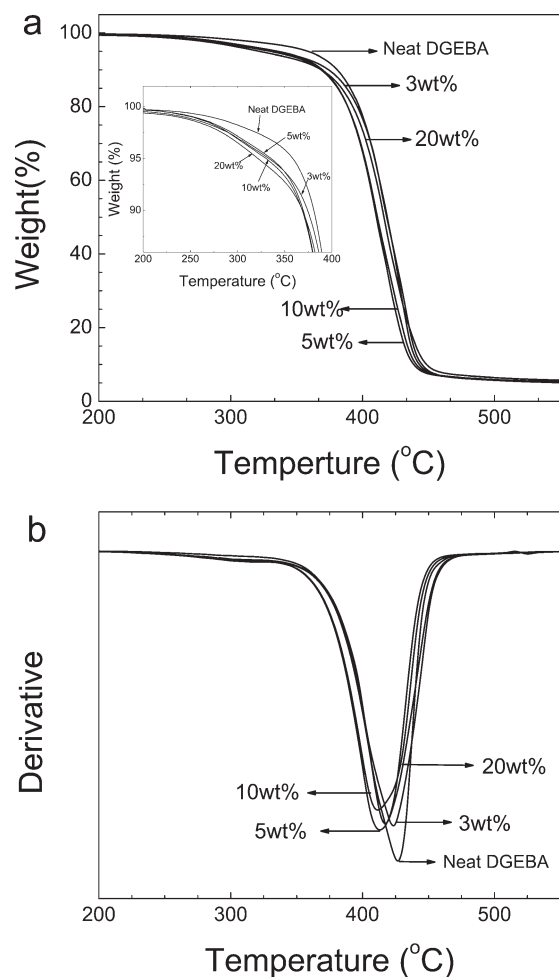


Figure 6. TGA (a) and DTG (b) curves of DGEBA/HBPEE hybrids with different HBPEE loading.

in thermal stability. The slightly drop in T_{d5} with increasing HBPEE loading could be explained by the higher density of ester structures, which can undergo β -elimination reactions through labile ester groups⁵⁰ in the networks of cured samples. The DGEBA/HBPEE hybrids display good thermal stability, although there is a slight drop in the T_{d5} . The maximum temperatures of decomposition for all samples are above 400°C. It is also noted that the residuals at 700°C increase with increasing HBPEE loading. This may be explained by the mass incorporation of the triphenyl structures arising from HBPEE, which has better heat resistance and high char yield compared with the neat DGEBA.

Mechanical Properties of DGEBA/HBPEE Hybrids

The addition of HBPEE into the DGEBA strongly affects the mechanical properties of the final cured hybrids, and the results are summarized in Table III. It can be found that the reactive HBPEE is highly efficient in enhancing the impact strength, tensile strength, elongation at break, and flexural strength. The impact strength reaches 35.2 kJ/m² when the HBPEE content is 5 wt %, which is twice of that of the neat DGEBA. Furthermore, the tensile strength of hybrids is apparently promoted after the introduction of HBPEE. When the loading is 5 wt %, the tensile strength reaches 82.2 MPa, which is a 19% increase compared with 69.1 MPa of the neat DGEBA, and then it reaches a plateau value with further addition. Meanwhile, the elongation at break reaches 11.1% and increases by 150% at 5 wt % HBPEE loading. In addition, the flexural strength also increases with the increase in HBPEE contents and has a similar trend with tensile strength. When the loading is 10 wt %, the flexural strength reaches 139.1 MPa and increases by 23% compared with that of the neat epoxy. The remarkable increases in all mechanical properties show that reactive HBPEE is a very effective modifier in improving the toughness and reinforcing the neat DGEBA epoxy.

As mentioned in the “Introduction” section, the improvements in toughness were often accompanied by a decrease in T_g s. Although there are many reports involving the usage of hyperbranched molecules as modifiers for E-51 type epoxy, only a limited number of studies reported all three properties (i.e., the tensile strength, the toughness and the glass transition temperatures), and their results are summarized in Table IV.^{40,52–55} It is clearly seen that, in all those cases, the improvements in mechanical properties are always accompanied by apparently decreasing in T_g s. In contrast, the reactive HBPEE modifier in this study exhibits balanced performance: notable improvements in mechanical properties at lower loading, moreover, still maintaining its high T_g . It is worth noting that the results, in our previous study,³¹ showed the optimum properties at 20 wt % loading. The toughness of the as-modified epoxy materials was improved, but their T_g s decreased by 18% and the tensile strength was not promoted. In contrast, in this study, the hybrids containing 5 wt % HBPEE has reached the optimum balanced performance, and both the impact strength and tensile strength are improved without compromise of T_g . Thus, compared with our previous study, we make a further progress in devising a new modifier, which is much more efficient in toughening and reinforcing the epoxy matrices while maintains a high T_g value. Such a progress can be ascribed to the successful design of hyperbranched molecular skeletons with more rigid aromatic rings.

Table III. Mechanical Properties of DGEBA/HBPEE Hybrids

Samples	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)	Flexural strength (MPa)
Neat DGEBA	69.1 ± 3.2	4.4 ± 0.6	19.1 ± 3.2	112.8 ± 2.2
3 wt % HBPEE	79.7 ± 2.7	7.6 ± 0.3	24.3 ± 1.6	132.7 ± 2.3
5 wt % HBPEE	82.2 ± 1.1	11.1 ± 0.3	35.2 ± 3.8	136.6 ± 3.0
10 wt % HBPEE	82.4 ± 1.3	10.5 ± 0.4	29.8 ± 3.9	139.1 ± 1.2
20 wt % HBPEE	82.7 ± 1.6	10.1 ± 0.3	29.0 ± 2.2	139.3 ± 3.1

Table IV. Properties of Toughened Epoxy by Various Hyperbranched Polymers

References	Backbones of HBPs	Optimum conc. (wt %)	Curing agent	Impact strength		Tensile strength		T _g		Phase separation
				Value	Changes	Value (MPa)	Changes	Value (°C)	Changes	
31,41,53	polyester	9	DETA	48.3 kJ/m ²	168% ↑ ^a	76.0	18% ↑	56	30% ↓ ^b	No
32	polyether	20	TETA	40.6 kJ/m ²	142% ↑	64.5	No change	89	18% ↓	No
54	Polyglycerol	20	TETA	20.2 kJ/m ²	35% ↑	51.2	10% ↑	-/-	-/-	Yes
55	Boltorn H30	10	MeTHPA	31.2 kJ/m ²	20% ↑	83.4	No change	-/-	No change	No
56	Boltorn E1	20	HHPA	K _{IC} ^c : 1.22 MPa·m ^{0.5}	85% ↑	-/-	-/-	130	18% ↓	Yes
Our study	HBPEE	5	MeHHPA	35.2 kJ/m ²	84% ↑	82.2	19% ↑	135	1% ↑	No

^a ↑ represents the increase of the value.

^b ↓ represents the decrease of the value.

^c The fracture toughness.

In most reports,^{30,31,40,52,54,55} the hyperbranched modifiers used in epoxy systems were mainly constructed by masses of flexible or aliphatic chains in the backbones. As is well known, to much flexible chains in the epoxy matrices will lower the T_g of materials, although they have an acceptable toughening effect. Especially in references 30, 40, and 52, although the impact strength increased by 168%, the T_g was declined to 56°C by which is a 30% decrease. However, in this study, the big improvement of

impact strength is achieved without the compromise of T_g, because HBPEE/DGEBA hybrids have more rigid skeletons and higher cross-linking density than that of the neat DGEBA. In this study, the increase in toughness could be attributed to the introduction of free volumes or molecule-scale cavities arising from hyperbranched polymers with few flexible chains in the backbones,^{56,57} which can absorb an appreciable amount of energy under impacting. However, because of the more rigid

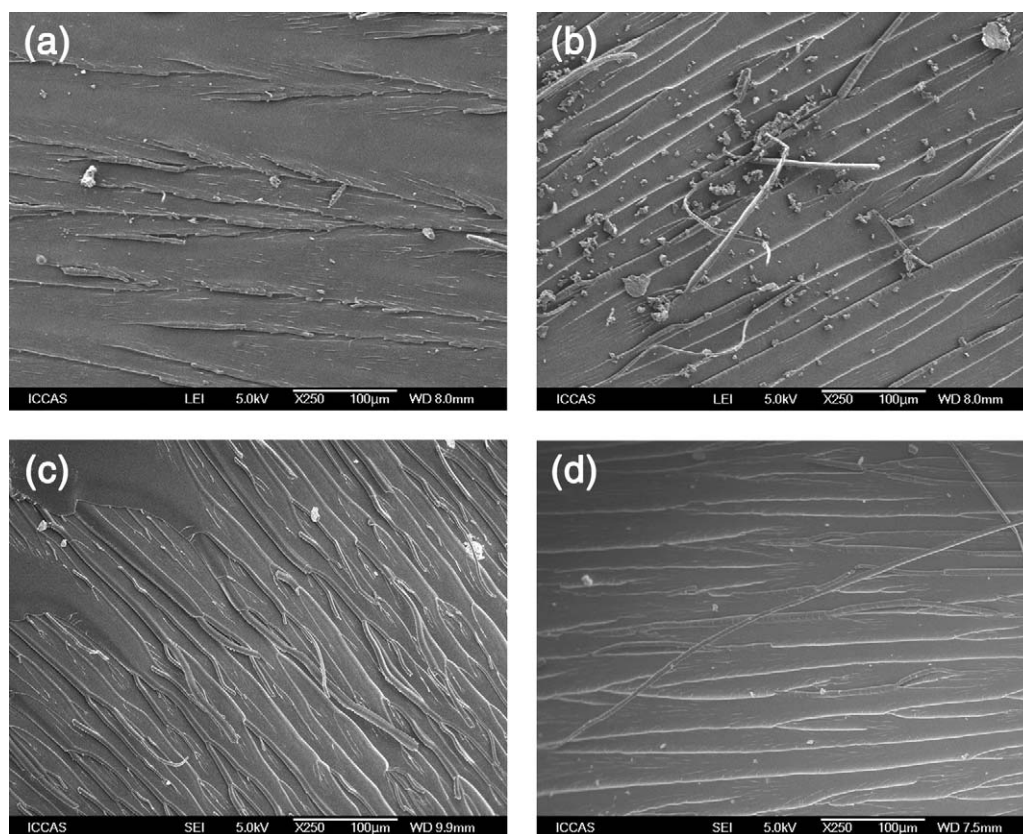


Figure 7. SEM images of fracture surface morphology of DGEBA/HBPEE hybrids with different HBPEE contents: (a) neat DGEBA, (b) 3 wt % HBPEE loading, (c) 5 wt % HBPEE loading, (d) 20 wt % HBPEE loading.

units and higher cross-linking density brought by the reactive HBPEE, excessive HBPEE may have adverse effects on the toughness. The improvement of elongation at break shows the enhanced ductility by introduction of HBPEE. The presence of free volumes provides room for the chains to move when subjected to a tensile force, which contributes to an increase in the elongation at break as the HBPEE content increases.⁵⁴ However, the higher crosslink density restrict the mobility of the chain segment and has negative impact on the elongation at break, which leads to a decrease in toughness at higher loading of HBPEE. The increase in tensile strength of DGEBA/HBPEE can partially be explained by the higher cross-linking density, as evident by the higher rubbery plateau modulus, and its rigid skeletons of HBPEE macromolecules. In addition, both the tensile strength and flexural strength firstly increase and then level off with increasing HBPEE loading. This trend could be attributed to the trade-off between the positive effects from the higher cross-linking density and more rigid backbones of HBPEE and the negative effects from the additional internal defects.

Fracture Surface Morphology of Cured Hybrid Systems

The SEM images of the fracture surfaces are shown in Figure 7. The fracture surface of the neat DGEBA [Figure 7(a)] shows flat and smooth morphology, which is typical for a brittle failure. For the fracture surfaces of hybrids [Figure 7(b–d)], the surfaces become increasingly rougher and show signs of fibril formations. When the HBPEE was added into epoxy, the fracture surface becomes rougher with more fibrils, suggesting that the impact specimens break more yieldingly. The fibrils, which are caused by the excessive energy associated with the relatively fast crack growth and shear steps connecting different fracture planes, are ways of absorbing excessive energy in a very brittle material. It has been suggested that the rough fracture surface or fibrils are the results of the coalescence of microcracks.^{58,59} The increasing fibrils on the fracture surfaces at higher HBPEE loadings are consistent with the improvement in toughness measured from unnotched impact tests.

We note that no particles or cavities are observed on the fracture surfaces morphology, indicating that no obvious phase separation occurs, which is consistent with the single peaks in DMA measurements. Because of the reactivity of HBPEE modifier, HBPEE participate into the cross-linking networks as a chemical cross-linking points, forming a homogenous system after curing.

CONCLUSIONS

Hyperbranched polyether epoxy (HBPEE) was successfully synthesized by one-step $A_2 + B_3$ proton transfer polymerization. Considering the versatile and low-cost raw material, easy operations, and high yield (>72%), it is a facile approach to synthesize such a reactive epoxy-ended hyperbranched polymer. It was proved to be an efficient modifier in toughening and reinforcing DGEBA epoxy resin without sacrificing its T_g . At 5 wt % HBPEE loading, the hybrids showed excellent balanced mechanical properties. Compared with the neat DGEBA, the impact strength, tensile strength, elongation at break, and flexural strength of DGEBA/HBPEE hybrids were increased by

approximately 84, 19, 152, and 21%, respectively. Furthermore, the T_g increased with increasing HBPEE loading, and in the meanwhile, the DGEBA/HBPEE hybrids displayed good thermal stability. With the increase of HBPEE contents, the free volume of hybrids increases; and the molecule-scale cavities or free volumes in the cured hybrids could facilitate the formation of the fibrils and led to an increase in the toughness. In addition, there were no phase separation in the hybrids, which were discussed by DMA, TMA, and SEM results. Both the tensile strength and flexural strength firstly increase and then level off with increasing HBPEE loading. This trend could be attributed to the trade-off between the positive effects from the higher cross-linking density (confirmed by DMA) and more rigid backbones of HBPEE and the negative effects from the additional internal defects. Compared with earlier investigations, the new modifier shows an overall improvement in impact strength, tensile strength, elongation at break, flexural strength and T_g s without phase separation and sacrificing thermal properties. Therefore, reactive HBPEE macromolecule could be considered as a promising additive in toughening and reinforcing the epoxy matrices simultaneously without compromise of the thermal properties.

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