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ARTICLE TYPE

Dependence of epoxy toughness on the backbone structure of hyperbranched polyether modifiers

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Synthesis of epoxide-terminated hyperbranched polyethers (EHBPEs) with different backbone stiffness and molecular weight (MW) are obtained using simple one-pot A₂+B₃ approach. When used as tougheners for DGEBA/TETA system, non-phase-separated cured networks are always obtained. Effects of MW and backbone stiffness on the toughening performance were systematically investigated. Among the EHBPEs studied, EHBPE-4C which has the lowest MW and stiffest backbone and EHBPE-10C which has the highest MW and most flexible backbone can simultaneously improve toughness, tensile strength, and T_g. In contrast, addition of EHBPE-6C and EHBPE-8C, which have medium MW and backbone stiffness, lead to incomplete cure and cannot improve or worsen the toughness and tensile strength. Both stiffness and MW of hyperbranched polyether play important roles in determining the crosslink density and structure of non-phase-separated networks, which dictate the toughness strength and T_g of toughened epoxy.

Introduction

Epoxy resins are widely used as matrix resins for coatings, adhesives, composites, and electronic materials.¹ However, in some applications, the inadequate toughness or elongation at break of epoxy materials limit their wider applications. Various modifiers have been used to toughen epoxy, including liquid rubber, core-shell particles, and engineering plastics.² Addition of those modifiers lead to phase-separated morphologies, and effects of toughening are related to the final morphology (*e.g.*, size and distribution) of cured networks, which depends on the interfacial chemistry and cure schemes.³ Oftentimes, the improvement of toughness is achieved at expenses of processability, tensile strength, and glass transition temperature (T_g). In addition, effects of toughening, which are dictated by the final phase-separated morphologies, are susceptible to changes in cure schemes and heat transfer and are thus unfavorable for processing. In many fiber-reinforced composites and microelectronic applications, phase-separated morphology can be undesirable because of the limited processing flexibility (viscosity and processing window *etc.*) and interfacial effects. Thus, improving toughness (without sacrificing tensile strength and T_g) of cure epoxy materials without forming phase-separated morphology is very crucial for those applications.

In the past two decades, hyperbranched polymers (HBPs) begin to emerge as a new type of promising tougheners for epoxy.⁴ When HPBs are used as tougheners, they can act either as non-reactive modifiers or reactive modifiers. When severed as non-reactive modifiers, the phase-separated phases are mainly responsible for the improved toughness, which is similar to liquid rubber tougheners. Recently, reactive hyperbranched modifiers,

especially those with epoxide terminal groups, attract more attentions because they can improve both impact strength and tensile strength without forming phase-separated morphologies (PSM). Zhang et al.⁵ reported a series of epoxide-terminated HPBs which can improve toughness and tensile strength simultaneously without forming PSM, and *in-situ* reinforcing and toughening mechanism was proposed to explain the improved performances. However, huge reduction in T_g was found which restrict its usefulness. In order to obtain epoxy materials with balanced improvements in mechanical properties without scarifying T_g, Jin and Park⁶ prepared a hyperbranched polyimide (HBPI) which can toughen DGEBA without reducing T_g. However, the reported HBPI modifiers are costly and have poor controllability. Our group also showed that two epoxide-terminated HPB modifiers with stiff backbone structures were able to simultaneously improve toughness, tensile strength and T_g of DGEBA epoxy without forming FSM.⁷⁻⁸ Similar to HBPI, our previously reported hyperbranched modifiers suffer from relatively poor controllability. Recently, by taking advantage of competing reactions, we showed that better controllability can be achieved in HBPs synthesized using one-pot AB₂ approach.⁹ Thus, the better controllability in those systems allow us to further investigate effects of structure of hyperbranched tougheners on toughening performance in non-phase-separated epoxy.

Although several kinds of reactive HPBs were used as tougheners, some are not effective, and effects of toughening depend on several factors, including the stiffness of backbone structure, molecule weight (MW) and the reactivity of terminal groups. So far, for hyperbranched tougheners which form non-phase-separated cured networks, the relationship between the

structure of HPBs and toughening effect has not been investigated. In order to address this issue, controlled synthesis of a series of hyperbranched polyethers (HBPE) were synthesized using monomers of different space lengths through one-pot A_2+B_3 approach. The MW and degree of branching can be controlled well as in our previous system⁹, which is suitable for mass production. By varying the spacer length of monomers, a series of epoxide-terminated hyperbranched modifiers (EHBPEs) which has different backbone structures and MWs were obtained and used as tougheners for DGEBA/triethylenetetramine system. Effects of backbone structure and MW on toughening were then systematically investigated, and the relationship between the structure and toughening effects is proposed.

Experimental section

Materials

All chemicals (analytical pure) were purchased from Chinese suppliers and were used as received unless otherwise stated. Phenol (98%), triethylenetetramine (TETA), tetrabutyl ammonium bromide and p-toluenesulfonic acid (PTSA) were purchased from Tianjin Fuguang reagent Co. 1,2-dibromoethane (98%), 1,4-dibromobutane (98%), 1,6-dibromohexane (98%), 1,8-dibromooctane (98%) and 1,10-dibromodecane (98%) were purchased from Beijing Ouhe Technology Co. 4-hydroxybenzaldehyde (PHBA, 98%) were obtained from ZhongshengHuateng Reagent Co. Diglycidyl ether of bisphenol A (DGEBA) was purchased from Yueyang Resin Factory (epoxy equivalent weight, EEW=190.04 g/equiv.) Methyl sulfoxide-d (CD₃SOCD₃) used for NMR were purchased from Beijing InnoChem Science & Technology Co. All other solvents and reagents were purchased from Beijing reagent Co. Ltd. N, N-dimethylformamide (DMF) was dried thoroughly before use.

Synthesis of triphenol methane

Detailed procedures for synthesizing triphenol methane can be found elsewhere.^{7,9} The obtained triphenol methane is a brick-red solid, and the yield was 70%. ¹H-NMR (600 MHz, acetone-d₆, δ): 5.33 (s, 1H, Ph₃CH), 6.76 (d, 6H, C₆H₄O), 6.94 (d, 6H, C₆H₄O), 8.15 (s, 3H, PhOH); ¹³C-NMR (600 MHz, acetone, δ): 54.32, 114.75, 130.06, 136.04, 155.50.

Typical procedure for synthesis phenol-terminated hyperbranched polyethers (HBPEs)

Phenol-terminated hyperbranched polyethers (HBPEs), which were synthesized from monomers with different space lengths (*i.e.*, n=4, 6, 8, and 10 as shown in Scheme 1), are denoted as HBPE-4C, HBPE-6C, HBPE-8C and HBPE-10C respectively; suffixes "-4C, 6C, 8C and -10C" denotes the different A₂ monomers. The procedures for synthesizing different HBPEs are same, and as an example, HBPE-4C is used in the following description.⁹ Triphenol methane (116.8 g, 0.4 mol, B₃ monomer), K₂CO₃ (165.6 g, 1.2 mol), 4.14 g KI and 600 mL DMF were added into a three-necked flask. Under mechanical stirring, reactants were heated to 80 °C. Then 1,4-dibromobutane (64.8 g, 0.3 mol, A₂ monomer) was added dropwise within 12 h, and the mixture was allowed to react for another 6 h. After cooling to room temperature, the mixture was acidified with hydrochloric acid and filtered. The filtrate was precipitated into water to

remove DMF and residual salts. The crude product was dissolved in THF and added dropwise into 2:1 ethanol/water solution under strong agitation. The precipitate was collected, washed with ethanol, and dried under vacuum at 90 °C to give a brick red solid product with the yield of 73%. ¹H-NMR (600 MHz, (methyl sulfoxide)-d₆, δ): 1.77-1.87 (br, OCH₂(CH₂)₂CH₂O), 3.88-4.01 (br, OCH₂(CH₂)₂CH₂O), 5.24-5.39 (br, CHPh₃), 6.64-7.01 (br, C₆H₄O). ¹³C-NMR (600 MHz, (methyl sulfoxide)-d₆, δ): 25.46, 53.55, 67.00, 114.05, 114.99, 129.72, 129.76, 134.98, 136.44, 136.69, 136.93, 155.42, 155.48, 156.72, 156.77, 156.92.

Typical procedure for synthesis epoxide-terminated hyperbranched polyether (EHBPE)⁹

90.2 g of HBPE-4C and 13.1 g of TBAB (as the catalyst) were dissolved in 856 g of ECH. The mixture was heated to 80 °C for 3 h under a dry nitrogen atmosphere. Using a peristaltic pump, 18.1 g of NaOH and 42.1 g of H₂O were added dropwise into the mixture during 3 h, and the resultant mixture was kept at 80 °C for another 2 h. After cooling to room temperature, the mixture was washed with hot water (>70 °C) for three times to remove the residual salt. The resultant mixtures were dried with Mg₂SO₄ and then were precipitated into ethanol. The precipitate was washed with ethanol and dried under vacuum at 90 °C. The obtained EHBPE-4C was a light yellow solid with the yield of 75%. ¹H-NMR (600 MHz, (methyl sulfoxide)-d₆, δ): 1.70-1.85 (br, OCH₂(CH₂)₂CH₂O), 2.60-2.70 (br, CH₂-O), 2.75-2.85 (br, CH₂-O), 3.20-3.33 (br, CH-O), 3.69-3.81 (br, CH₂-O), 3.83-4.02 (br, CH₂-O), 4.19-4.30 (br, CH₂-O), 5.26-5.42 (br, Ph₃CH), 6.70-7.00 (br, C₆H₄O).

Other EHBPEs, such as EHBPE-6C, EHBPE-8C and EHBPE-10C, were synthesized using the same method but with different HBPEs.

Preparation of DGEBA/HBPEE Hybrid Epoxy Curing Systems

Different amounts (*i.e.*, 3, 5, 10, and 20 total wt%) of EHBPEs and appropriate amounts of THF were dissolved in DGEBA under mechanical stirring at 60 °C. After homogeneous mixtures were obtained, THF was removed in a vacuum oven at 80 °C. Stoichiometric amounts of TETA (curing agent) were added in hybrid epoxy mixtures under continuously stirring at room temperature and then cured in silicone rubber moulds. The cure schedule followed a three-step procedure: cure at room temperature for 12 h, 100 °C for 2 h, and 190 °C for 2 h. After cure, samples were allowed to cool down naturally to room temperature. The chemical structures of DGEBA epoxy and TETA are shown in Scheme 2.

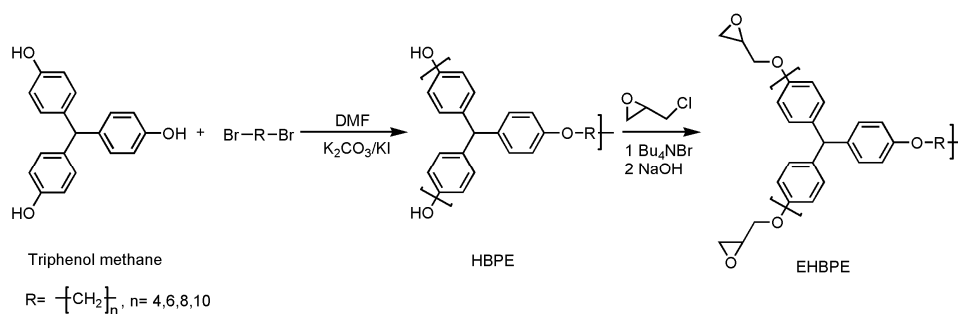
Instrumentation

MWs of EHBPEs were determined using a Waters 515-2410 gel permeation chromatography (GPC) system which was calibrated using linear polystyrene calibration standards and with tetrahydrofuran (THF) as the eluent. The epoxy equivalent weights (EEW) were determined by titration using the HCl-acetone method.¹⁰ Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-600 spectrometer (600 MHz). Chemical shifts of ¹H and ¹³C NMR peaks were reported in ppm; in all NMR measurements, CD₃SOCD₃ were used as solvents. Fourier transform infrared spectroscopy (FTIR) spectra were

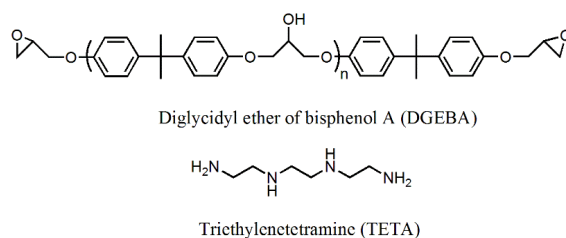
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Scheme 1 Synthesis route of EHBPE with different space lengths of 4C, 6C, 8C and 10C.



Scheme 2 Chemical structures of DGEBA epoxy and TETA.

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collected on a Bruker Tensor 37 spectrophotometer using the potassium bromide (KBr) disc technique.

Dynamic mechanical properties of cure samples were measured using a TA Q800 Dynamic Mechanical Analyzer (DMA) in the single cantilever mode at 1 Hz. The sample size was 35.0 mm×12.8 mm×3.2 mm, and measurements were performed on heating runs from 50 to 220 °C at 5 °C/min. T_g values of HBPEs were determined on second heating runs (10 K/min) using a DSC-1 (Mettler-Toledo, Switzerland) differential scanning calorimeter (DSC) under a dry nitrogen atmosphere (40 ml/min); when operated in the temperature-modulated mode, an amplitude of 0.5 K and a heating rate of 2 K/min were used. Thermal stability was measured using a PerkinElmer Pyris-1 thermo gravimetric analyzer (TGA) from 50 to 800 °C at a heating rate of 10 K/min under nitrogen. All measurements were performed at 25±3 °C unless otherwise stated. Linear coefficients of thermal expansion (LCTE) were measured using a TMA/SDTA841e (Mettler-Toledo, Switzerland) Thermal Mechanical Analyzer (TMA) during cooling from 190 to 50 °C at 2 K/min.

The tensile strength of cured hybrids was characterized by an Instron 1185 test machine according to ISO 527:1993. Unnotched impact strength tests were performed on a CeastResil impact tester according to ISO 179:1982 1BA type test specimens. After impact tests, fracture surfaces were coated with platinum and then scanned by a JEOL JSM-6700 Scanning Electron Microscopy (SEM) at 5 kV.

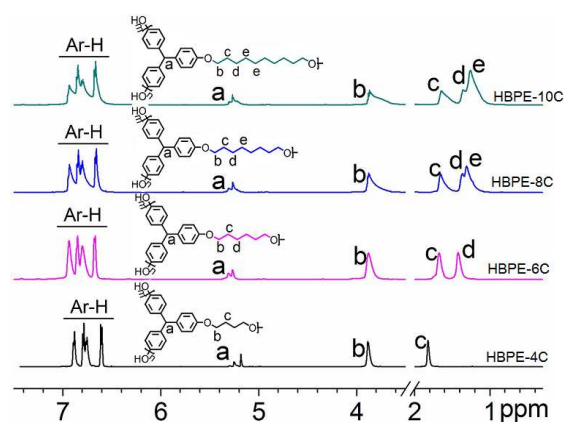


Fig. 1 ^1H NMR spectra of HBPEs obtained from monomers with different space lengths (*i.e.*, 4C, 6C, 8C, and 10C).

Results and discussion

Synthesis section

(1) Synthesis of polymers

In our previous work, controlled synthesis of HBPEs were realized through one-pot polymerization of AB_2 monomers with different space lengths, and better controllability is attributed to competing reactions between AB_2 monomers.⁹ Our previous results clearly showed that the competition reaction between substitution and elimination can lead to a fast kinetically-controlled steady state, *i.e.*, better controllability and scalability, as compared with hyperbranched synthesized using conventional

one-pot approach. In addition, we also demonstrated that the molecular weight of hyperbranched polymers can simply be “programmed” by choosing proper monomer concentrations, temperature, and feeding additional batches of monomers. In this work, HBPEs with the similar chemical structure were prepared using A_2+B_3 method instead which use commercially available monomers. Almost all HBPs prepared from the A_2+B_3 method suffer from poor controllability;¹¹ however, as will be shown later, for our reacting systems, the competing reactions between A_2+B_3 can indeed result in better controllability which is new way to produce large amounts of HBPs in a more controllable and economical way. The structure of HBPEs with different space lengths has been confirmed by NMR, and the results are shown in Fig. 1. To insure that terminal groups are phenol groups, excessive triphenol methane was added. Those terminal groups were then converted to epoxide groups to ensure better compatibility with DGEBA.

(2) Characterization of polymers

As expected, the MW of HBPEs stabilizes in a short time (less than 6 h) after monomer addition finished. By comparing the corresponding peaks in the ^1H NMR spectra of HBPE-4C (Fig. 1) with that of a model molecule, 4-bromo-1-butene, new double bonds (C=C) were found in HBPE-4C (Fig. 2). Fast stabilization in MWs were also observed in HBPEs synthesized using AB_2 monomers;⁹ similarly, competing reactions between elimination and substitution reactions are found to be responsible.¹² Furthermore, no obvious -Br groups were found in NMR spectra (Fig. 2), suggesting that most -Br groups were converted to unreactive C=C groups. In traditional one-pot synthesis of HBPs, MW is sensitive to local reaction conditions, such as mixing and heat transfer.¹³ However, in our reacting systems, the terminating side reaction inactivates propagating species and halts the reaction in several hours. As a result, the final products are not sensitive to the variations in local reaction conditions and result in better controllability and scalability.

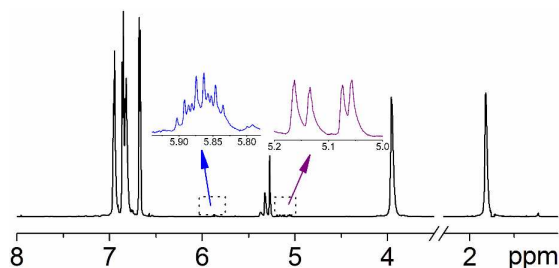


Fig. 2 ^1H NMR spectrum of HBPE-4C. Insets show enlarged views of the boxed parts.

MWs were determined using GPC which was calibrated using linear polystyrene standards in the corresponding MW range. Although MWs of HBP determined from GPC may be smaller than actual values, recent studies show that the determined MW is actually very close to true values when it is not very high (*ca.* 10.0×10^3 g/mol).¹⁴ HBPs show notable deviations only when the MW is high, and the backbone structure is stiff. In our HBPEs, the MW is not very high, and the backbone structure is not very stiff. Thus, no notable deviations from actual values are expected. As shown in Table 1, the average polymerization degree (DP) increases with space length (from 4C to 10C). Monomers with

longer space lengths tend to be less affected by the substitution (or steric hindrance) effects and result in higher DP. On the other hand, intermolecular cyclization may occur in monomers with long space lengths (8C and 10C), which restricts further increase of DP. For HBPE-2C (results not shown), the obtained MW is very low ($<1 \times 10^3$ g/mol), which is mainly due to the pronounced steric hindrance effect of monomer and low boiling point (*ca.* 131 °C) of A_2 monomer.

(3) Degree of branching of HBPEs

According to Hawker and Fréchet, the degree of branching (DB) can be defined as $DB = (D + T) / (D + T + L)$, where D, T, and L are the relative amounts of dendritic, terminal, and linear units, respectively.¹⁵ As shown in the ^1H NMR results (Fig. 1), chemical shifts of Ph_3CH proton (~ 5.3 ppm) are affected differently by the dendritic, linear, and terminal units and thus split into different peaks. However, those peaks cannot be used directly for integration due to peak overlapping. Assuming Gaussian distributions, peaks corresponding to each structural unit can be deconvoluted. A typical convolution result for HBPE-6C is shown Fig. 3. For HBPEs with longer space length (*i.e.*, HBPE-8C and HBPE-10C), intermolecular cyclization may occur and lead to an overestimation of DB. On the other hand, as the space length increases, three peaks (~ 5.3 ppm) overlap and are difficult to be deconvoluted. Thus, only DB values of HBPE-4C and HBPE-6C are calculated, which are 0.62 and 0.58, respectively.

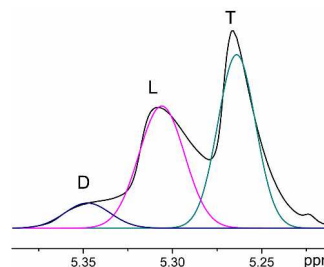


Fig. 3 Typical curve-fitting results of HBPE-6C showing the deconvolution of each structural unit.

(4) Terminal group modification

The structure of EHBPEs were confirmed by NMR and FTIR measurements. Taking EHBPE-4C as an example, the characterization results are shown in Figs. 4(a) and 4(b). All corresponding peaks are observed in ^1H -NMR spectrum. After terminal group modification, absorption peaks of phenol groups in FTIR spectrum can hardly be seen, and new peak corresponding to epoxy group at 914 cm^{-1} is observed. By choosing *ca.* 1506 cm^{-1} as internal standard peak, the extend of chemical modification was obtained by integrating the peak area at *ca.* 3400 cm^{-1} , and more than 98% of terminal phenol groups in HBPE-4C and HBPE-6C have been successfully converted to epoxy groups. However, as for HBPE with higher molecular weight, *i.e.*, HBPE-10C, there are still at least 10% of terminal phenol groups have not been successfully converted to epoxy groups. This can be explained by the fact that some terminal groups bury in the inside of hyperbranched molecules and have less chance to involved into the reaction. In addition, T_g values of EHBPEs as determined by second heating runs (10 K/min) of

DSC are shown in Table 1 and Fig. 5. Clearly, T_g decreases with increasing space length, indicating that T_g is largely determined by monomer space length rather than DP or MW.

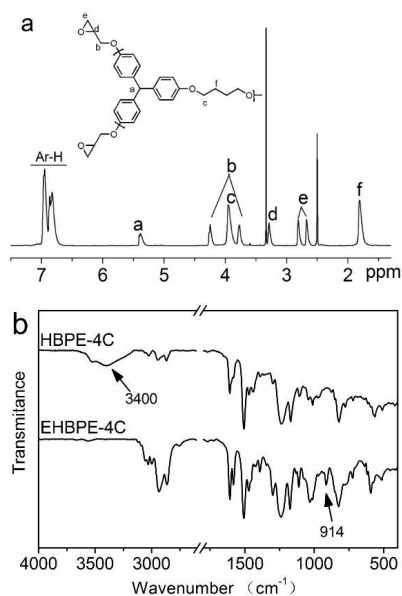


Fig. 4 (a) ^1H NMR spectra of EHBPE-4C; (b) FTIR spectra of HBPE-4C and EHBPE-4C.⁹

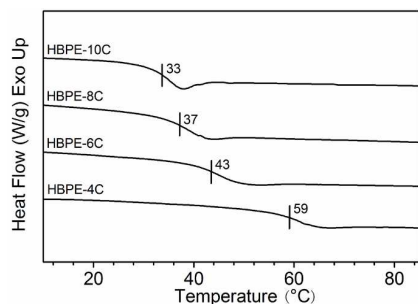


Fig. 5 DSC heating runs of different EHBPEs with different space lengths.

Table 1 Characterization results of epoxy-terminated EHBPEs.

Entry	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w ($\text{g}\cdot\text{mol}^{-1}$)	PDI	T_g ($^{\circ}\text{C}$)
EHBPE-4C	2.3×10^3	7.6×10^3	3.3	59
EHBPE-6C	3.0×10^3	9.6×10^3	3.2	43
EHBPE-8C	3.3×10^3	10.9×10^3	3.3	37
EHBPE-10C	6.0×10^3	18.6×10^3	3.1	33

Curing and performance sections

(1) FTIR characterizations

FTIR spectra of TETA, cured neat system (without EHBPE addition), and cured hybrids containing 5wt% loading of different EHBPEs are shown in Figs. 6a and 6b. TETA shows a broad band in the range of 3700 to 2600 cm^{-1} , corresponding to the different reactive hydrogen atoms. In the neat system and the hybrid containing 5% EHBPE-4C, the peak at ca. 3200 cm^{-1} disappear; however, for hybrids containing other EHBPE modifiers, the peak at ca. 3200 cm^{-1} remains, suggesting that some reactive hydrogen atoms are not fully reacted during cure. Mezzenga et al.¹⁶ have shown that significant incomplete cure can result when primary amines are used to cure hyperbranched epoxy as a result of the strong steric hindrance brought by bulky

hyperbranched molecules. In addition, some reactive terminal groups are buried in the inside of EHBPE molecules (*i.e.* 6C, 8C and 10C with higher MW), which could also contribute to the incomplete cure.

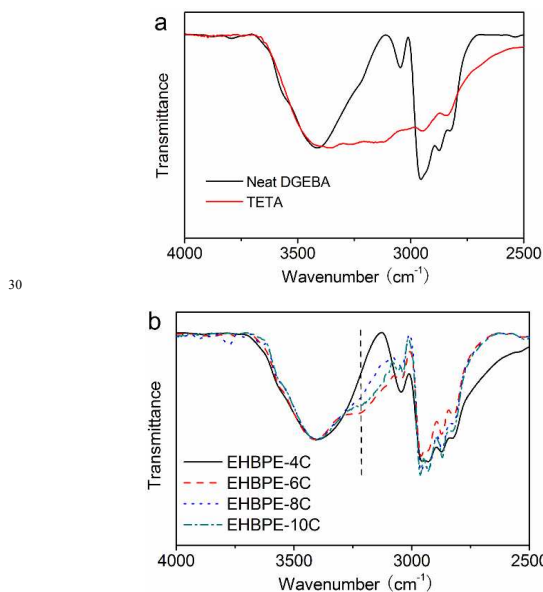


Fig. 6 (a) FTIR spectra of cured neat system and TETA. (b) FTIR spectra of hybrids at 5% loadings of different EHBPEs.

(2) DMA characterizations

The storage moduli (E') and loss tangent ($\tan\delta$) of cured neat system and hybrids containing 3%, 5%, 10% and 20% EHBPE, as a function of temperature are shown in Figs. 7a, 7b, 7c and 7d. For clarity, we only show data of EHBPE-4C and EHBPE-10C, which have biggest structure differences (in terms of MW and stiffness) for easy comparison. According to rubber elasticity, the rubbery plateau modulus (E_r) is proportional to average crosslinking density.¹⁷ As shown in Figure 7a, E_r increases with increasing EHBPE-4C loading. In contrast, as EHBPE-10C loading increases, (Fig. 7c), E_r first decreases and then increases. The different trends could be attributed to three factors: the number of reactive terminal groups, steric hindrance, and backbone structure. EHBPE-4C has relatively less terminal groups and steric hindrance and can thus be more effectively crosslinked into the network, which leads to higher crosslink density. In contrast, although EHBPE-10C has more terminal groups, which could increase the crosslink density (if fully reacted), the larger steric hindrance and possibility of chain back folding could actually lead to lower crosslink density (*i.e.*, more incomplete cure).

As shown in Fig. 7b and Table 2, T_g increases with EHBPE-4C loading, which is related to increases in crosslink density and the backbone stiffness. In contrast, as the EHBPE-10C loading increases, T_g first increases and then decreases (Fig. 7d). At low loadings ($\leq 3\%$), EHBPE-10C are fully surrounded by DGEBA molecules, and the crosslinked density is mainly determined by the higher functionality of hyperbranched modifier rather than its steric hindrance, which lead to an increase in T_g . At higher loadings, the steric hindrance effects in EHBPE-10C become more dominant and lead to significant incomplete cure,¹⁶ which lower the final T_g . In addition, the flexible backbone of EHBPE-

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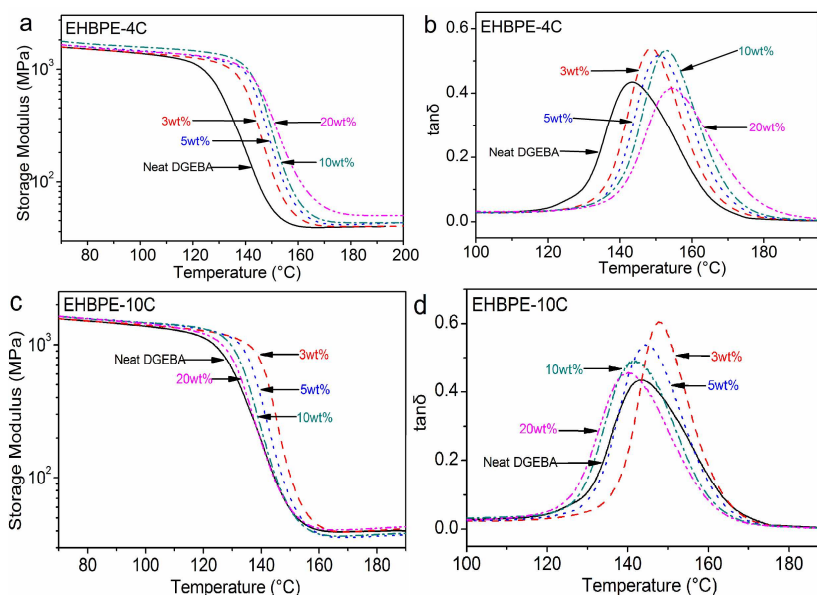


Fig. 7 DMA results of DGEBA/EHBPEs hybrids at different EHBPE loadings. Storage modulus (a) and $\tan\delta$ (b) as a function of temperature at different EHBPE-4C loadings; storage modulus (c) and $\tan\delta$ (d) as a function of temperature at different EHBPE-10C loadings.

10C can show dilution effect and lead to additional decrease in

⁵ T_g .

The $\tan\delta$ of all hybrids show only one peak, and the peak corresponding to pure EHBPEs are not found. Thus, in all hybrids, no sign of phase separation is found. In addition, no additional T_g , which corresponds to pure EHBPEs, is found (data not shown) in the temperature-modulated mode of DSC. The found single peaks in $\tan\delta$ are consistent with results of Zhang et al.⁵ and our previous work^{7,8,18}. The good miscibility can be explained by structural similarity between EHBPE modifiers and DGEBA and by the higher reactivity of terminal epoxide group in EHBPE, which ensures the incorporation of EHBPE (into the crosslink network) in the early stage of cure and prevent phase separation.¹⁹

The full width at half maxima (FWHM) of $\tan\delta$ may reveal additional information such as miscibility and homogeneity and is listed in Table 2. At 3%, 5%, and 10% loadings, FWHM of hybrids containing EHBPE-4C are all narrower than that of the neat system, suggesting that addition of EHBPE-4C appears to result in a more homogeneous network. Similar narrowing in FWHM (see Table 2) is also observed in hybrids containing EHBPE-6C and EHBPE-8C. At 20% loading, FWHM becomes wider and is similar to that of the neat system. A closer inspection of the peak shape reveals that they are not symmetrical, which is more obvious in the neat system and in the hybrid at 20% loading. For hybrids containing EHBPE-10C, narrowing in FWHM is only observed at 3% and 5% loadings, which can be related to the large steric hindrance effect in EHBPE-10C.

Table 2 Thermal properties of DGEBA/EHBPEs hybrids.

Sample	T_g^a (°C)	T_g^b (°C)	FWHM ^c of $\tan\delta$ (°C)	E_r (MPa)
Neat DGEBA	126.4	143.4	22.5	39.7
3wt% EHBPE-4C	129.0	148.5	17.8	40.1
5wt% EHBPE-4C	128.3	151.0	18.5	41.8
10wt% EHBPE-4C	131.5	152.6	18.5	43.4
20wt% EHBPE-4C	135.4	154.1	22.9	50.5
3wt% EHBPE-10C	127.1	147.9	14.9	39.9
5wt% EHBPE-10C	128.3	145.1	18.8	36.1
10wt% EHBPE-10C	126.9	141.9	20.6	36.8
20wt% EHBPE-10C	123.6	140.0	22.4	40.9
5wt% EHBPE-6C	123.8	144.0	17.1	36.1
5wt% EHBPE-8C	127.6	151.5	15.1	40.6

^a Obtained from DSC method.

³⁵ ^b Calculated from DMA method using the peak of $\tan\delta$.

^c The full width at half maxima of $\tan\delta$.

(3) TMA characterizations

Based on the free volume theory²⁰, the free volume at temperature T (f_T) is expressed as

$$f_T = f_g + \Delta\alpha_v(T - T_g)$$

where $\Delta\alpha_v = \alpha_{v,r} - \alpha_{v,g}$ is the difference between volumetric coefficients of thermal expansions (CTE) in rubbery and glassy states, and f_g is the fractional free volume at T_g . Thus, $\Delta\alpha_v$ is directly related to the fractional free volume, which has been confirmed by positron annihilation lifetime spectroscopy (PALS) measurements.^{8,21} As shown in Table 3, for hybrids containing EHBPE-4C, α_g decreases at lower loadings ($\leq 10\%$) and then increases at 20% loading; in contrast, α_r first increases than decreases at 20% loading. For hybrids containing EHBPE-10C,

α_g only decreases at 3% loadings and then steady increases at higher loadings; α_r shows a big increase at 3% loading then slowly decreases at higher loading. The resultant $\Delta\alpha$ values which are related to the fractional free volume of hybrids were also reported in Table 3. For hybrids containing EHBPE-4C, $\Delta\alpha$ increases with EHBPE-4C loading up to 10% and then decreases at 20% loading. For hybrids containing EHBPE-10C, $\Delta\alpha$ shows a notable increase at 3% loading then continuous to decrease with further loading. The explanations for the different trends are given below.

Table 3 Coefficients of linear thermal expansion of different hybrids.

Sample	$\alpha_g (\times 10^{-6} \cdot K^{-1})$	$\alpha_r (\times 10^{-6} \cdot K^{-1})$	$\Delta\alpha = \alpha_r - \alpha_g (\times 10^{-6} \cdot K^{-1})$
Neat DGEBA	91.8	187.9	96.1
3wt% EHBPE-4C	90.7	192.2	101.5
5wt% EHBPE-4C	88.3	193.0	104.7
10wt% EHBPE-4C	85.7	199.6	113.8
20wt% EHBPE-4C	90.3	194.5	104.2
3wt% EHBPE-10C	88.5	206.6	118.1
5wt% EHBPE-10C	88.8	198.5	109.7
10wt% EHBPE-10C	90.6	197.8	107.2
20wt% EHBPE-10C	94.9	193.2	98.3
5wt% EHBPE-6C	88.2	211.3	123.1
5wt% EHBPE-8C	87.2	202.9	115.7

Theoretically, adding of multi-functional HBPs should increase the crosslink density; however, if the terminal groups of HBPs cannot reacted fully, for example due to the steric hindrance, addition of HBPs can actually lead to significant incomplete cure and lower the average crosslink density. At low loadings, effects of steric hindrance are marginal, and the crosslink density increases with loading, which is especially true for EHBPE-4C which has low MW; the free volume inside and between HBP molecules can be effectively fixed and leads to an increase in $\Delta\alpha$. However, at high loadings, the steric hindrance plays a more important role and lead to incomplete cure, which lowers the average crosslink density and creates “defects” in networks. When high loadings of EHBPE-10C, which has higher MW and more flexible backbone, is added, more defects could be created, which facilitate the backfolding of unreacted chain ends and leading to decreases in α_r and $\Delta\alpha$. We note that at 5% loading, the hybrid with 5% EHBPE-6C loading has the highest $\Delta\alpha$ among all other hybrids at 5% loading, which is to the more “defects” due to steric hindrance and the relative stiff backbone. Those defects and lower crosslink density can compromise mechanical properties which will be shown in later section.

(4) Mechanical properties

Effects of EHBPE addition on mechanical properties are shown in Fig. 8. Both EHBPE-4C and EHBPE-10C are found to be

effective tougheners for DGEBA/TETA reacting system. At 5% loadings of EHBPE-4C and EHBPE-10C, impact strengths of cured hybrids become higher than 40 kJ/m². At the same time, the variation of elongation at break at different EHBPE loadings is similar with that of impact strength. In addition, the tensile strength of the hybrid containing 5% EHBPE-10C remains unchanged; and that of the hybrid containing 5% EHBPE-4C increases to 72.1 MPa, which is slightly higher than that of the neat system (66.9 MPa). The simultaneous improvements in impact strength, tensile strengths, and T_g indicate that EHBPE-4C and EHBPE-10C are effective all-purpose tougheners. In contrast, as shown in Figs. 8a and 8b, addition of EHBPE-8C cannot improve mechanical performance, and addition of EHBPE-6C even decreases the impact and tensile strength. Possible explanations for the counter-productiveness will be given next.

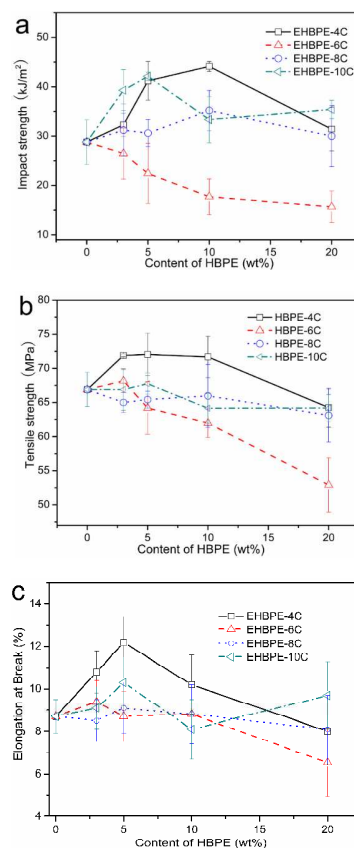


Fig. 8 Effects of EHBPE loading on (a) impact strength (b) tensile strength and (c) elongation at break of hybrids.

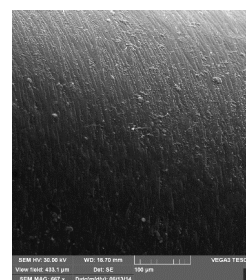


Fig. 9 SEM photographs of fracture surfaces of cured neat DGEBA.

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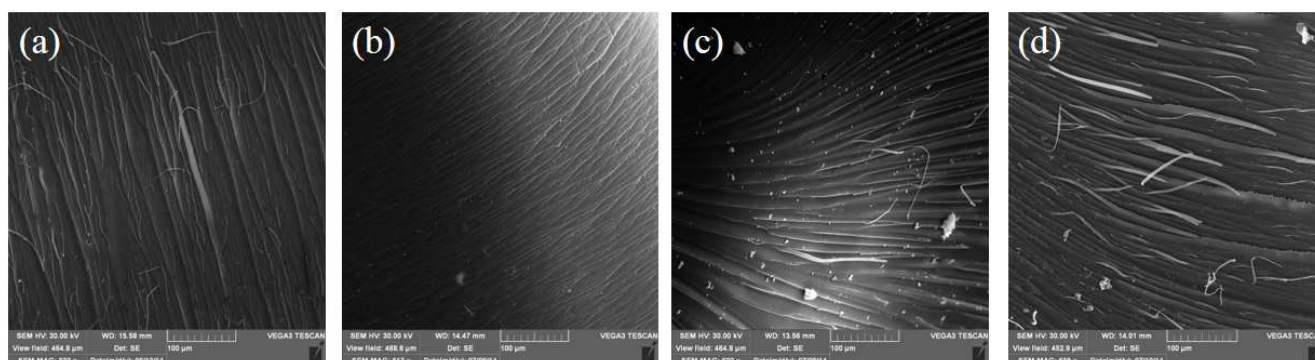


Fig. 10 SEM photographs of fracture surfaces of hybrids at 5% EHBPE loadings: (a) EHBPE-4C; (b) EHBPE-6C; (c) EHBPE-8C; (d) EHBPE-10C.

(5) Fracture surface and mechanisms

SEM images of fracture surfaces after impact tests are shown in Figs. 9 (for neat DGEBA) and 10 (for different hybrids at 5% loading). All images were obtained at the rear ends (far away from the breaking points) of fracture surfaces. The smooth and glossy surface of neat DGEBA suggests a brittle failure with little deformation, which is consistent with its low impact strength. In contrast, fibrils are found in hybrids containing EHBPE-4C and EHBPE-10C (see Fig. 10). Fibrils are signs of shear yielding which can absorb energy and increase toughness.²² However, fracture surfaces of hybrids containing EHBPE-6C and EHBPE-8C are relative smooth, which is consistent with their low impact strengths.

For HBP-toughened epoxy materials that do not form phase-separated morphologies, the toughening mechanism has been explained by the *in-situ* toughening mechanism, *i.e.*, increased free volume and deformation of cavities.^{5,23,24} In our systems, the *in-situ* toughening mechanism can still be operative. However, we believe that other mechanisms can also contribute. We note that in terms of toughening, EHBPE-6C and EHBPE-8C are not effective as EHBPE-4C and EHBPE-10C, which again could be related to the different structure of cured network. It is expected that defects due to incomplete cure can lower the crosslink density and weaken the integrity of the network, which compromise mechanical properties. As explained before, hybrids containing proper amounts of EHBPE-4C can be effectively cured and form more homogeneous network. However, when TETA is cured with EHBPE-6C, which has more terminal groups and more steric hindrance, there are more unreacted terminal groups (see Fig. 6b), which creates defects and higher apparent “free volume” and $\Delta\alpha$ (see Table 3). The less crosslinked structure and larger defects compromise mechanical performance. As the space length increases, the backbone becomes more flexible, and the terminal groups gain more freedom to be able to react with curing agents and decrease the possibility of defects. In addition, flexible units in network can be beneficial in toughness. Thus, EHBPE-10C which has the most flexible backbone also show good toughening effect despite its high MW and more terminal groups. As a result, it is concluded that the backbone

structure and density of terminal groups are important parameters that can shape the final cured network. When designing an effective hyperbranched toughener, loading amount, backbone stiffness, and density of terminal groups are important considerations, because the balance between those parameters can affect the crosslink density, fixed more free volume, and defects in cured network.

Conclusions

Thanks to the competing elimination side reaction, facile controlled synthesis of four types hyperbranched polyethers with different space length (4C, 6C, 8C and 10C) are realized using one-pot A_2+B_3 approach. Due to the different length and reactivity of A_2 monomers, the molecular weight of EHBPE increases with increasing space length. After the terminal group modification, epoxide-terminated hyperbranched polyethers (EHBPE) were obtained, which were then used to study the effects of MW and backbone structure on toughening efficiency.

Among the four types of EHBPEs tougheners, EHBPE-4C, which has the lowest MW and stiff backbone, and EHBPE-10C, which has the highest MW and flexible backbone, are found to be effective tougheners, which can improve toughness without sacrificing tensile strength and T_g . In contrast, EHBPE-6C and EHBPE-8C cannot improve the toughness. Results from DMA, DSC, FTIR, TMA and SEM suggest that the differences in backbone structure (esp. backbone stiffness) and the number of terminal group can lead to different network structure, including average crosslink density, homogeneity, fractional free volume and defects, which result in quite different toughness. Balanced considerations on MW, backbone structure of hyperbranched reactive tougheners are necessary in order to achieve the simultaneous improvements in toughness, strength and T_g .

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Notes and references

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- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
- ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
- J. LeMay, F. Kelley, In *Advances in Polymer Science*, Springer: Berlin/Heidelberg, 1986; R. S. Bouer, In *Epoxy Resin Chemistry*, American Chemical Society: Washington DC, 1983; J. Xin, P. Zhang, K. Huang, J. Zhang, *RSC Adv.*, 2014, **4**, 8525.
 - L. Boogh, B. Pettersson, J.-A. E. Månson, *Polymer*, 1999, **40**, 2249.
 - I. Kelnar, J. Rotrekl, L. Kaprálková, J. Hromádková, A. Strachota, *J. Appl. Polym. Sci.*, 2012, **125**, 3477; Y. L. Liang, R. A. Pearson, *Polymer*, 2010, **51**, 4880; X. L. Jiang, Y. Fan, *J. Appl. Polym. Sci.*, 2012, **124**, 2423.
 - X. Zhang, *Polym. Int.*, 2011, **60**, 153; D. Foix, A. Serra, L. Amparore, M. Sangermano, *Polymer*, 2012, **53**, 3084; M. Morell, X. Ramis, F. Ferrando, Y. Yu, A. Serra, *Polymer*, 2009, **50**, 5374.
 - D. Zhang, Y. Chen, D. Jia, *Polym. Compos.*, 2009, **30**, 918.
 - F. L. Jin, S. J. Park, *J. Polym. Sci. Part B: Polym. Phys.*, 2006, **44**, 3348.
 - L. Luo, Y. Meng, T. Qiu, X. Li, *J. Appl. Polym. Sci.*, 2013, **130**, 1064.
 - J. Lv, Y. Meng, L. He, T. Qiu, X. Li, H. Wang, *J. Appl. Polym. Sci.*, 2013, **128**, 907; L. Luo, Y. Meng, T. Qiu, Z. Li, J. Yang, X. Cao, X. Li, *Polym. Compos.*, 2013, **34**, 1051.
 - T. Liu, X. Geng, Y. Nie, R. Chen, Y. Meng, X. Li, *RSC Adv.*, 2014, **4**, 30250; T. Liu, Y. Nie, R. Chen, L. Zhang, Y. Meng, X. Li, *J. Mater. Chem. A*, 2014, DOI: 10.1039/C4TA04841E.
 - C. Gong, J. M. J. Fréchet, *Macromolecules*, 2000, **33**, 4997; GB/T 1678-1981: China: 1981.
 - D. Yan, C. Gao, H. Frey, In *Hyperbranched Polymers: Synthesis, Properties, and Applications*, John Wiley & Sons, Inc: Hoboken, New Jersey, 2011; Chap. 1; T. Liu, Y. Meng, X. Wang, H. Wang, X. Li, *RSC Adv.*, 2013, **3**, 8269-8275; Q. Zhu, F. Qiu, B. Zhu, X. Zhu, *RSC Adv.*, 2013, **3**, 2071-2083; X. Xiao, S. Lu, B. Qi, C. Zeng, Z. Yuan, J. Yu, *RSC Adv.*, 2014, **4**, 14928-14935.
 - J. Miller, In *Aromatic Nucleophilic Substitution*, Amsterdam, Elsevier, 1968.
 - P. J. Flory, In *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, New York, 1953; Chap. IV.
 - C. J. Hawker, E. E. Malmström, C. W. Frank, J. P. J. Kampf, *J. Am. Chem. Soc.*, 1997, **119**, 9903-9904.
 - C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4583.
 - R. Mezzenga, L. Boogh, J.-A. E. Månson, *Macromolecules*, 2000, **33**, 4373.
 - L. E. Nielsen, R. F. Landel, eds., In *Mechanical Properties of Polymers and Composites*, 2nd Ed., Chap. 4, Boca Raton: CRC Press, 1994.
 - J. Lv, Y. Meng, L. He, X. Li, H. Wang, *Chinese J. Polym. Sci.*, 2012, **30**, 493; L. Ma, H. Wang, L. He, X. Li, *Chinese J. Polym. Sci.*, 2011, **29**, 300.
 - Q. Li, X. Li, Y. Meng, *Thermochim. Acta*, 2012, **69**, 549.
 - G. Strobl, In *The Physics of Polymers: Concepts for Understanding Their Structures and Behavior*, Springer-Verlag: Berlin, 2007.
 - D. Ratna, G. P. Simon, *J. Appl. Polym. Sci.*, 2010, **117**, 557.
 - D. Ratna, R. Varley, R. K. S. Raman, G. P. Simon, *J. Mater. Sci.*, 2003, **38**, 147; R. J. Varley, *Polym. Int.*, 2004, **53**, 78; R. Mezzenga, J.-A. E. Månson, *J. Mater. Sci.*, 2001, **36**, 4883.
 - B. L. Burton, and J. L. Bertram, Chap. 10 "Design of tough epoxy thermosets", in C.B Arends ed., In *Polymer Toughening*, New York: Marcel Dekker, Inc., 1996.
 - D. Zhang, H. Wu, T. Li, A. Zhang, Y. Peng, F. Jing, *Polym. Compos.*, 2011, **32**, 36.